Basic aspects of the spin-Restricted Ensemble-referenced Kohn-Sham (REKS) method

What is the REKS method?

REKS method is based on ensemble DFT, not the usual KS DFT

Advantages of ensemble DFT

Non-dynamic (static) electron correlation

- bond breaking
- bi- and poly-radicals
- symmetry forbidden reactions
- magnetic coupling

Variational (not response) excited states

- S_1/S_0 crossings
    - avoided crossings
    - conical intersections
- excited state orbital relaxation
    - conjugated π-systems
    - charge transfer excitations

Part 1

Ground States

Content

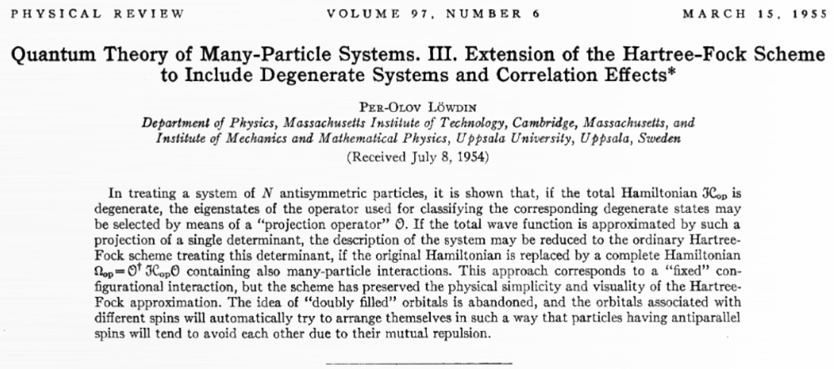
- Electron correlation
  - Dynamic and static (non-dynamic) correlation
  - Examples of non-dynamic correlation
  - Multi-reference wavefunction methods

- Density functional theory
  - Standard Kohn-Sham DFT; KS-DFT
  - Ensemble DFT; eDFT
  - eDFT and non-dynamic correlation

- Practical implementation of eDFT
  - REKS method for ground states
    - derivation
    - benchmarking
    - extensions

Electron correlation

introduced by P.-O. Löwdin in 1954



PHYSICAL REVIEW VOLUME 97, NUMBER 6 MARCH 15, 1955

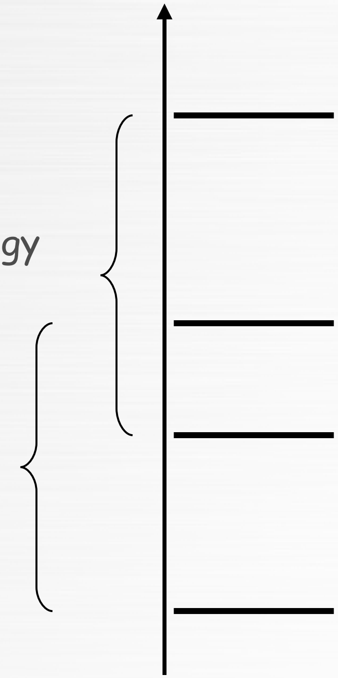
Quantum Theory of Many-Particle Systems. III. Extension of the Hartree-Fock Scheme to Include Degenerate Systems and Correlation Effects*

PER-OLOV LÖWDIN
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts, and
Institute of Mechanics and Mathematical Physics, Uppsala University, Uppsala, Sweden

(Received July 8, 1954)

In treating a system of N antisymmetric particles, it is shown that, if the total Hamiltonian $\mathcal{H}_{op}$ is degenerate, the eigenstates of the operator used for classifying the corresponding degenerate states may be selected by means of a "projection operator" $\mathcal{O}$. If the total wave function is approximated by such a projection of a single determinant, the description of the system may be reduced to the ordinary Hartree-Fock scheme treating this determinant, if the original Hamiltonian is replaced by a complete Hamiltonian $\Omega_{op}=\mathcal{O}^{\dagger}\,\mathcal{H}_{op}\mathcal{O}$ containing also many-particle interactions. This approach corresponds to a "fixed" configurational interaction, but the scheme has preserved the physical simplicity and visuality of the Hartree-Fock approximation. The idea of "doubly filled" orbitals is abandoned, and the orbitals associated with different spins will automatically try to arrange themselves in such a way that particles having antiparallel spins will tend to avoid each other due to their mutual repulsion.

characterizes deviation from independent particles model



Hartree-Fock (finite basis set)

finite basis correlation energy

Hartree-Fock (complete basis set)

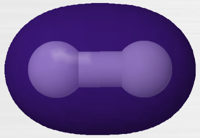
post Hartree-Fock (finite basis set)

CBS correlation energy

CBS full CI (FCI) or Schrödinger equation

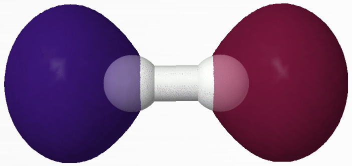
Hartree-Fock description of H_2

bonding MO



$$\sigma_g = \mathcal{N}_{\sigma_g}\left(\chi_A + \chi_B\right)$$

anti-bonding MO



$$\sigma_u = \mathcal{N}_{\sigma_u}\left(\chi_A - \chi_B\right)$$

The ground state HF wave function: $\Phi_0 = \hat{\mathcal{A}}\,\sigma_g^{\alpha}(1)\sigma_g^{\beta}(2)$

In the dissociation limit: $\chi_A \sim 1s_A\,,\ \chi_B \sim 1s_B\,,\ \mathcal{N}_{\sigma_g} = \dfrac{1}{\sqrt{2}}$

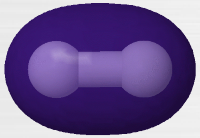
$$\Phi_0 \sim \frac{1}{2}\hat{\mathcal{A}}\Big(\underbrace{1s_A^{\alpha}\,1s_B^{\beta} + 1s_B^{\alpha}\,1s_A^{\beta}}_{\text{covalent configuration}} + \underbrace{1s_A^{\alpha}\,1s_A^{\beta} + 1s_B^{\alpha}\,1s_B^{\beta}}_{\text{ionic configuration}}\Big)$$

$$\mathrm{H} - \mathrm{H} \qquad {}^{+}\mathrm{H} - \mathrm{H}^{-} \longleftrightarrow {}^{-}\mathrm{H} - \mathrm{H}^{+}$$

50/50 mix of covalent (right) and ionic (wrong) configurations

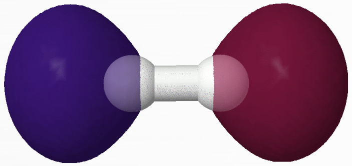
Doubly excited configuration of H$_2$

bonding MO



$$\sigma_g = \mathcal{N}_{\sigma_g}\left(\chi_A + \chi_B\right)$$

anti-bonding MO



$$\sigma_u = \mathcal{N}_{\sigma_u}\left(\chi_A - \chi_B\right)$$

The doubly excited wave function:

$$\Phi_{11}^{22} = \hat{\mathcal{A}}\,\sigma_u^{\alpha}(1)\sigma_u^{\beta}(2)$$

In the dissociation limit:

$$\chi_A \sim 1s_A\,,\ \chi_B \sim 1s_B\,,\ \mathcal{N}_{\sigma_u} = \frac{1}{\sqrt{2}}$$

$$\Phi_{11}^{22} \sim \frac{1}{2}\hat{\mathcal{A}}\Big(\underbrace{-1s_A^{\alpha}\,1s_B^{\beta} - 1s_B^{\alpha}\,1s_A^{\beta}}_{\text{covalent configuration}} + \underbrace{1s_A^{\alpha}\,1s_A^{\beta} + 1s_B^{\alpha}\,1s_B^{\beta}}_{\text{ionic configuration}}\Big)$$

$\mathrm{H - H}$ $\quad$ ${}^{+}\mathrm{H - H}^{-} \longleftrightarrow {}^{-}\mathrm{H - H}^{+}$

covalent configuration enters with opposite sign

Configuration mixing in H_2

Take a linear combination of the two configurations:

$$\Psi_{CID} = \sqrt{1-\lambda^2}\,\Phi_0 - \boxed{\lambda}\,\Phi_{11}^{22}$$

variational parameter

In the dissociation limit: $\lambda = \frac{1}{\sqrt{2}}$

$$\Psi_{CID} = \frac{1}{\sqrt{2}}\Phi_0 - \frac{1}{\sqrt{2}}\Phi_{11}^{22} = \frac{1}{\sqrt{2}}\hat{A}\underbrace{\left(1s_A^{\alpha}\,1s_B^{\beta} + 1s_B^{\alpha}\,1s_A^{\beta}\right)}_{\text{covalent configuration} \quad \mathrm{H - H}}$$

Generalized Valence Bond Perfect (spin-)Pairing (GVB-PP) wavefunction

Electron correlation in H_2

Correlated motion of two electrons

$$P(\vec{r}_1,\vec{r}_2) \neq P(\vec{r}_1)P(\vec{r}_2)$$

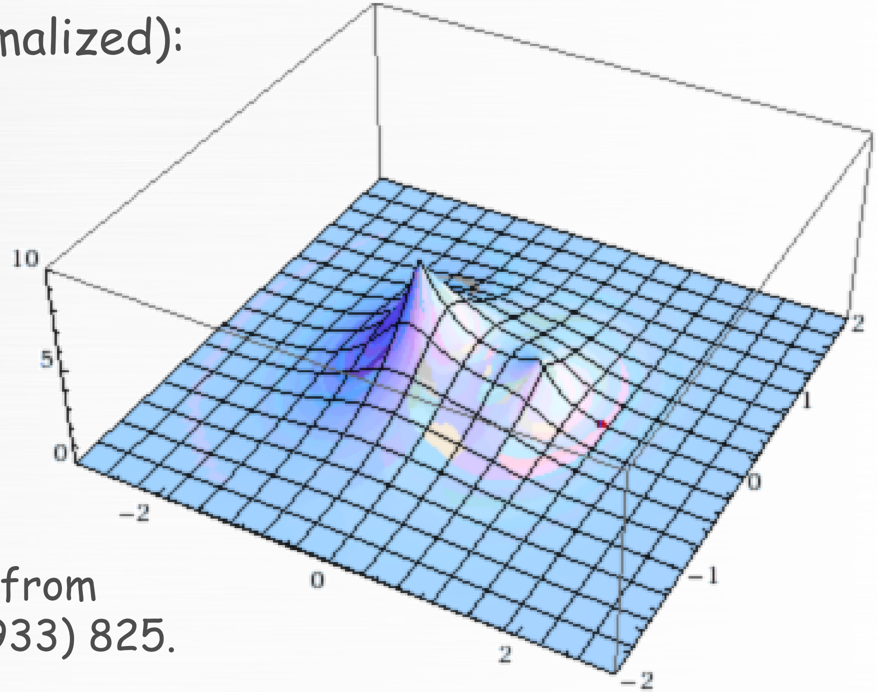
In the ground state of H_2

$$P(\vec{r}_1,\vec{r}_2) = \left|\Psi(\vec{r}_1,\vec{r}_2)\right|^2$$

Conditional probability (un-normalized):

$$P(\vec{r}_2|\vec{r}_1 = \vec{R}) = \left|\Psi(\vec{R},\vec{r}_2)\right|^2$$

Probability distribution for electron 2
provided that electron 1 resides at R.

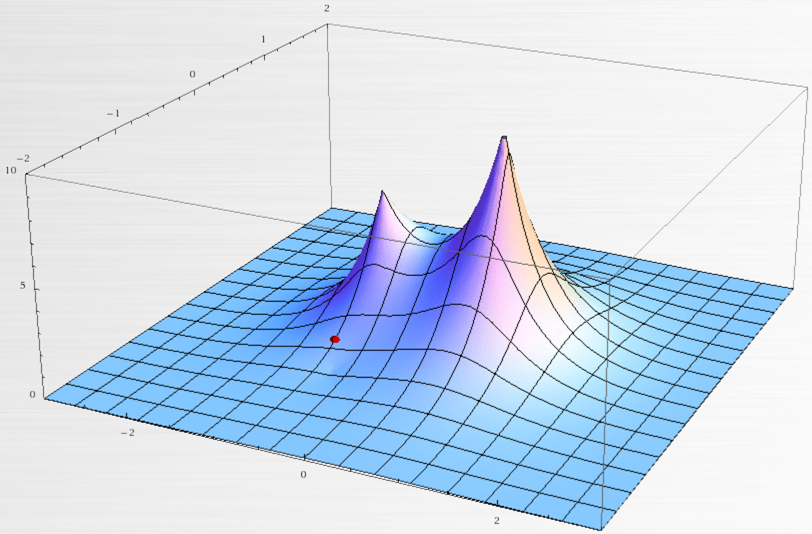


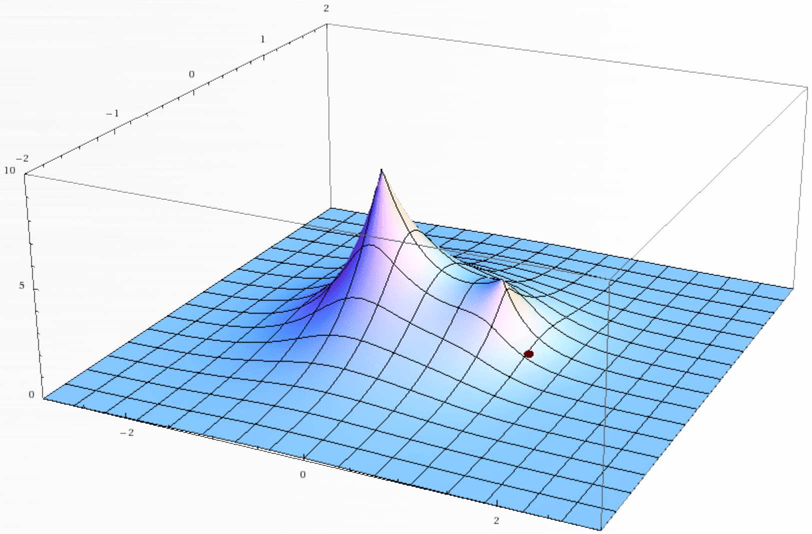
Explicitly correlated wave function from
H. James and A. Coolidge, JCP, 1 (1933) 825.

Electron correlation in H_2

Conditional probability (un-normalized): $P\left(\vec{r}_2 | \vec{r}_1 = \vec{R}\right) = \left|\Psi\left(\vec{R}, \vec{r}_2\right)\right|^2$

Probability distribution for electron 2 provided that electron 1 resides at R.





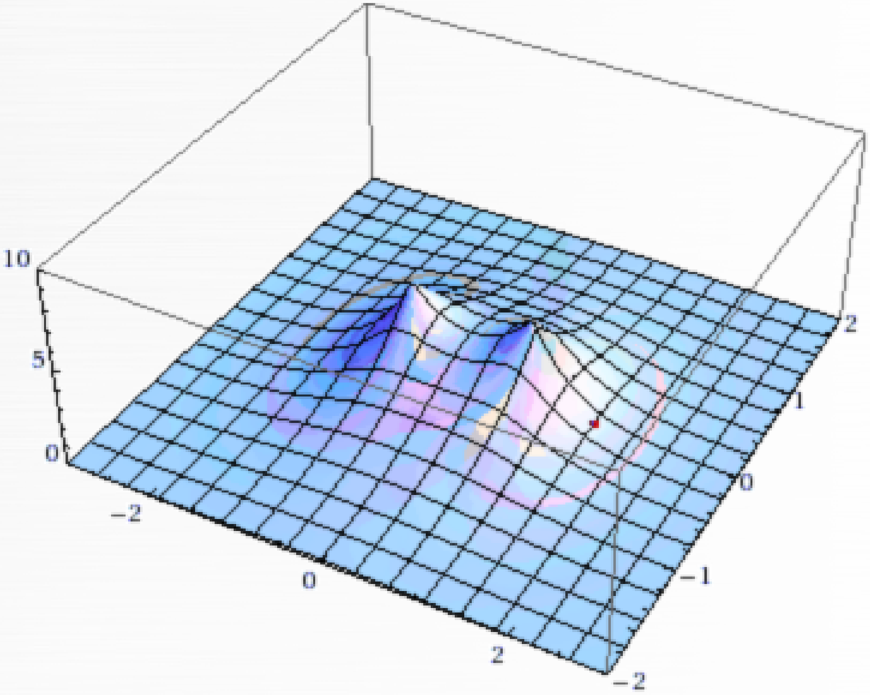
Explicitly correlated wave function from H. James and A. Coolidge, JCP, 1 (1933) 825.

Probability distribution from HF wave function

Conditional probability (un-normalized): $P^{HF}\left(\vec{r}_2|\vec{r}_1=\vec{R}\right)=\left|\Phi_0\left(\vec{R},\vec{r}_2\right)\right|^2$

Probability distribution for electron 2 provided that electron 1 resides at R.

Probability distribution of the second electron is independent on the position of the first electron.



"Breathing" does not count as correlation. This is because the P^{HF} is un-normalized.

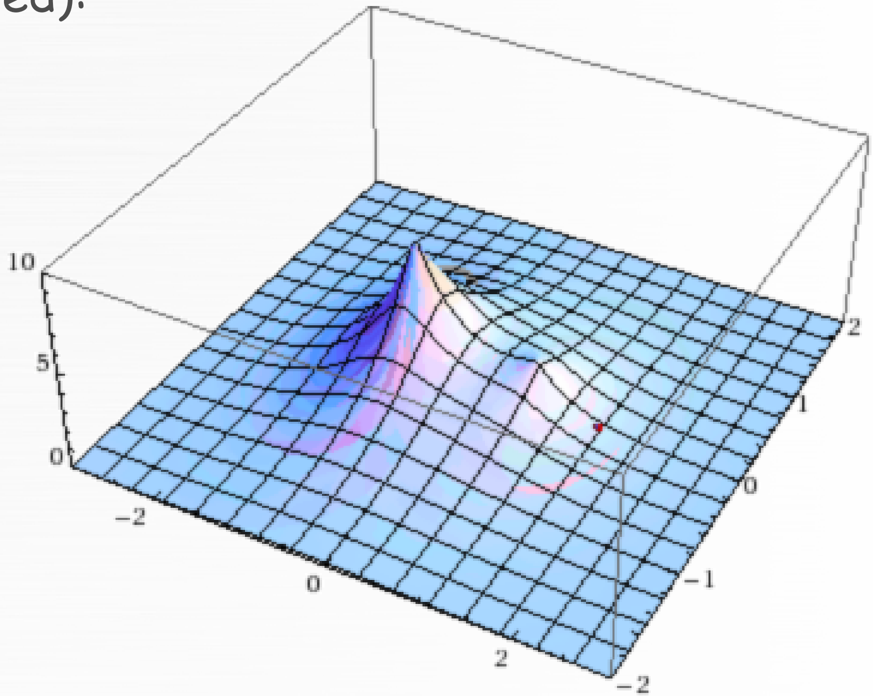
Configuration mixing in H_2

GVB-PP (2-config.) wave function:

$$\Psi_{GVB-PP} = \sqrt{1-\lambda^2}\,\Phi_0 - \lambda\,\Phi_{11}^{22}$$

Conditional probability (un-normalized):

$$P^{CID}\left(\vec{r}_2 | \vec{r}_1 = \vec{R}\right) = \left|\Psi_{CID}\left(\vec{R}, \vec{r}_2\right)\right|^2$$

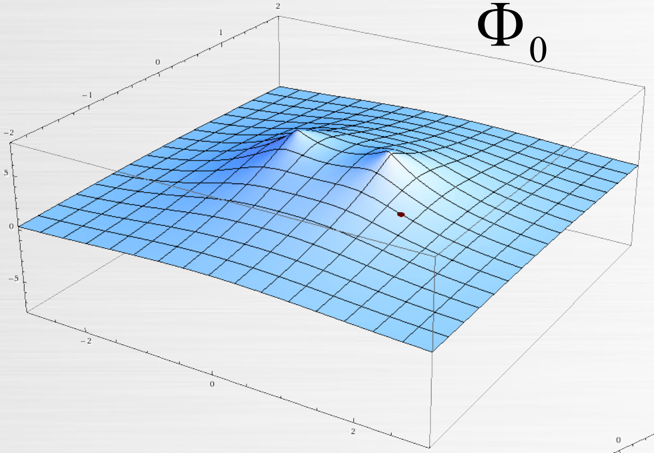


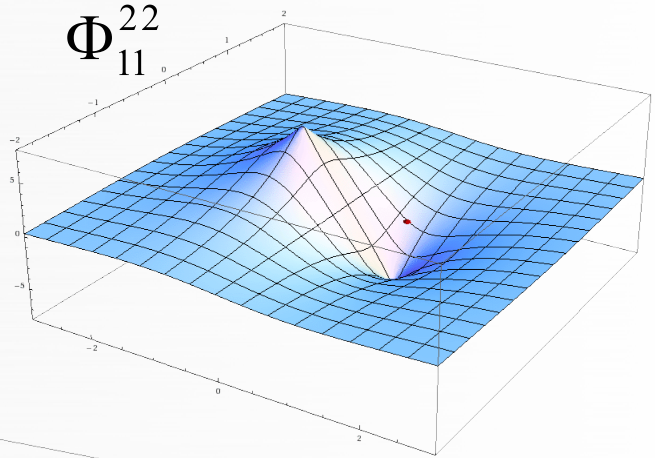
Configuration mixing brings in the electron correlation!

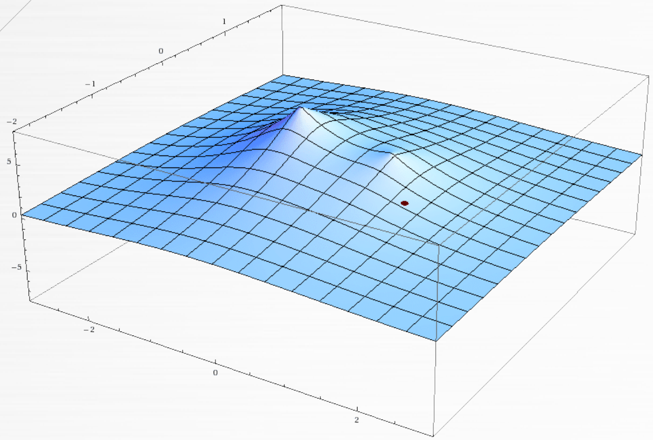
Configuration mixing in H_2

GVB-PP wave function:

$$\Psi_{GVB-PP} = \sqrt{1-\lambda^2}\,\Phi_0 - \lambda\,\Phi_{11}^{22}$$


Φ_0


Φ_{11}^{22}


Ψ_{GVB-PP}

Fermi correlation in open shell wave functions

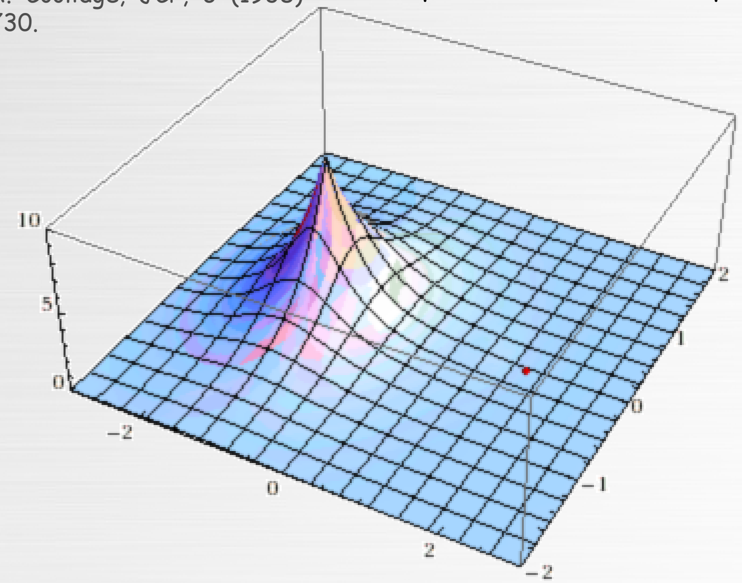
Fermi correlation: Correlation due to the Pauli principle (w.f. antisymmetry).

Motion of the same-spin electrons is correlated at the HF level.

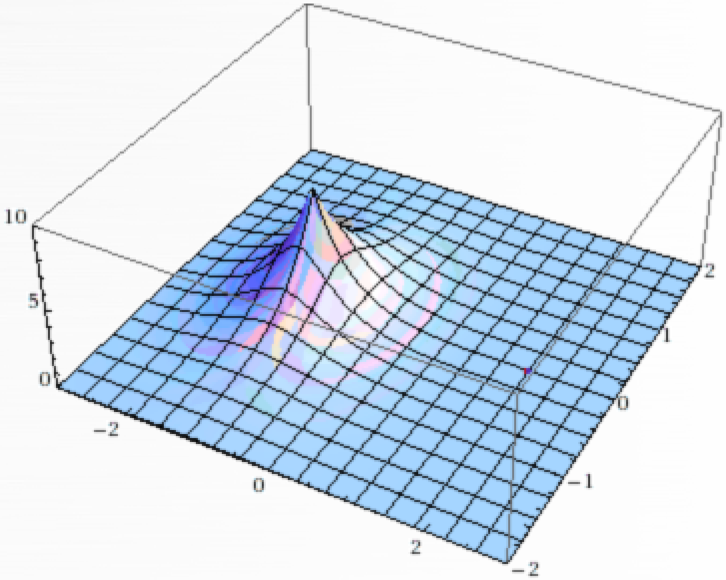
Example: Triplet state of H_2

Explicitly correlated wave function from H. James and A. Coolidge, JCP, 6 (1938) 730.

$$\left|\Psi^{T}_{exact}\left(\vec{R},\vec{r}_2\right)\right|^2$$



$$\left|\Phi^{T}_{HF}\left(\vec{R},\vec{r}_2\right)\right|^2=\left|\hat{A}\,\sigma^{\alpha}_{g}(1)\sigma^{\alpha}_{u}(2)\right|^2$$



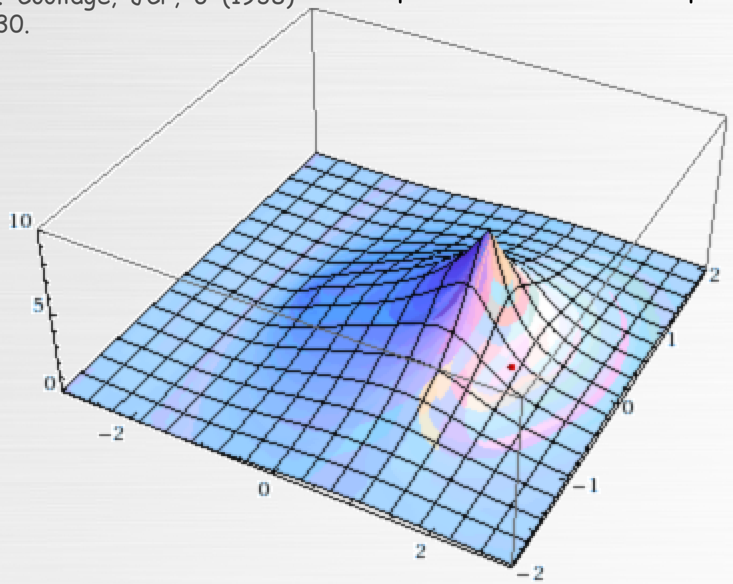
Fermi correlation in open shell wave functions

Fermi correlation: Correlation due to the Pauli principle (w.f. antisymmetry).

Another example: Open-Shell Singlet (OSS) ${}^{1}\Sigma_{u}^{+}$ state of H_2

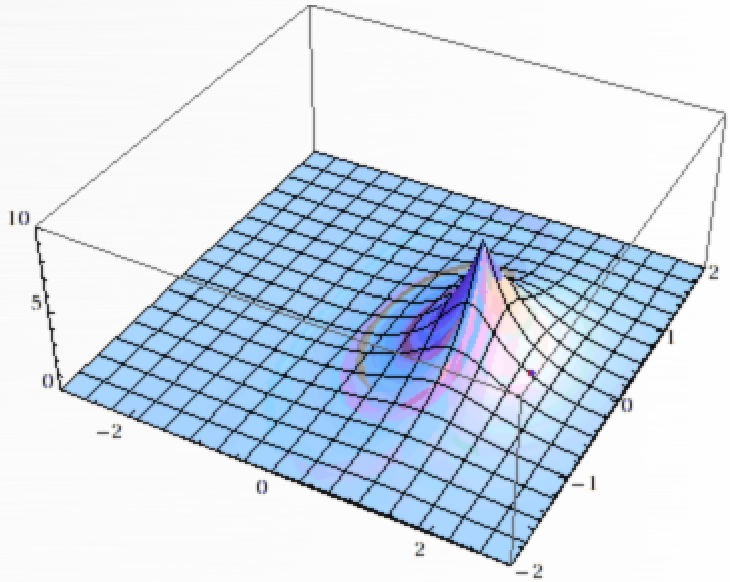
Explicitly correlated wave function from H. James and A. Coolidge, JCP, 6 (1938) 730.

$$\left|\Psi_{exact}^{OSS}\left(\vec{R},\vec{r}_2\right)\right|^2$$



Two-configurational wave function

$$\left|\Phi_{HF}^{OSS}\left(\vec{R},\vec{r}_2\right)\right|^2=\left|\frac{1}{\sqrt{2}}\left(\hat{A}\,\sigma_g^{\alpha}(1)\sigma_u^{\beta}(2)-\hat{A}\,\sigma_g^{\beta}(1)\sigma_u^{\alpha}(2)\right)\right|^2$$



Electron correlation

O. Sinanoğlu (1964) Adv. Chem. Phys. 6:315-412

$$E_{corr} = \left\langle \Phi_{HF} \middle| \hat{H} - E_{HF} \middle| \Psi \right\rangle$$

correlation energy

intermediate normalization $\left\langle \Phi_{HF} \middle| \Psi \right\rangle = 1$

$$\Psi = \Phi_{HF} + \sum_{\substack{i\\a}} C_i^a \Phi_i^a + \sum_{\substack{i<j\\a<b}} C_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{\substack{i<j<k\\a<b<c}} C_{ijk}^{abc} \Phi_{ijk}^{abc} + \dots$$

$$E_{corr} = \sum_{\substack{i<j\\a<b}} C_{ij}^{ab} \left\langle \Phi_{HF} \middle| \hat{H} - E_{HF} \middle| \Phi_{ij}^{ab} \right\rangle = \sum_{i<j} \varepsilon_{ij}$$

pairwise interactions in H;
only pair correlations survive

Dynamic and non-dynamic electron correlation

dynamic correlation

single reference wavefunction

$$\Psi \approx \Phi_{HF}$$

RS perturbation theory is valid

$$E_{corr} \approx \sum_{\substack{i<j \\ a<b}} \frac{\left| \left\langle \Phi_{HF} \middle| \hat{H} - E_{HF} \middle| \Phi_{ij}^{ab} \right\rangle \right|^2}{E_{HF} - E_{ij}^{ab}} + \dots$$

non-dynamic (static) correlation

multi reference wavefunction

$$\Psi \approx C_0 \Phi_0 + C_1 \Phi_1 + \dots$$

$$C_0 \approx C_1 \approx C_p$$

RS perturbation theory is <u>not valid</u>

(near) zero denominators

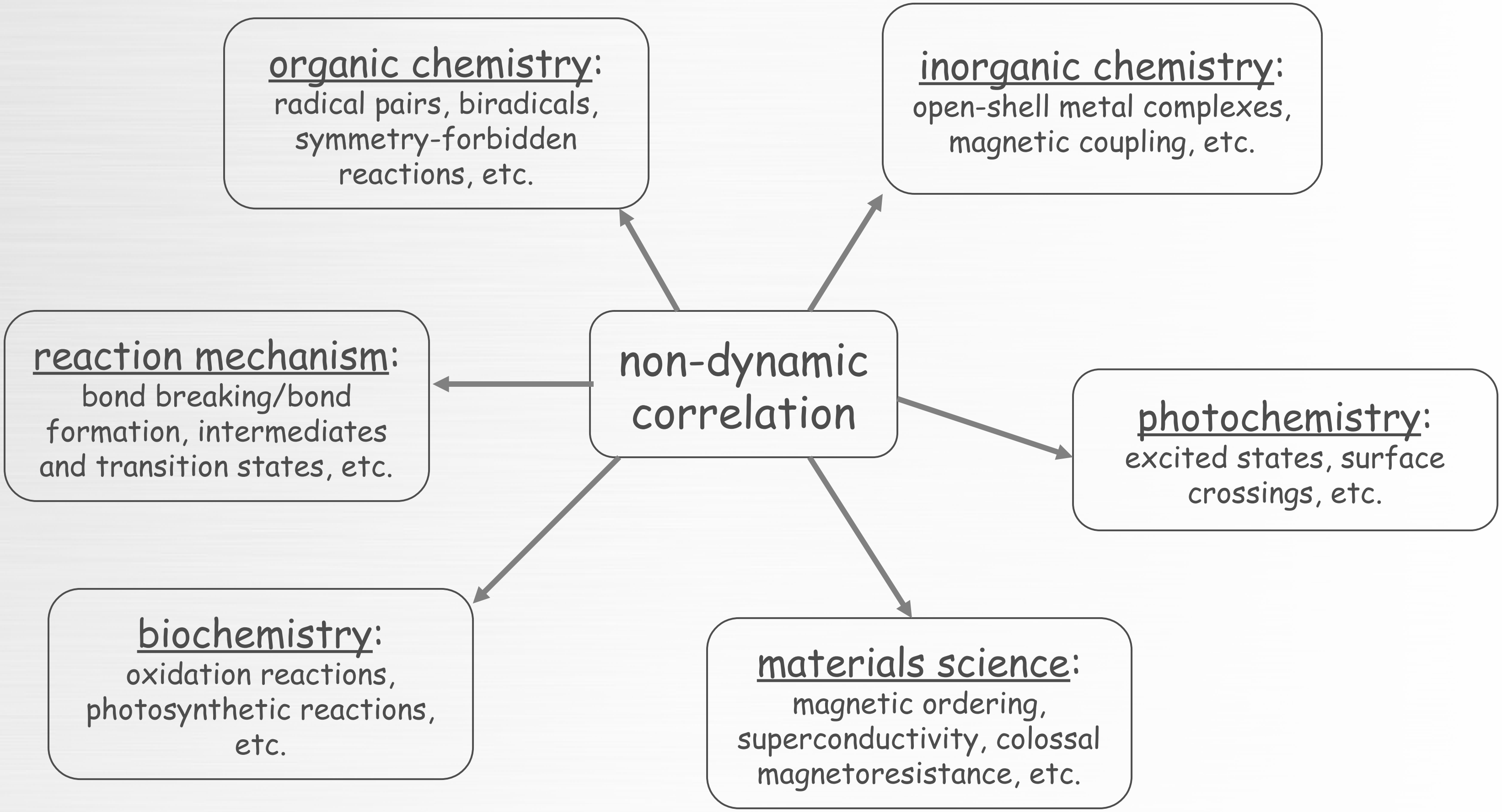
$$E_0 \approx E_1 \approx E_p$$

divergent PT series

Non-dynamic electron correlation

Electron correlation – deviation from mean-field approximation

Non-dynamic correlation – multi-reference wavefunction…



non-dynamic correlation

<u>organic chemistry</u>: radical pairs, biradicals, symmetry-forbidden reactions, etc.

<u>inorganic chemistry</u>: open-shell metal complexes, magnetic coupling, etc.

<u>reaction mechanism</u>: bond breaking/bond formation, intermediates and transition states, etc.

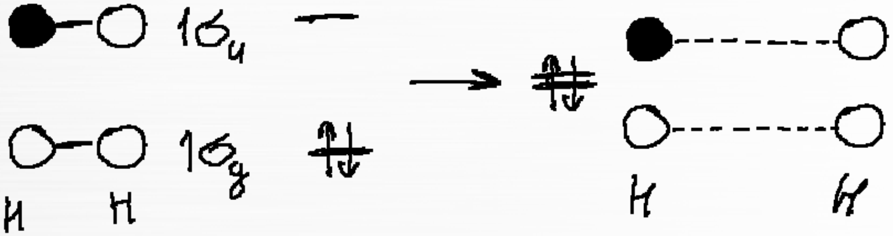
<u>photochemistry</u>: excited states, surface crossings, etc.

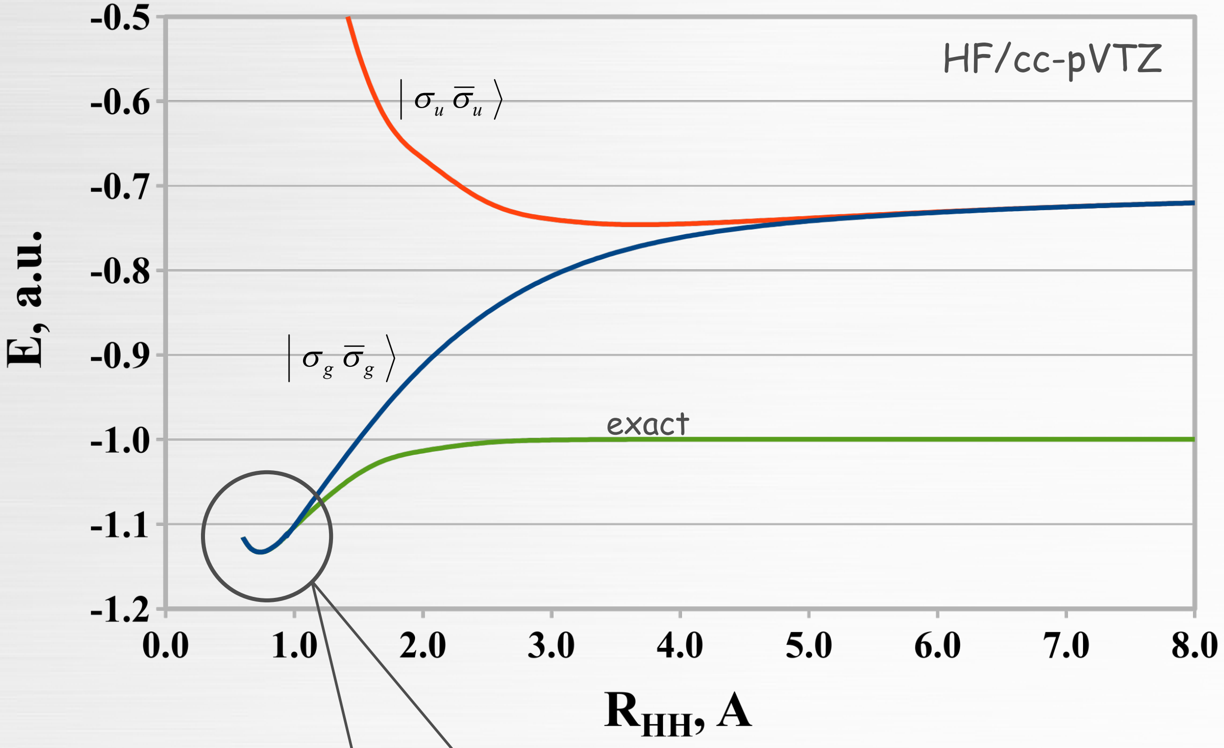
<u>biochemistry</u>: oxidation reactions, photosynthetic reactions, etc.

<u>materials science</u>: magnetic ordering, superconductivity, colossal magnetoresistance, etc.

Examples of non-dynamic electron correlation

Bond breaking in H_2



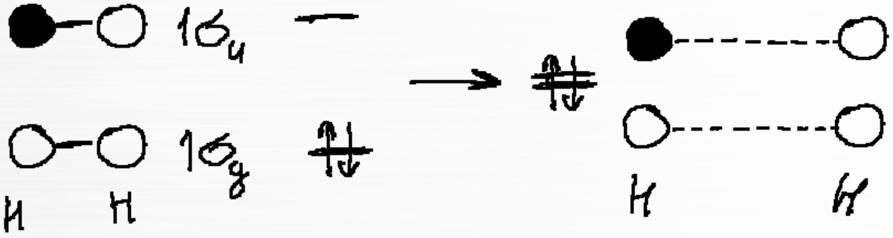


PT is valid here

PT is no loner valid at stretched bondlength

Examples of non-dynamic electron correlation

Bond breaking in H_2



second order correlation energy:

$$E_{corr}^{(2)} = \sum_{\substack{i<j\\ a<b}} \frac{\left| \left\langle \Phi_{HF} \middle| \hat{H} - E_{HF} \middle| \Phi_{ij}^{ab} \right\rangle \right|^2}{E_{HF} - E_{ij}^{ab}}$$

expectation values:

$$E_{HF} = \left\langle \sigma_g \overline{\sigma}_g \middle| \hat{H} \middle| \sigma_g \overline{\sigma}_g \right\rangle \qquad E_{ij}^{ab} = \left\langle \sigma_u \overline{\sigma}_u \middle| \hat{H} \middle| \sigma_u \overline{\sigma}_u \right\rangle$$

coupling term:

$$\left\langle \Phi_{HF} \middle| \hat{H} - E_{HF} \middle| \Phi_{ij}^{ab} \right\rangle = \left\langle \sigma_g \overline{\sigma}_g \middle| r_{12}^{-1} \middle| \sigma_u \overline{\sigma}_u \right\rangle = K_{gu}$$

exchange integral

Slater-Condon rules

vacuum state: $\Phi_0 = \hat{\mathcal{A}}\left(\phi_1^{\sigma_1}\,\phi_2^{\sigma_2}\ldots\phi_i^{\sigma_i}\ldots\phi_j^{\sigma_j}\ldots\right)$

single substitution: $\Phi_i^a = \hat{\mathcal{A}}\left(\phi_1^{\sigma_1}\,\phi_2^{\sigma_2}\ldots\phi_a^{\sigma_a}\ldots\phi_j^{\sigma_j}\ldots\right)$

double substitution: $\Phi_{ij}^{ab} = \hat{\mathcal{A}}\left(\phi_1^{\sigma_1}\,\phi_2^{\sigma_2}\ldots\phi_a^{\sigma_a}\ldots\phi_b^{\sigma_b}\ldots\right)$

Hamiltonian: $\hat{H} = \sum_i \hat{h}(i) + \sum_{i<j} r_{ij}^{-1}$

$$\left\langle \Phi_0 \middle| \hat{H} \middle| \Phi \right\rangle = \sum_i^{occ} h_{ii} + \sum_{i<j}^{occ}\left(\langle i\,j \,|\, i\,j\rangle - \langle i\,j \,|\, j\,i\rangle\right)$$

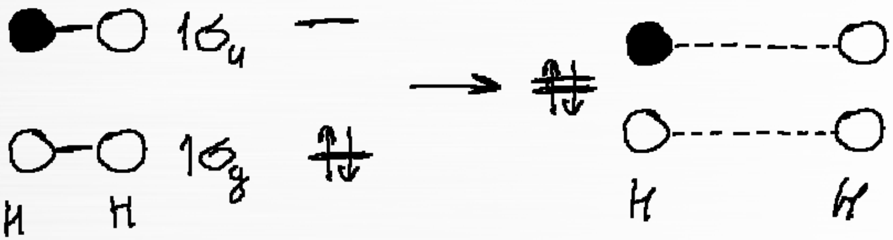
$$\left\langle \Phi_0 \middle| \hat{H} \middle| \Phi_i^a \right\rangle = h_{ia} + \sum_k^{occ}\left(\langle i\,k \,|\, a\,k\rangle - \langle i\,k \,|\, k\,a\rangle\right) = \left\langle i \middle| \hat{F} \middle| a \right\rangle$$

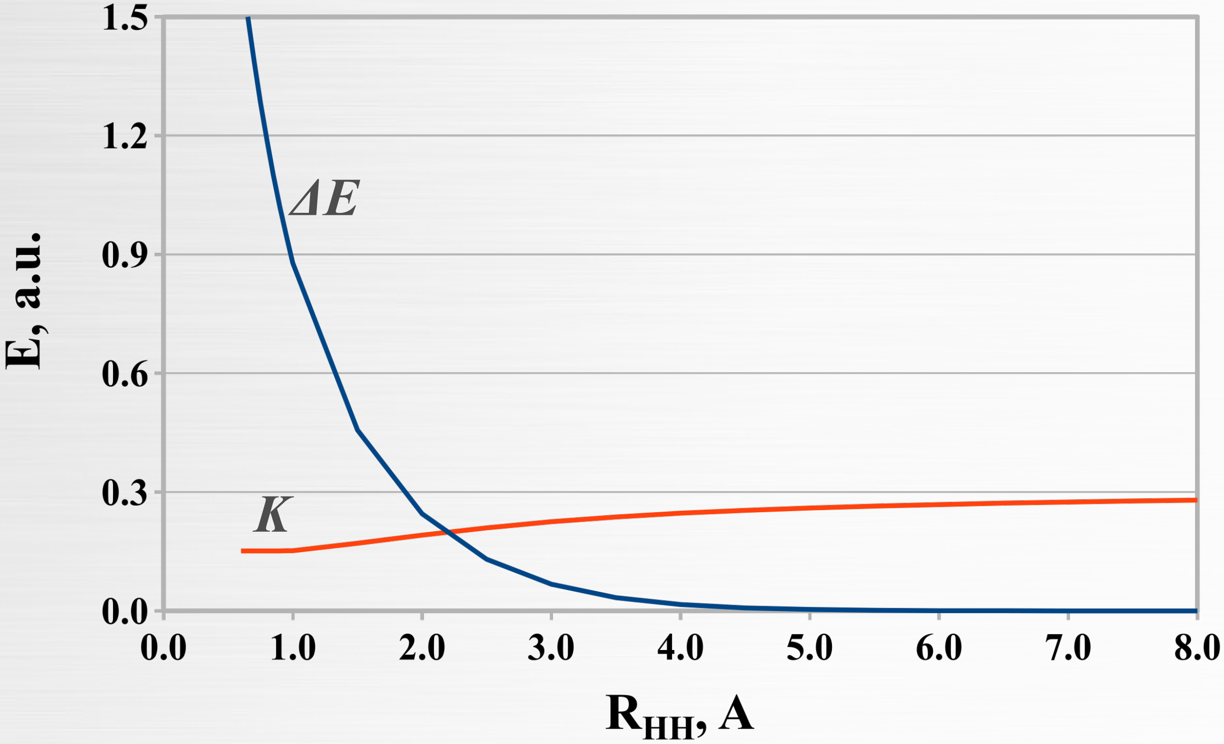
$$\left\langle \Phi_0 \middle| \hat{H} \middle| \Phi_{ij}^{ab} \right\rangle = \langle i\,j \,|\, a\,b\rangle - \langle i\,j \,|\, b\,a\rangle$$

two-electron integral: $\langle i\,j \,|\, p\,q\rangle = \iint d\vec{r}_1 d\vec{r}_2\, r_{12}^{-1}\, \phi_i^{\sigma_i *}(\vec{r}_1)\,\phi_p^{\sigma_p}(\vec{r}_1)\,\phi_j^{\sigma_j *}(\vec{r}_2)\,\phi_q^{\sigma_q}(\vec{r}_2)$

Examples of non-dynamic electron correlation

Bond breaking in H_2





when $\Delta E \sim K$,
PT series blows up

need to remove the
(near) degeneracy

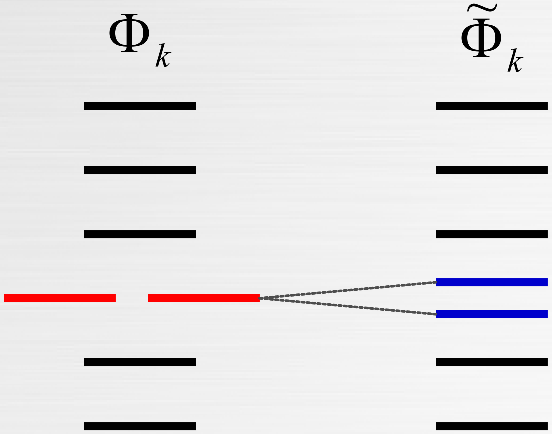
Quasi-degenerate perturbation theory

Let $\hat{H} = \hat{H}_0 + \lambda \hat{V}$ (λ - perturbation parameter)

and $\hat{H}_0 \Phi_k = E_k \Phi_k\,, \quad \Phi_k, \Phi_{k'}, \ldots \in \mathrm{H}_d\,, \quad E_k = E_{k'} = \ldots$

where H_d is a d-fold degenerate subspace

then
$$\begin{pmatrix} \langle \Phi_k|\hat{V}|\Phi_k\rangle & \langle \Phi_k|\hat{V}|\Phi_{k'}\rangle & \cdots \\ \langle \Phi_{k'}|\hat{V}|\Phi_k\rangle & \langle \Phi_{k'}|\hat{V}|\Phi_{k'}\rangle & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}\begin{pmatrix}\tilde{\Phi}_k\\ \tilde{\Phi}_{k'}\\ \vdots \\ \vdots\end{pmatrix} = \begin{pmatrix} U_k & 0 & \cdots & \cdots \\ 0 & U_{k'} & \cdots & \cdots \\ \vdots & \vdots & \ddots & \\ \vdots & \vdots & & \ddots\end{pmatrix}\begin{pmatrix}\tilde{\Phi}_k\\ \tilde{\Phi}_{k'}\\ \vdots\\ \vdots\end{pmatrix}$$



degeneracy lifted → NDPT is good again

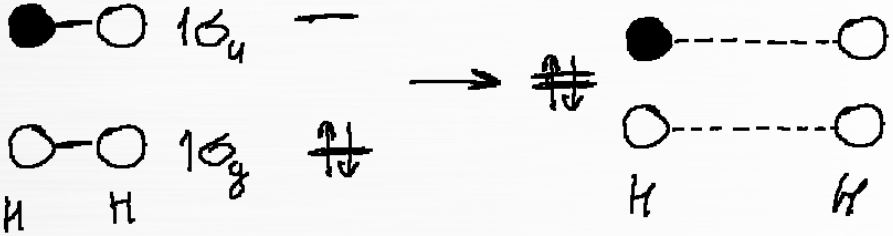
NDPT uses renormalized perturbation

$$\hat{W} = \hat{P}_d \hat{V} \hat{P}_d + \hat{P}_d \hat{V} \frac{\hat{Q}_d}{E - \hat{H}_0} \hat{V} \hat{P}_d\,; \quad \hat{P}_d = \sum_{k \in \mathrm{H}_d} |\, k \rangle\langle k\,|\,; \quad \hat{Q}_d = 1 - \hat{P}$$

remove what was already taken into account

Examples of non-dynamic electron correlation

Bond breaking in H_2



Apply QDPT and solve 2X2 secular problem

$$\begin{pmatrix} E_{HF} & K_{gu} \\ K_{gu} & E_{ij}^{ab} \end{pmatrix} \begin{pmatrix} \tilde{\Phi}_0 \\ \tilde{\Phi}_2 \end{pmatrix} = \begin{pmatrix} E_0 & 0 \\ 0 & E_2 \end{pmatrix} \begin{pmatrix} \tilde{\Phi}_0 \\ \tilde{\Phi}_2 \end{pmatrix}$$

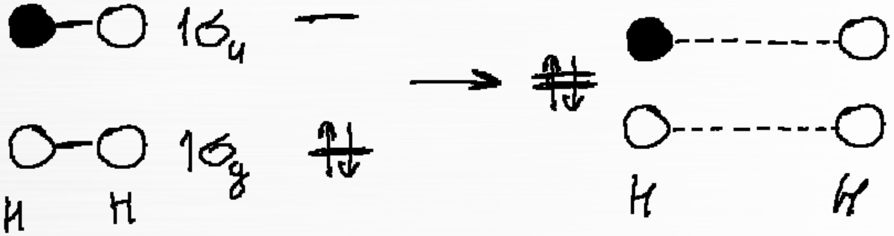
Eigenvalues:

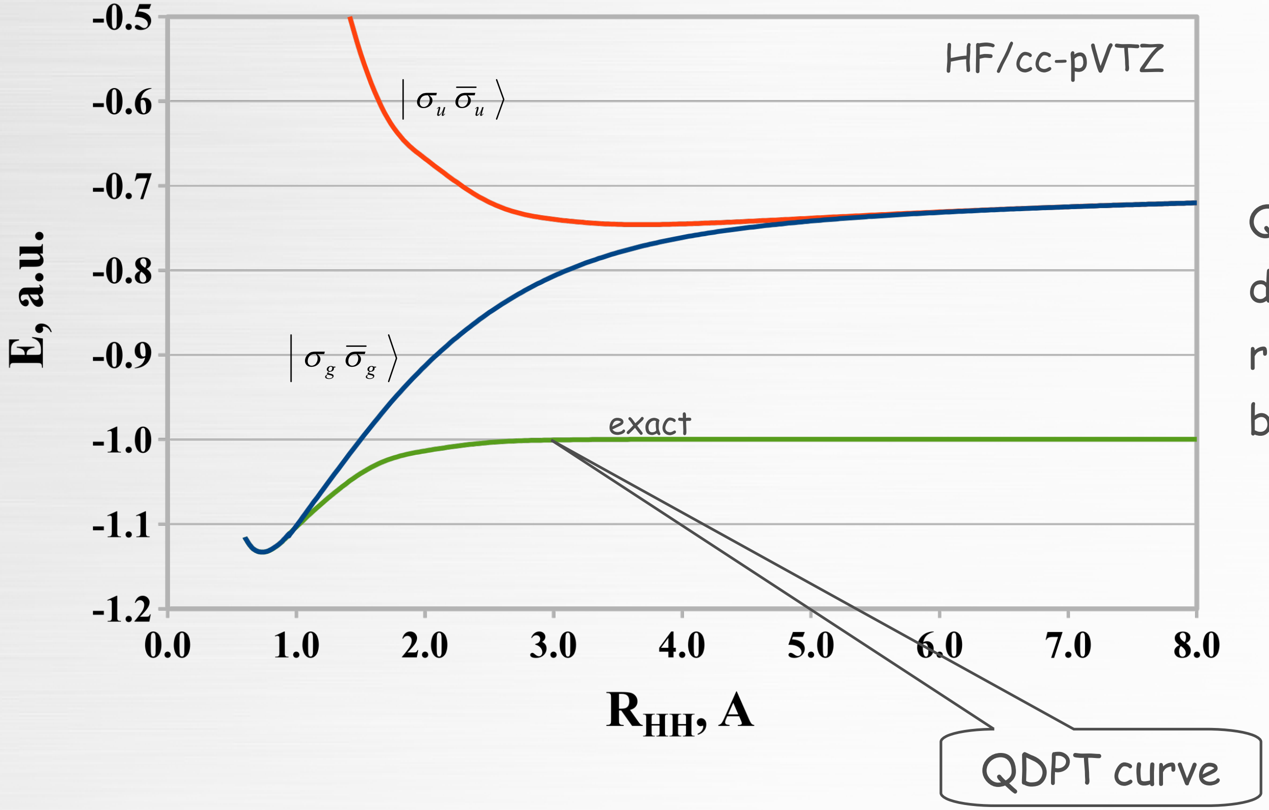
$$E_{0,2} = \tfrac{1}{2}\left(E_{HF} - E_{ij}^{ab}\right) \mp \tfrac{1}{2}\sqrt{\left(E_{HF} - E_{ij}^{ab}\right)^2 + 4\,K_{gu}^2}$$

Non-linear in energies and couplings

Examples of non-dynamic electron correlation

Bond breaking in H$_2$

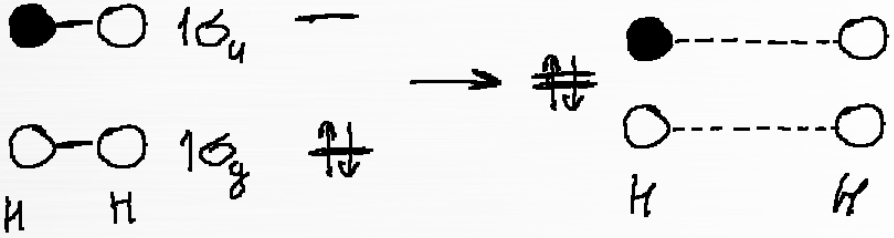




QDPT lifts the degeneracy and recovers the exact behavior

Examples of non-dynamic electron correlation

Bond breaking in H_2



2X2 QDPT secular problem
$$\begin{pmatrix} E_{HF} & K_{gu} \\ K_{gu} & E_{ij}^{ab} \end{pmatrix} \begin{pmatrix} \tilde{\Phi}_0 \\ \tilde{\Phi}_2 \end{pmatrix} = \begin{pmatrix} E_0 & 0 \\ 0 & E_2 \end{pmatrix} \begin{pmatrix} \tilde{\Phi}_0 \\ \tilde{\Phi}_2 \end{pmatrix}$$

new eigenfunctions – linear conbinations of old functions

$$\tilde{\Phi}_0 = C_{00}\,\Phi_{HF} + C_{20}\,\Phi_{ij}^{ab} \qquad \tilde{\Phi}_2 = C_{02}\,\Phi_{HF} + C_{22}\,\Phi_{ij}^{ab}$$

then $E_0 = C_{00}^2\,E_{HF} + C_{20}^2\,E_{ij}^{ab} + 2\,C_{00}\,C_{20}\,K_{gu}\;;\quad C_{00} > 0; C_{20} < 0$

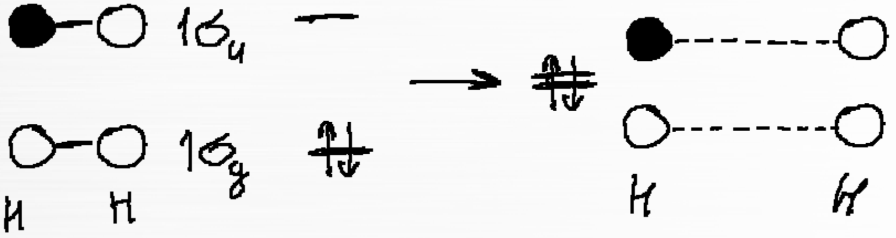
because $\Phi_{HF} = \left|\,\sigma_g\,\bar{\sigma}_g\,\right\rangle \qquad \Phi_{ij}^{ab} = \left|\,\sigma_u\,\bar{\sigma}_u\,\right\rangle \longrightarrow 2\,C_{00}^2 = n_g \qquad 2\,C_{20}^2 = n_u$

$$E_0 = \frac{n_g}{2}E_{HF} + \frac{n_u}{2}E_{ij}^{ab} - \left(n_g\,n_u\right)^{1/2} K_{gu}$$

energy is a function of orbital's fractional occupation numbers (FONs)

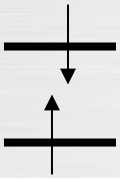
Examples of non-dynamic electron correlation

Bond breaking in H_2

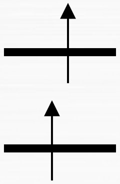


energies and coupling terms:

$$E_0 = \frac{n_g}{2} E_{HF} + \frac{n_u}{2} E_{ij}^{ab} - \left(n_g \, n_u \right)^{1/2} K_{gu}$$



$$E_{bs-u} = \varepsilon_g + \varepsilon_u + J_{gu}$$



$$E_T = \varepsilon_g + \varepsilon_u + J_{gu} - K_{gu}$$

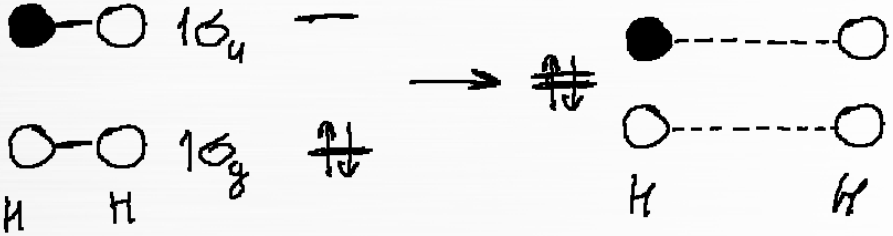
$$K_{gu} = E_{bs-u} - E_T$$

$$E_0 = \frac{n_g}{2} E_{HF} + \frac{n_u}{2} E_{ij}^{ab} - \left(n_g \, n_u \right)^{1/2} \left(E_{bs-u} - E_T \right)$$

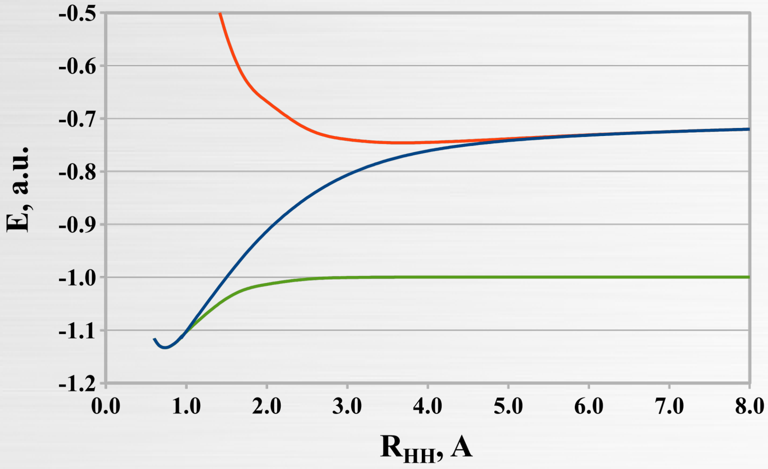
linear in energies only

Examples of non-dynamic electron correlation

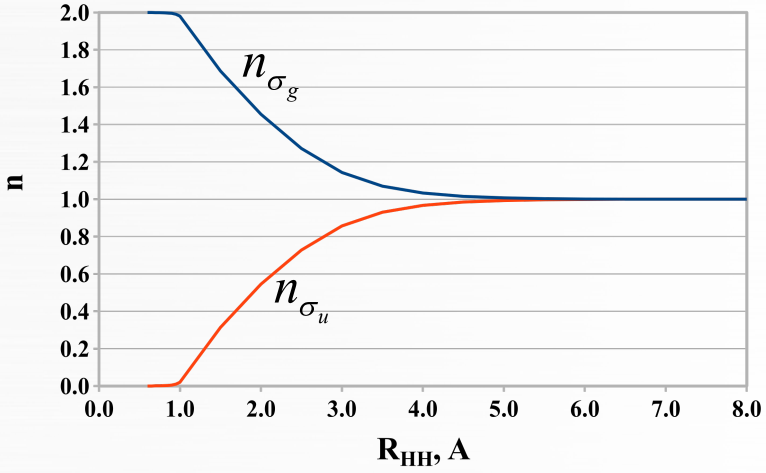
Bond breaking in H_2



energies



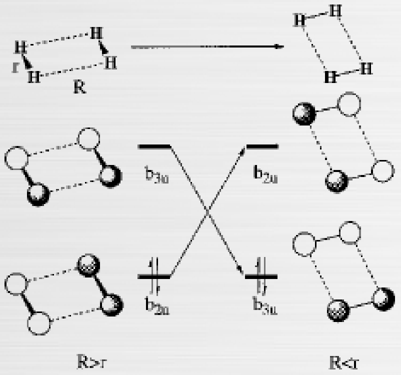
FONs in the exact energy

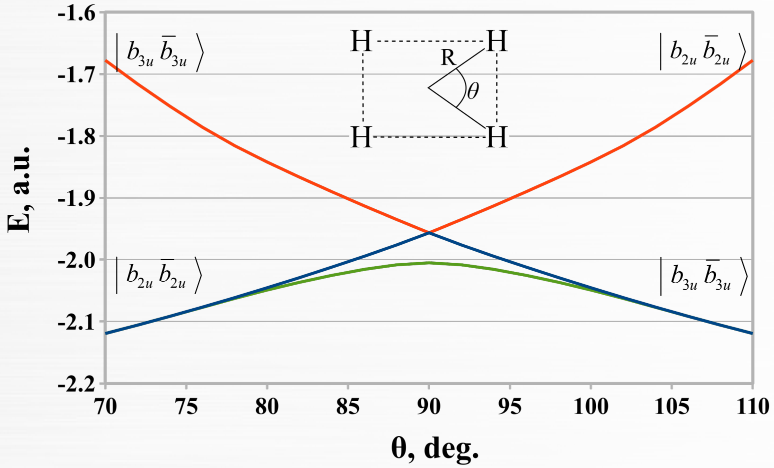


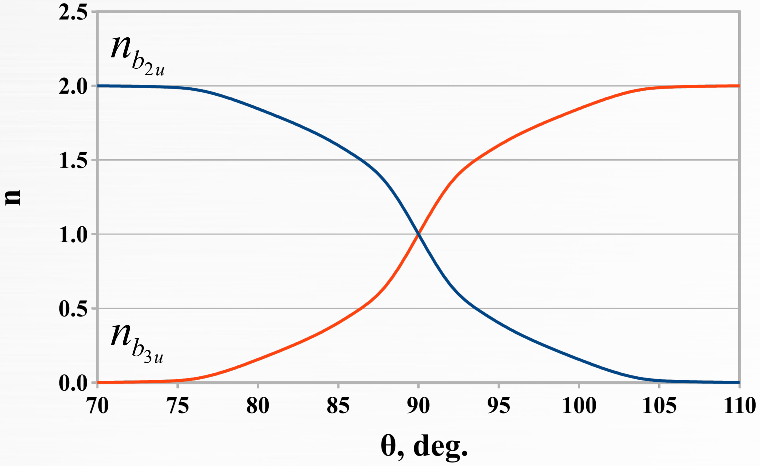
As bond breaks, FONs rapidly deviate from 2 and 0; converge at 1

Examples of non-dynamic electron correlation

Symmetry forbidden reaction: Automerization of rectangular H_4



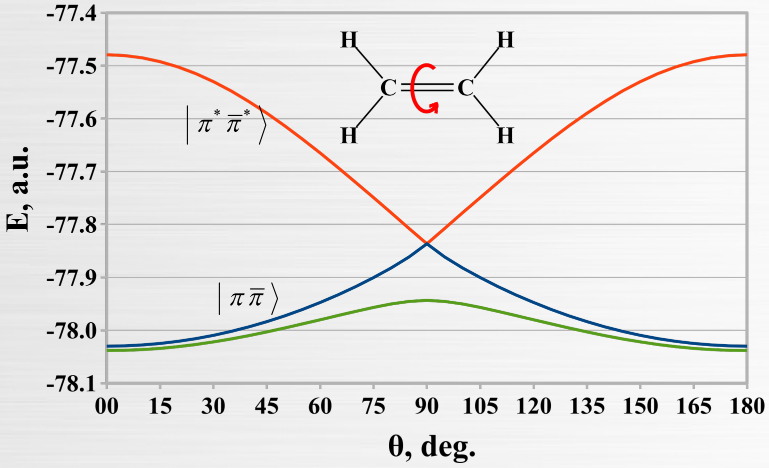


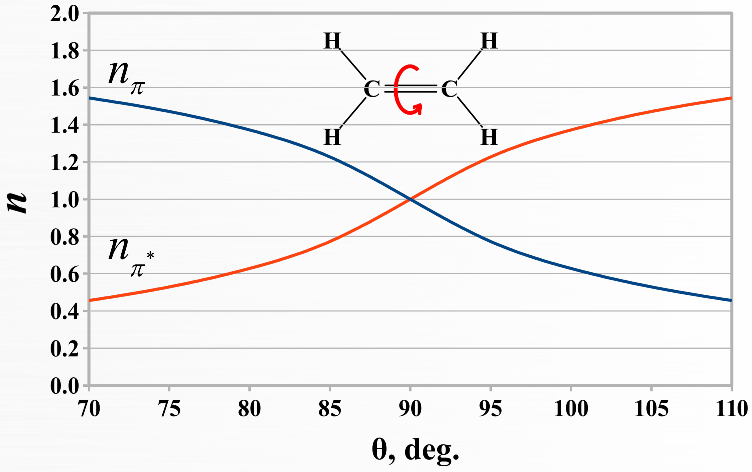


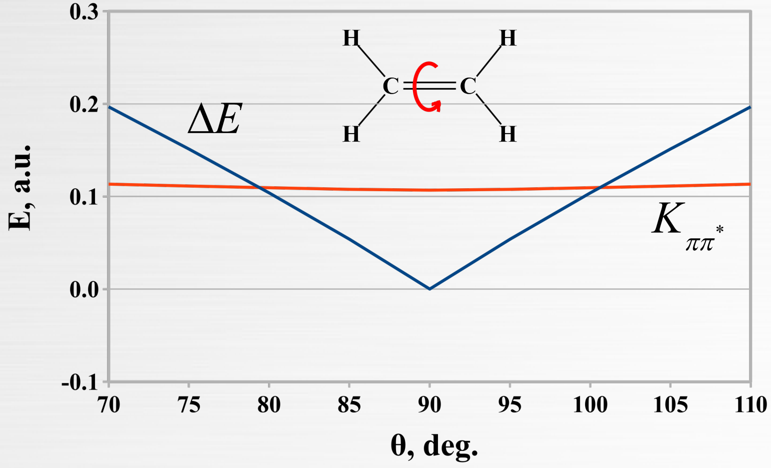
non-dynamic correlation sets in long before the degeneracy occurs

Examples of non-dynamic electron correlation

Double bond torsion of C_2H_4







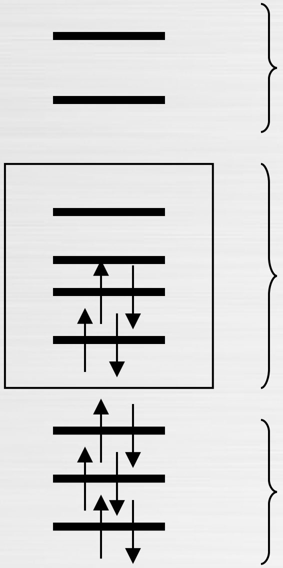
Multi-configurational wavefunction methods

complete-active
space wavefunction

$$\Psi_{CAS} = \sum_{(I,A)} C_I^A \, \hat{E}_I^A \left| \phi_1^{\sigma_1} \phi_2^{\sigma_2} \ldots \phi_N^{\sigma_N} \right\rangle$$

excitation operators
(spin-symmetry adapted)

$$\hat{E}_I^A ; \quad I \in \{i, ij, ijk, \ldots\}; \, A \in \{a, ab, abc, \ldots\}$$



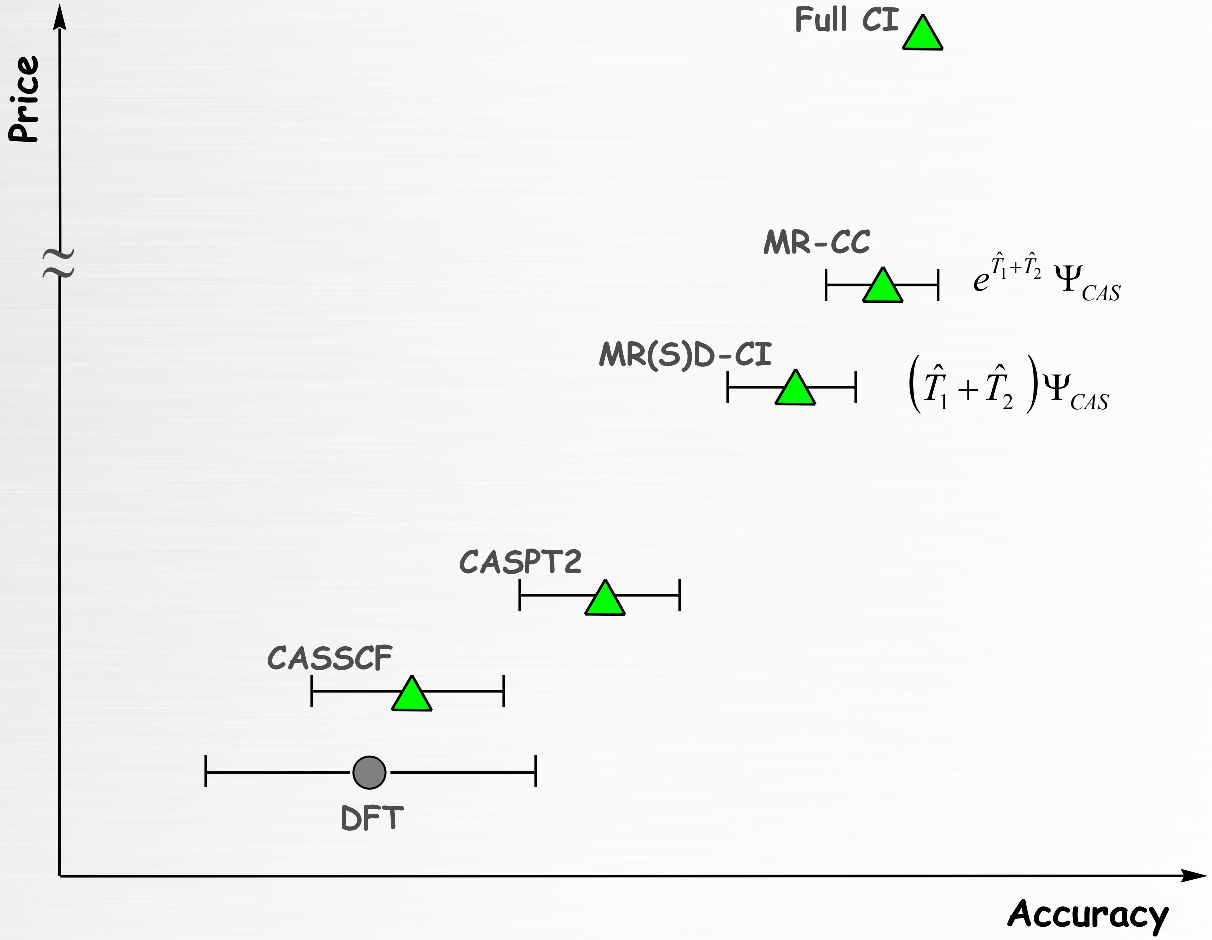
vacant orbitals — no excitations to this space

active orbitals — all possible (spin-adapted) excitations in this space

core orbitals — no excitations from this space

$$E_{CAS} = \left\langle \Psi_{CAS} \middle| \hat{H} \middle| \Psi_{CAS} \right\rangle$$ is minimized w.r.t. both C_I^A and $\phi_k^{\sigma_k}$

Computational methods for non-dynamic correlation



Standard Kohn-Sham DFT

Hohenberg-Kohn theorem:

Ground state energy is uniquely defined by the ground state density $\boldsymbol{\rho}$

$E[\rho]$ is it a functional?

Kohn-Sham method:

Assumes that any $\boldsymbol{\rho}$ can be mapped onto the ground state (single Slater determinant) of a non-interacting system (KS reference system)

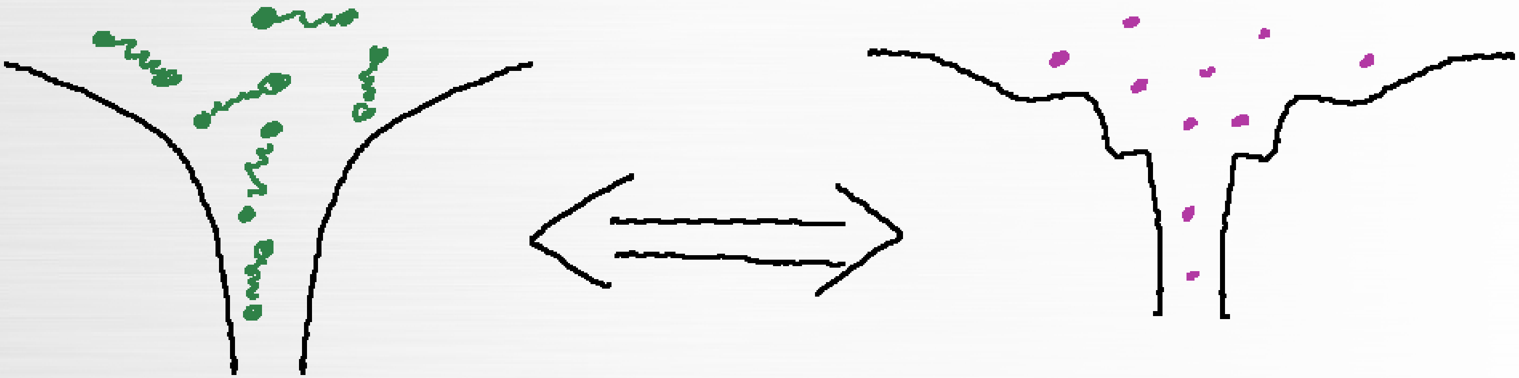
$$\rho \Leftrightarrow \rho_S$$

single determinant density

Adiabatic connection: Often used to justify KS method and construct XC functionals

W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965)

Kohn-Sham method in DFT

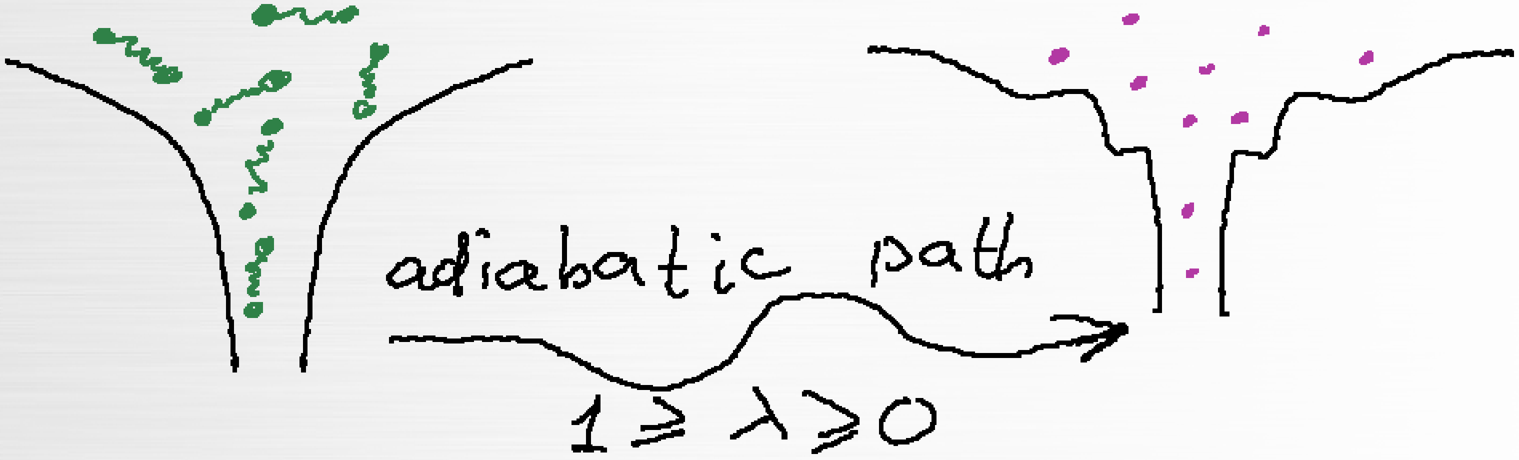


$\lambda = 1$ $\lambda \cdot V_{ee}$ $\lambda = 0$

V_{ext} V_s

ρ_0 ρ_s

Adiabatic connection in Kohn-Sham method



- System remains in the ground state
- Finite gap btw the G.S. and the 1st E.S.
- Pert. theory remains valid along the path

$$E_1 - E_0 = \int_0^1 \frac{dE_\lambda}{d\lambda} d\lambda$$

$\lambda = 1$ $\lambda \cdot V_{ee}$ $\lambda = 0$

J. Harris, PRA 29, 1648 (1984)

Kohn-Sham method in DFT

Assumptions

- ρ_s is a single determinant density
- V_s exists

physical density $\rho_0 = \rho_s$ non-interacting density

ρ_s from N lowest eigenfunctions of $V_s(\vec{r}) = V_{ext}(\vec{r}) + \dfrac{\delta E_{Hxc}[\rho]}{\delta \rho(\vec{r})}$

$$\begin{aligned} E[\rho_0] &= T_s[\rho_0] + \int \rho_0(\vec{r}) V_{ext}(\vec{r}) d\vec{r} + J[\rho_0] + E_{xc}[\rho_0] \\ &= T_s[\rho_0] + \int \rho_0(\vec{r}) V_{ext}(\vec{r}) d\vec{r} + E_{Hxc}[\rho_0] \end{aligned}$$

total energy of
interacting system

Can be solved at a mean-field cost, if E_{Hxc} is known (usually, approximated)

$$E_{Hxc} = \int_0^1 \frac{dE_\lambda}{d\lambda} d\lambda - \int \left(V_{ext}(\vec{r}) - V_s(\vec{r})\right) \rho(\vec{r}) d\vec{r}$$

can be obtained from adiabatic connection

KS DFT vs. Ensemble DFT for ground states

	KS DFT	Ensemble DFT
Applicability:	ground state only	ground and excited states
Existence of V_{xc}:	assumed	rigorously proved
Non-interacting reference:	single-determinant; fixed occupations	multi-reference; fractional occupations
Bond breaking:	brakes symmetry and/or wrong	doesn’t brake symmetry

Ensemble DFT (eDFT)

<u>Ground states</u>:

S. M. Valone	(1980)
E. H. Lieb	(1983)
H. & R. Englisch	(1984)

Any physical density can be mapped onto *ensemble* density

$$\rho \Leftrightarrow \rho_{ens} = \sum_k \omega_k \, \rho_k$$

Exact functional (E.H.Lieb):

$$F(\rho) = \sum_k \omega_k \, F(\rho_k)$$

<u>Excited states</u>:

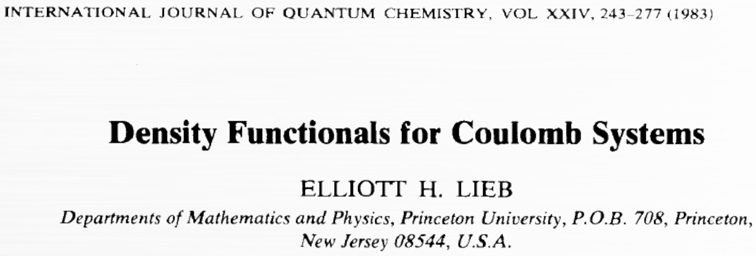
Gross, Oliveira, Kohn (1988): variational principle for ensembles of ground and excited states

$$\sum_k \omega_k \left\langle \Phi_k \middle| \hat{H} \middle| \Phi_k \right\rangle \geq \sum_k \omega_k \, E_k$$

basis for variational DFT for excited states

Basic ideas of eDFT

The most important work:



INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY, VOL XXIV, 243–277 (1983)

Density Functionals for Coulomb Systems

ELLIOTT H. LIEB

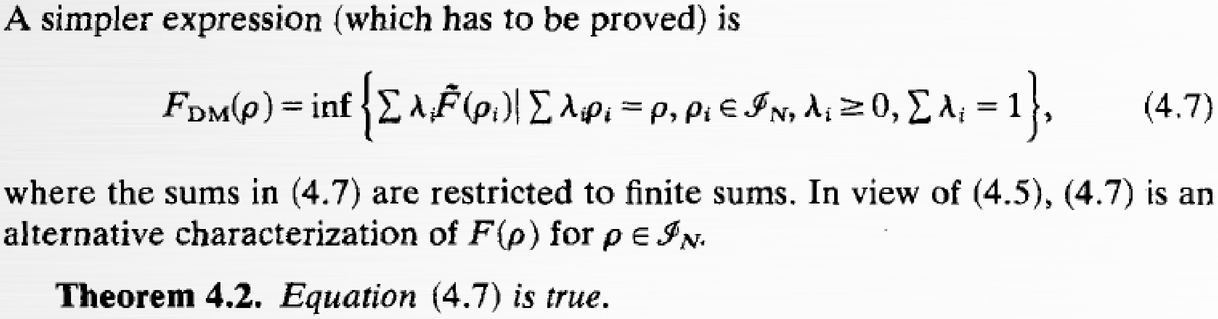
Departments of Mathematics and Physics, Princeton University, P.O.B. 708, Princeton, New Jersey 08544, U.S.A.

The most important results:

Hohenberg-Kohn functional F_{HK} – not defined for all densities, not convex

Levy's constrained search functional $\tilde{F}$ – not convex

Ensemble functional F_{DM} – the one and only that has all the desired properties



A simpler expression (which has to be proved) is

$$F_{\rm DM}(\rho) = \inf\left\{\sum \lambda_i \tilde{F}(\rho_i) \,\middle|\, \sum \lambda_i \rho_i = \rho, \rho_i \in \mathcal{I}_N, \lambda_i \geq 0, \sum \lambda_i = 1\right\}, \qquad (4.7)$$

where the sums in (4.7) are restricted to finite sums. In view of (4.5), (4.7) is an alternative characterization of $F(\rho)$ for $\rho \in \mathcal{I}_N$.

Theorem 4.2. *Equation* (4.7) *is true.*

F_{DM} is defined for any density, is convex and differentiable (H. & R. Englisch, 1984)

Feasibility of eDFT

Practical proof of feasibility:

construct the KS potential V_s from the exact density ρ

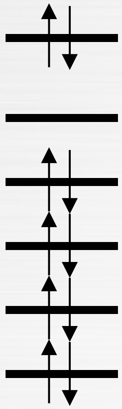
solve $\left(-\frac{1}{2}\nabla^2 + V_s(\vec{r})\right)\phi_i(\vec{r}) = \varepsilon_i\,\phi_i(\vec{r})$ under the constraint

$$\rho_s(\vec{r})\left\{=\sum_i^{occ} 2\left|\phi_i(\vec{r})\right|^2\right\} \equiv \rho(\vec{r})$$

E.-J. Baerends et al., (1998):	molecular systems H_2+H_2, C_2, CH_2
R. C. Morrison (2002):	Be-like atomic systems

not a ground state!!!

holes below
the Fermi level



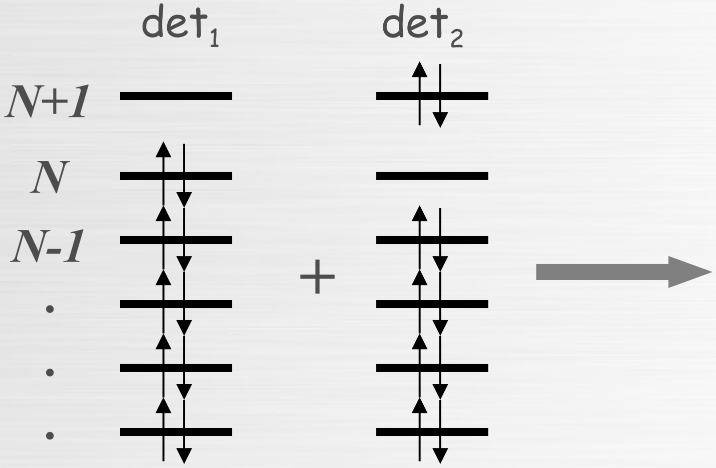
OR

Fractional Occupation Numbers

only a few KS orbitals with FONs

FONs in eDFT

Let $\rho_K(\vec{r}) = \sum_i^{occ} 2\left|\phi_i(\vec{r})\right|^2$ density of a single KS determinant



$$\rho_1(\vec{r}) = \sum_{i=1}^{N-1} 2\left|\phi_i(\vec{r})\right|^2 + 2\left|\phi_N(\vec{r})\right|^2$$

$$\rho_2(\vec{r}) = \sum_{i=1}^{N-1} 2\left|\phi_i(\vec{r})\right|^2 + 2\left|\phi_{N+1}(\vec{r})\right|^2$$

$$\begin{aligned}\rho_{ens}(\vec{r}) &= \lambda_1\,\rho_1(\vec{r}) + \lambda_2\,\rho_2(\vec{r}) \\ &= \sum_{i=1}^{N-1} 2\left|\phi_i(\vec{r})\right|^2 + 2\lambda_1\left|\phi_N(\vec{r})\right|^2 + 2\lambda_2\left|\phi_{N+1}(\vec{r})\right|^2\end{aligned}$$

FONs result from *ensemble* of KS densities

$$\rho_{ens} = \sum_k \lambda_k\,\rho_k \quad \longrightarrow \quad \rho_{ens} = \sum_i^{occ} n_i\left|\phi_i\right|^2$$

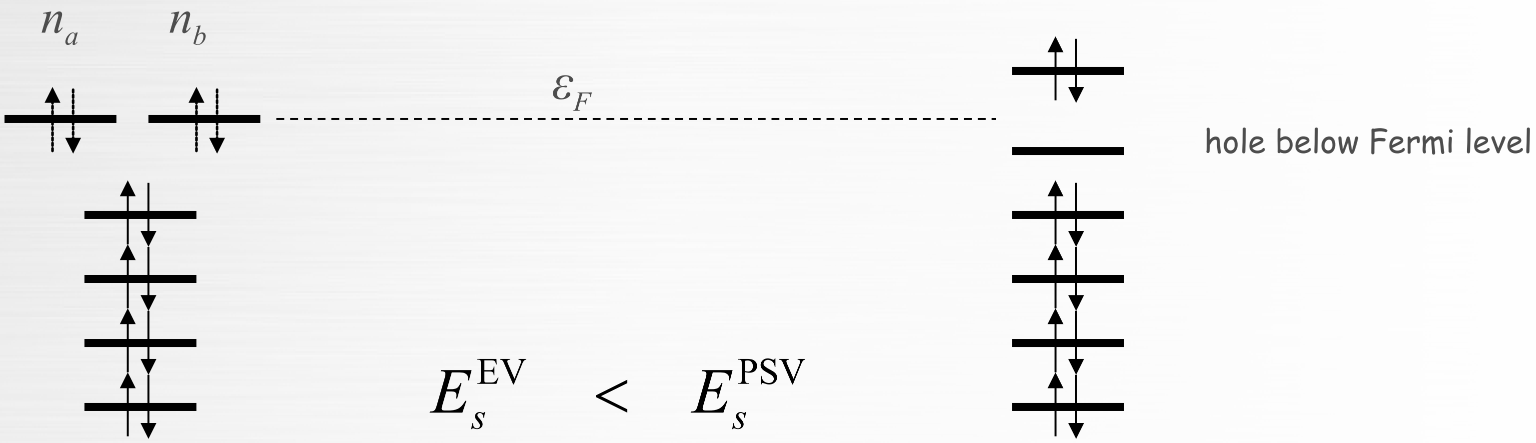
KS orbitals in eDFT

Giesbertz, Baerends (2010): Fractionally occupied KS orbitals become degenerate

$$\varepsilon_k = \mu + \frac{\partial E}{\partial n_k} \qquad \frac{\partial E}{\partial n_k} = 0; \quad 0 < n_k < 2$$

ensemble KS state

pure KS state



$$E_s^{\mathrm{EV}} \quad < \quad E_s^{\mathrm{PSV}}$$

$$\rho_s^{\mathrm{EV}} \quad = \quad \rho \qquad\qquad \rho_s^{\mathrm{PSV}} \quad \approx \quad \rho$$

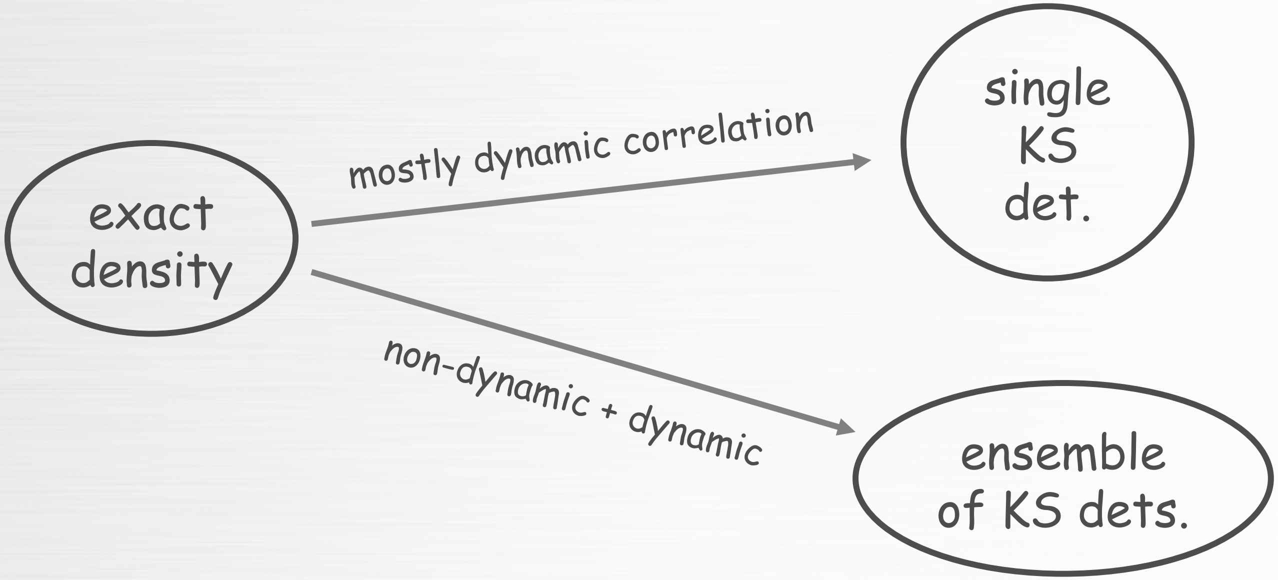
P. R. T. Schipper, O. Gritsenko & E.J. Baerends (1998; 1999)

eDFT and non-dynamic correlation

Ullrich, Kohn (2001)
van Leeuwen (2003)

not all exact densities can be mapped onto single KS determinant

some need ensemble KS densities



Non-dynamic correlation (WFT) → ensemble representation (DFT)

eDFT and XC functionals

usual approximate XC functionals – single KS det. densities

DFT energy: $E[\rho]=T_s[\rho]+\int\rho(\vec{r})V_{ext}(\vec{r})d\vec{r}+J[\rho]+E_{xc}[\rho]$

Classical Coulomb repulsion: $J[\rho]=\frac{1}{2}\int d\vec{r}_1\,d\vec{r}_2\;r_{12}^{-1}\,\rho(\vec{r}_1)\rho(\vec{r}_2)$

Let: $\rho_{ens}(\vec{r})=\lambda_a\,\rho_a(\vec{r})+\lambda_b\,\rho_b(\vec{r})+\ldots$

then

$$J[\rho_{ens}]=\tfrac{1}{2}\int d\vec{r}_1\,d\vec{r}_2\;r_{12}^{-1}\,\rho_{ens}(\vec{r}_1)\rho_{ens}(\vec{r}_2)$$

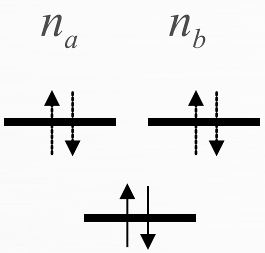
$$=\frac{\lambda_a^2}{2}\int\frac{\rho_a(\vec{r}_1)\rho_a(\vec{r}_2)}{r_{12}}d\vec{r}_2\,d\vec{r}_1+\quad\ldots\quad\frac{\lambda_a\,\lambda_b}{2}\int\frac{\rho_a(\vec{r}_1)\rho_b(\vec{r}_2)}{r_{12}}d\vec{r}_2\,d\vec{r}_1+\quad\ldots$$

cross terms (ghost terms, Gross et al, 2002) – should not appear in ensemble energy

$$E(\rho_{ens})=\sum_k\lambda_k\,E(\rho_k)$$

usual XC functionals do not eliminate ghost terms – wrong energies with FONs

eDFT XC functional for simple (2e,2o) model



non-interacting ($\lambda = 0$): ensemble
degenerate φ_a and φ_b

quasi-degenerate
PT ($\lambda \approx 0$):

$$\left\| \begin{matrix} E^{\lambda}_{a\bar{a}} & \Delta^{\lambda}_{ab} \\ \Delta^{\lambda}_{ab} & E^{\lambda}_{b\bar{b}} \end{matrix} \right\|$$

$$\Delta^{\lambda}_{ab} = \lambda \langle aa \,|\, bb \rangle = \left(E^{\lambda}_{a\bar{b}} - E^{\lambda}_{ab} \right)$$

exchange integral as energy difference

lowest root at $\lambda \approx 0$:

$$E = \frac{n^{\lambda}_a}{2} E^{\lambda}_{a\bar{a}} + \frac{n^{\lambda}_b}{2} E^{\lambda}_{b\bar{b}} - \left(n^{\lambda}_a \, n^{\lambda}_b \right)^{1/2} \left(E^{\lambda}_{a\bar{b}} - E^{\lambda}_{ab} \right)$$

λ-integration of
the lowest root

- FONs replaced by median values (λ-independent)
- no further degeneracies along the λ-path

energy of interacting ($\lambda = 1$)
strongly correlated system

$$E = \frac{n_a}{2} E^{DFT}_{a\bar{a}} + \frac{n_b}{2} E^{DFT}_{b\bar{b}} - \left(n_a \, n_b \right)^{1/2} \left(E^{DFT}_{a\bar{b}} - E^{DFT}_{ab} \right)$$

λ-Integration of eDFT energy

Hamiltonian: $$\hat{H}^{\lambda} = -\tfrac{1}{2}\sum_{i}\nabla_i^2 + \sum_{i} V_{ext}^{\lambda}\left(\vec{r}_i\right) + \lambda \sum_{i<j} r_{ij}^{-1}$$

Energy of configuration $\left|a\bar{a}\right\rangle$: $$E_{a\bar{a}}^{\lambda} = -\tfrac{1}{2}\sum_{k}\left\langle \phi_k \left|\nabla^2\right| \phi_k \right\rangle + \int d\vec{r}\,\rho\left(\vec{r}\right) V_{ext}^{\lambda}\left(\vec{r}\right) + E_{Hxc}^{\lambda}$$

Derivative w.r.t. λ: $$\frac{d\,E_{a\bar{a}}^{\lambda}}{d\,\lambda} = \int d\vec{r}\,\rho\left(\vec{r}\right)\frac{d\,V_{ext}^{\lambda}}{d\,\lambda} + \frac{d\,E_{Hxc}^{\lambda}}{d\,\lambda}$$

Expand the secular matrix: $$\begin{pmatrix} E_{a\bar{a}}^{\lambda} & \Delta_{ab}^{\lambda} \\ \Delta_{ab}^{\lambda} & E_{b\bar{b}}^{\lambda} \end{pmatrix} = \begin{pmatrix} E_{a\bar{a}}^{0} & 0 \\ 0 & E_{b\bar{b}}^{0} \end{pmatrix} + \lambda \begin{pmatrix} \dfrac{d\,E_{a\bar{a}}^{\lambda}}{d\,\lambda} & \dfrac{d\,\Delta_{ab}^{\lambda}}{d\,\lambda} \\ \dfrac{d\,\Delta_{ab}^{\lambda}}{d\,\lambda} & \dfrac{d\,E_{b\bar{b}}^{\lambda}}{d\,\lambda} \end{pmatrix} + O\left(\lambda^2\right)$$

Lowest root (expansion): $$E^{\lambda} = \frac{n_a^{\lambda}}{2}E_{a\bar{a}}^{0} + \frac{n_b^{\lambda}}{2}E_{b\bar{b}}^{0} + \lambda\left(\frac{n_a^{\lambda}}{2}\frac{d\,E_{a\bar{a}}^{\lambda}}{d\,\lambda} + \frac{n_b^{\lambda}}{2}\frac{d\,E_{b\bar{b}}^{\lambda}}{d\,\lambda} - \left(n_a^{\lambda}\,n_b^{\lambda}\right)^{1/2}\frac{d\,\Delta_{ab}^{\lambda}}{d\,\lambda}\right)$$

λ-Integration of eDFT energy (continued)

Integrate: $E^1 - E^0 = \int_0^1 d\lambda \frac{dE^\lambda}{d\lambda}$ assuming that n_a and n_b do not depend on λ

$$= \int d\vec{r}\,\rho_{ens}(\vec{r})\left(V^1_{ext}(\vec{r}) - V^0_{ext}(\vec{r})\right) + \frac{n_a}{2}E^1_{Hxc}\left[a\bar{a}\right] + \frac{n_b}{2}E^1_{Hxc}\left[b\bar{b}\right] - \left(n_a\, n_b\right)^{1/2}\Delta^1_{ab}$$

$$E^1 = \frac{n_a}{2}E^0_{a\bar{a}} + \frac{n_b}{2}E^0_{b\bar{b}} + \int d\vec{r}\,\rho_{ens}(\vec{r})\left(V^1_{ext}(\vec{r}) - V^0_{ext}(\vec{r})\right) + \frac{n_a}{2}E^1_{Hxc}\left[a\bar{a}\right] + \frac{n_b}{2}E^1_{Hxc}\left[b\bar{b}\right] - \left(n_a\, n_b\right)^{1/2}\Delta^1_{ab}$$

$$\rho_{ens}(\vec{r}) = \frac{n_a}{2}\rho_a(\vec{r}) + \frac{n_b}{2}\rho_b(\vec{r})$$

$$E^0_{a\bar{a}} = -\tfrac{1}{2}\sum_k \left\langle \phi_k \middle| \nabla^2 \middle| \phi_k \right\rangle + \int d\vec{r}\,\rho(\vec{r})V^0_{ext}(\vec{r})$$

$$\begin{aligned} E^1 &= \frac{n_a}{2}\left[\left(E^0_{a\bar{a}} - \int d\vec{r}\,\rho_a(\vec{r})V^0_{ext}(\vec{r})\right) + \int d\vec{r}\,\rho_a(\vec{r})V^1_{ext}(\vec{r}) + E^1_{Hxc}\left[a\bar{a}\right]\right] \\ &+ \frac{n_a}{2}\left[\left(E^0_{b\bar{b}} - \int d\vec{r}\,\rho_b(\vec{r})V^0_{ext}(\vec{r})\right) + \int d\vec{r}\,\rho_b(\vec{r})V^1_{ext}(\vec{r}) + E^1_{Hxc}\left[b\bar{b}\right]\right] - \left(n_a\, n_b\right)^{1/2}\Delta^1_{ab} \\ &= \frac{n_a}{2}E^1_{a\bar{a}} + \frac{n_a}{2}E^1_{b\bar{b}} - \left(n_a\, n_b\right)^{1/2}\Delta^1_{ab} \end{aligned}$$

(final expression)

eDFT XC functional for simple (2e,2o) model

strong correlation

$(\uparrow\downarrow\ -),(-\ \uparrow\downarrow)$

2×2

$$\begin{Vmatrix} E_{a\bar{a}} & \Delta_{ab} \\ \Delta_{ab} & E_{b\bar{b}} \end{Vmatrix}$$

$n_a \sim n_b \sim 1$

$$E = \frac{n_a}{2} E_{a\bar{a}} + \frac{n_b}{2} E_{b\bar{b}} - \sqrt{n_a n_b}\,\Delta_{ab}$$

interpolation

$f(n_a, n_b)$

weak correlation

$- \ b$

$\uparrow\downarrow\ a$

$E_{a\bar{a}}$

$n_a \sim 2,\ n_b \sim 0$

$$E = \frac{n_a}{2} E_{a\bar{a}} + \frac{n_b}{2} E_{b\bar{b}} - (n_a n_b)\,\Delta_{ab}$$

Interpolation between strong and weak correlation

Inspect the usual KS DFT energy

$$E^{DFT} = \sum_{i}^{occ} n_i \left\langle i \middle| \hat{h} \middle| i \right\rangle + \sum_{i<j}^{occ} n_i n_j \left\langle i\, j \,\middle|\, i\, j \right\rangle + E_{xc}[\rho]$$

with the ensemble density

$$\rho_{ens} = \frac{n_a}{2}|\phi_a|^2 + \frac{n_b}{2}|\phi_b|^2$$

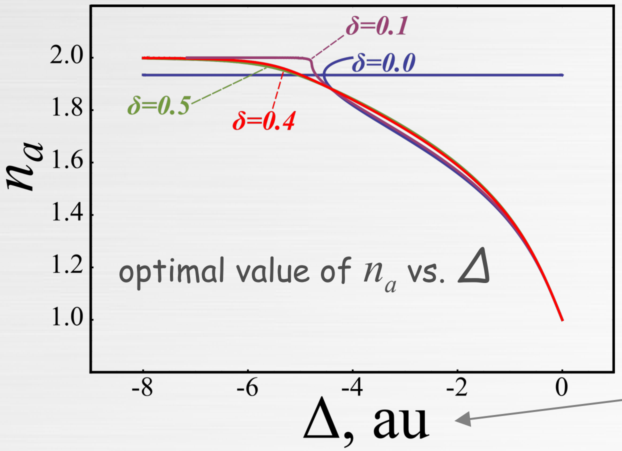
XC part is inseparable,
so only an approximation

$$E^{DFT}[\rho_{ens}] \approx \frac{n_a}{2}E_{a\bar{a}} + \frac{n_b}{2}E_{b\bar{b}} - n_a n_b\left(\tfrac{1}{2}E_{a\bar{a}} + \tfrac{1}{2}E_{b\bar{b}} - E_{a\bar{b}}\right)$$

Considering that it's valid near $n_a \sim 2$ and $n_b \sim 0$ shows linear dependence on $n_a{\cdot}n_b$

Interpolating function:

$$f(n_a, n_b) = (n_a \cdot n_b)^{1-\frac{n_a \cdot n_b + \delta}{2(1+\delta)}}$$



optimal value of n_a vs. Δ

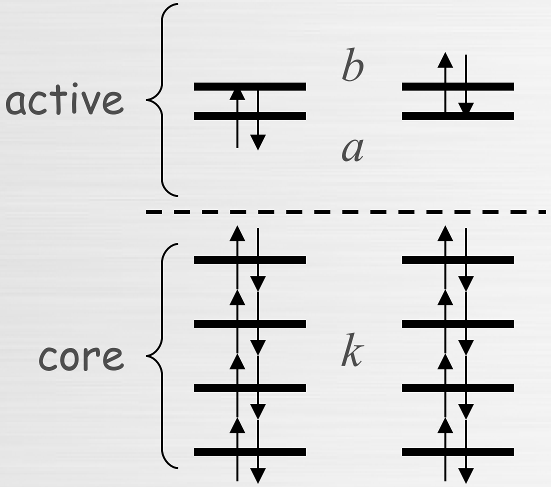
$\delta = 0.4$ - smooth transition btw single det. and ensemble

in a wide range of δ values, the ensemble energy quickly collapses to a single det. energy

$$\Delta = \left(E_{a\bar{a}} - E_{b\bar{b}}\right)/\Delta_{ab}$$

spin-Restricted Ensemble-referenced KS (REKS) method

REKS(2,2): 2 electrons in 2 active orbitals



Density:

$$\rho(\mathbf{r}) = \frac{n_a}{2}\rho_a(\mathbf{r}) + \frac{n_b}{2}\rho_b(\mathbf{r})$$

$$= \sum_k^{core} 2\,|\phi_k(\mathbf{r})|^2 + n_a|\phi_a(\mathbf{r})|^2 + n_b|\phi_b(\mathbf{r})|^2$$

Energy:

$$E = \frac{n_a}{2}E[\rho_{a\bar{a}}] + \frac{n_b}{2}E[\rho_{b\bar{b}}]$$

$$-\, f(n_a, n_b)\left(E[\rho_{a\bar{b}}] + E[\rho_{\bar{a}b}] - E[\rho_{ab}] - E[\rho_{\bar{a}\bar{b}}]\right)$$

all approximations are here

Energy is optimized w.r.t.

- KS orbitals
- fractional occupation numbers

M. Filatov and S. Shaik, CPL 304 (1999) 429
M. Filatov and S. Shaik, JPCA 104 (2000) 6628

REKS technology: orbital optimization

REKS(2,2): $E = \sum_L w_L \, E_L[\rho_L]$ $\qquad \rho(\vec{r}) = \sum_L w_L \, \rho_L(\vec{r}) = \sum_k^{core} 2\left|\phi_k(\vec{r})\right|^2 + n_a\left|\phi_a(\vec{r})\right|^2 + n_b\left|\phi_b(\vec{r})\right|^2$

$n_a + n_b = 2; \quad n_a = 2\cos^2\theta; \quad \frac{\partial E}{\partial \theta} = 0$ direct minimization, no constraints needed

$\frac{\delta}{\delta\phi_r}\left(E + \sum_{p,q} \varepsilon_{pq}\left(\delta_{qp} - \left\langle \phi_q \middle| \phi_p \right\rangle\right)\right) = 0$ orbitals' orthonormality constraints (Lagrange multipliers)

$\varepsilon_{pq} = \varepsilon^*_{qp}$ Hermiticity of ε – variational condition

Energy is not invariant w.r.t. rotation among all occupied orbitals, cannot diagonalize

$$\left\langle \phi_p \middle| n_q \hat{F}_q \middle| \phi_q \right\rangle = \left\langle \phi_q \middle| n_p \hat{F}_p \middle| \phi_p \right\rangle$$

$$\hat{F}_q = \sum_L w_L \frac{n^\alpha_{q,L}\,\hat{F}^\alpha_L + n^\beta_{q,L}\,\hat{F}^\beta_L}{n_q}$$

combined "Fock" operator (diagonalizable)

$$\begin{pmatrix} \ddots & \vdots & \vdots & \\ \cdots & \hat{F}_q & \frac{n_q\hat{F}_q - n_p\hat{F}_p}{n_q - n_p} & \cdots \\ \cdots & \frac{n_p\hat{F}_p - n_q\hat{F}_q}{n_p - n_q} & \hat{F}_p & \cdots \\ & \vdots & \vdots & \ddots \end{pmatrix}$$

can be arbitrary

zero when converged

spin-Restricted Ensemble-referenced KS (REKS) method

Spin-restricted ensemble-referenced KS (REKS) method (1998 →)

Uses ensemble representation for the density and energy

$$\rho = \sum_{k}^{n} \omega_k \, \rho_k \qquad\qquad E = \sum_{k}^{n} \omega_k \, E[\rho_k]$$

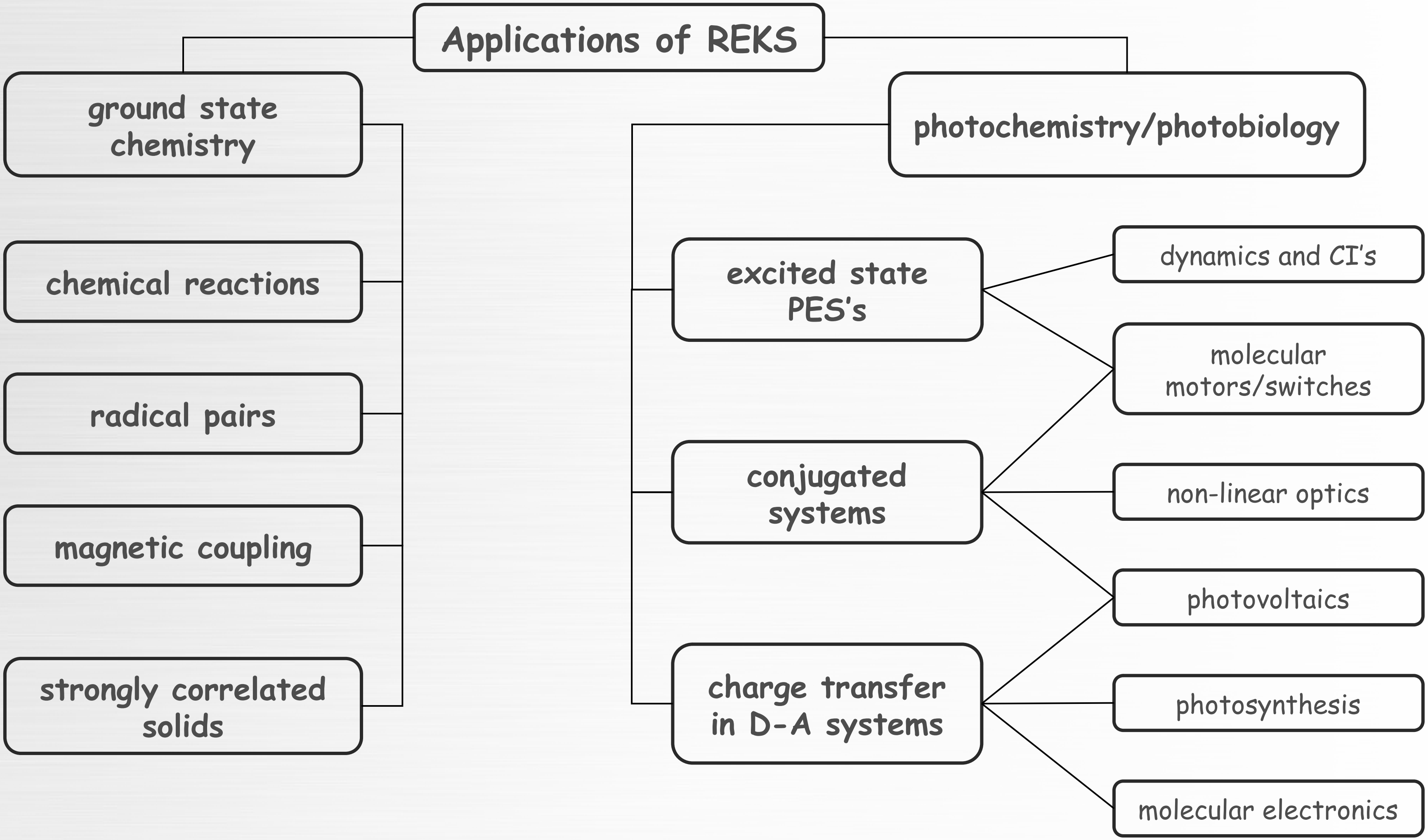
Designed to describe strong (static) correlation

Extended to excited states, state-averaged REKS (SA-REKS, 2008)

Can be used with any approximate density functional

Computational cost: mean-field cost (similar to the usual DFT)

Applications of REKS methodology



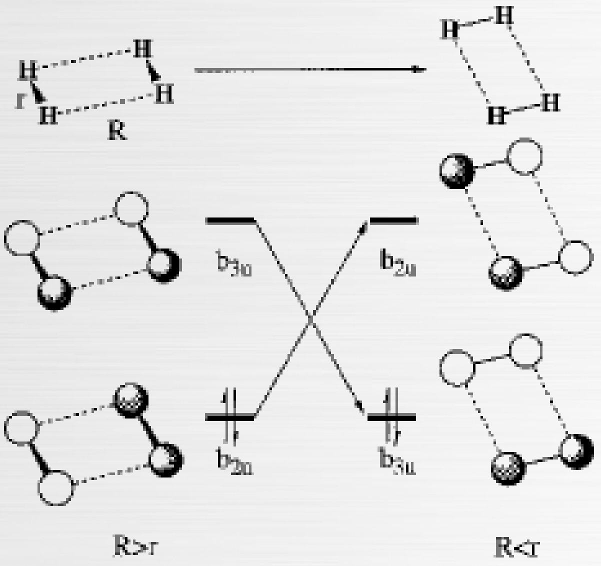
Applications of REKS

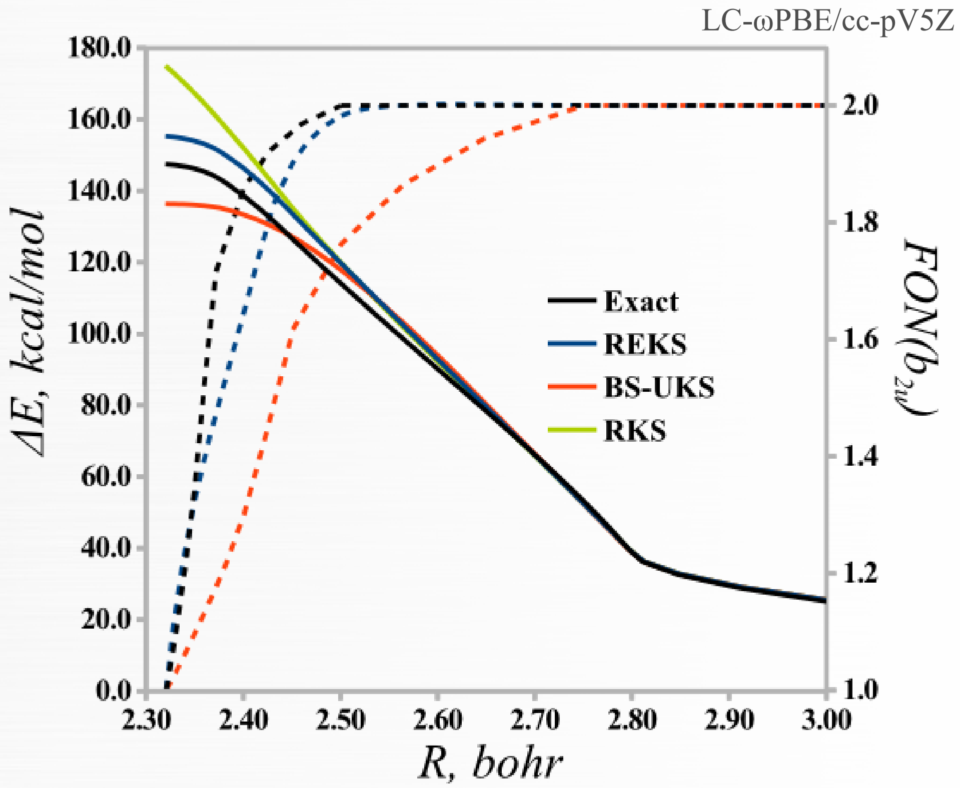
- **ground state chemistry**
  - **chemical reactions**
  - **radical pairs**
  - **magnetic coupling**
  - **strongly correlated solids**
- **photochemistry/photobiology**
  - **excited state PES's**
    - dynamics and CI's
    - molecular motors/switches
  - **conjugated systems**
    - molecular motors/switches
    - non-linear optics
    - photovoltaics
  - **charge transfer in D-A systems**
    - photovoltaics
    - photosynthesis
    - molecular electronics

Benchmarking REKS vs. exact eDFT

Model system: H_2+H_2 (D_{2h})

[2+2] cycloaddition; symmetry forbidden

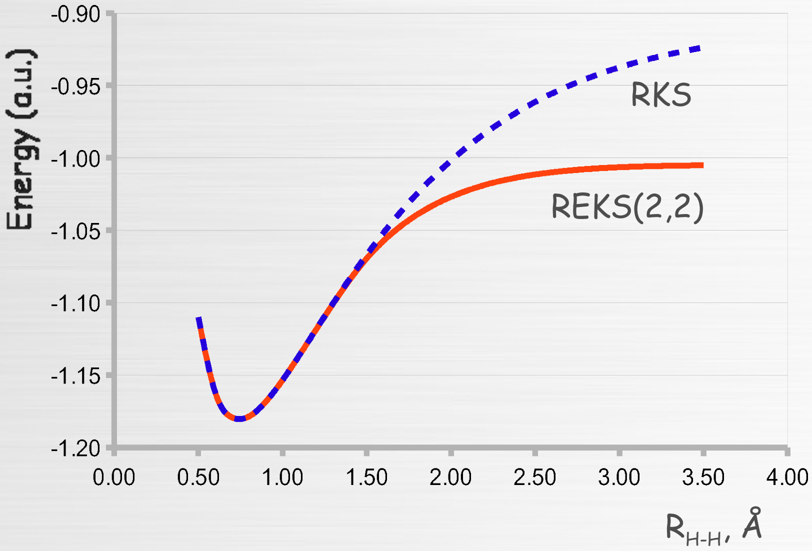




Exact KS DFT:	fractional orbital occupations (ensemble)
REKS:	accurate PES and orbital occupations
BS-UKS:	underestimates barrier, overestimates static correlation
Standard RKS:	fails completely

Applications of REKS: Bond dissociation

Bond stretching in H_2

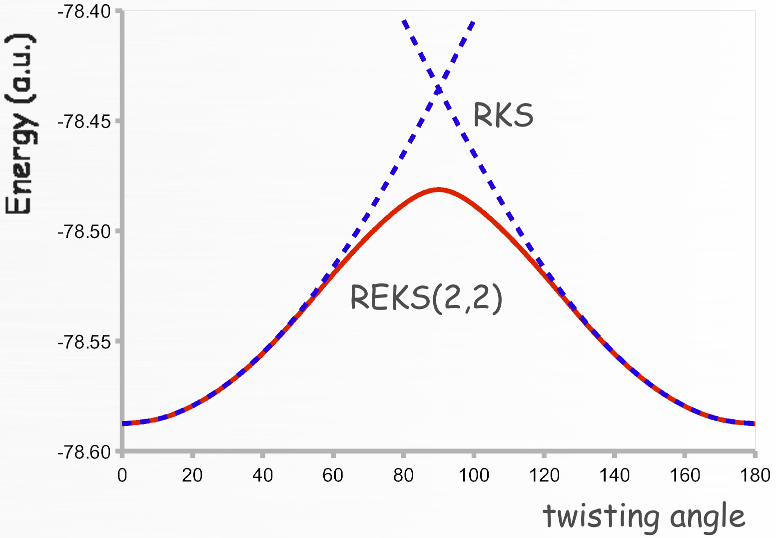


Total energy at R_{H-H} = 0.741 Å

E^{RKS} = -1.1786 a.u.
E^{REKS} = -1.1786 a.u.

B3LYP/aug-cc-pVQZ

Twisting about double bond in C_2H_4



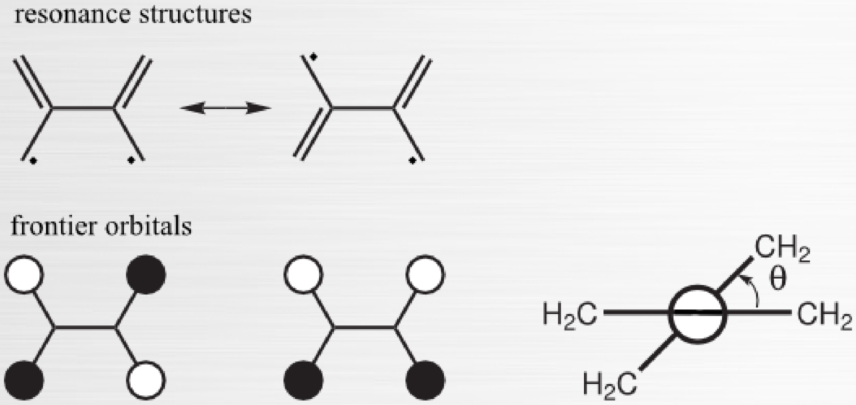
Total energy of planar ethylene

E^{RKS} = -78.5874 a.u.
E^{REKS} = -78.5874 a.u.

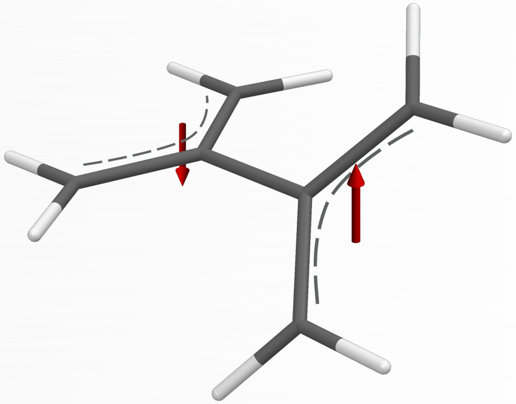
B3LYP/6-31G*

Applications of REKS: Tetramethyleneethane diradical

used in organic synthesis; as a ligand in metal complexes…



TME: singlet or triplet?

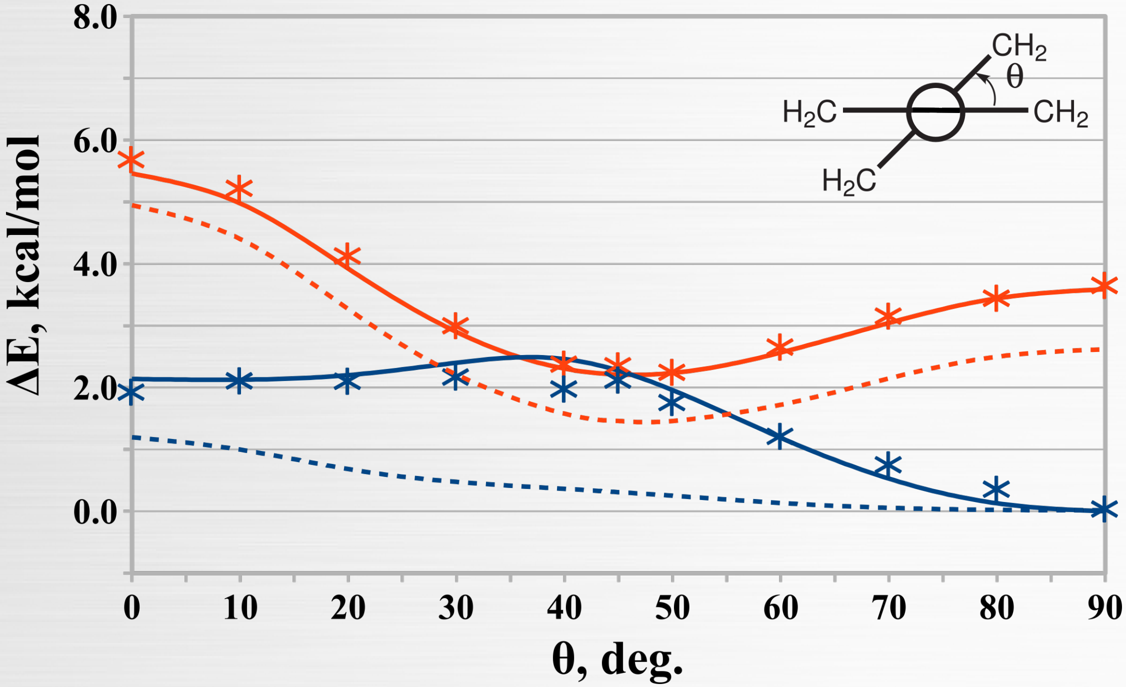


Matrix isolated TME: <u>triplet</u> EPR signal; linear CW plot (Dowd, 1970, 1986)

NIPE spectroscopy ($\mathrm{TME}^{\cdot -}$): <u>singlet</u> below (ca. 3 kcal/mol) triplet (Clifford et al., 1998)

Theory (CASSCF,CI, etc..): <u>singlet</u> always below triplet (Borden et al., 1987)

Applications of REKS: Tetramethyleneethane diradical



REKS: Filatov&Shaik, 1999

CASPT2: Caballol et al., 2000

QMC: Jordan et al., 2013
Barborini&Coccia, 2015

Singlet is a global energy minimum

Triplet is *meta-stable* at intermediate *θ* (trapping, slow relaxation)

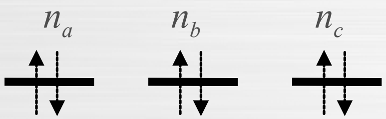
Reconciles theory and experiment (Lineberger&Borden, 2013)

Extending REKS to larger active spaces

for (a system with N fractionally occupied orbitals) {

non-interacting limit $\lambda = 0$:

for (N orbitals degenerate at Fermi level)
build N single CS determinants;



weakly interacting limit $\lambda \approx 0$:

apply quasi-degenerate PT;
rewrite E_0 through energies of single determinants;

$$\left\| \begin{matrix} E^{\lambda}_{a\bar{a}} & \Delta^{\lambda}_{ab} & \Delta^{\lambda}_{ac} \\ \Delta^{\lambda}_{ab} & E^{\lambda}_{b\bar{b}} & \Delta^{\lambda}_{bc} \\ \Delta^{\lambda}_{ac} & \Delta^{\lambda}_{bc} & E^{\lambda}_{c\bar{c}} \end{matrix} \right\|$$

$$E_0 = \sum_{p=1}^{N} \frac{n_p^{\lambda}}{2} E^{\lambda}_{p\bar{p}} + \sum_{p>q} \left(f_p \, f_q \right) \sqrt{n_p^{\lambda} \, n_q^{\lambda}} \left(E^{\lambda}_{pq} - E^{\lambda}_{p\bar{q}} \right)$$

carry out λ-integration:

assume (constant n_p's) && (no further degeneracies);
interpolation btw FON and CS;
E_0 for interacting particles;

$$E_0 = \sum_{p=1}^{N} \frac{n_p}{2} E^{DFT}_{p\bar{p}} + \sum_{p>q} \left(f_p \, f_q \right) f\left(n_p, n_q\right) \left(E^{DFT}_{pq} - E^{DFT}_{p\bar{q}} \right)$$

optimize:

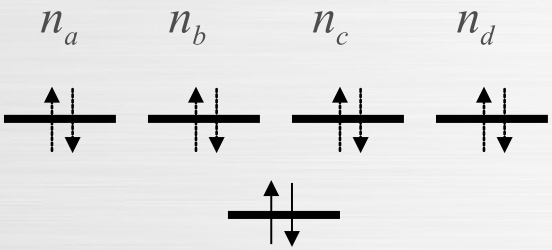
the orbitals and FONs;
enjoy;

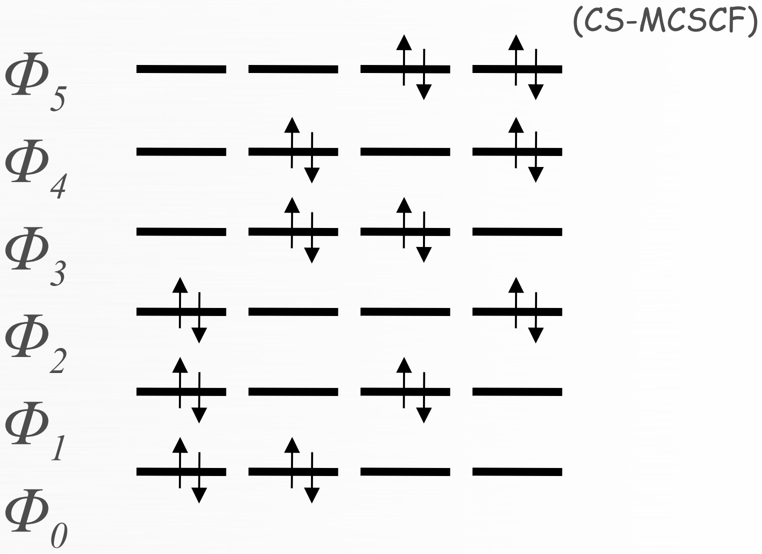
}

Extending REKS to larger active spaces

Active spaces (4,4), (6,6), etc.: Multiple bonds, polyradicals, metal complexes, etc.

$$n_a + n_b + n_c + n_d = 4$$





6x6 secular problem;
only 4 FON's;
no unique mapping of C's on FONs

<u>Idea</u>: use GVB to reduce the problem

$$\Psi^{GVB} = \hat{\mathcal{A}}\left[(core)\,\Psi^{NO}(1,2)\,\Psi^{NO}(3,4)\ldots\right]$$

$$\Psi^{NO}(1,2) = \sqrt{\frac{n_a}{2}}\left|\ldots\phi_a\bar{\phi}_a\right| - \sqrt{\frac{n_b}{2}}\left|\ldots\phi_b\bar{\phi}_b\right|$$

only pairs of natural orbitals (geminals) are needed

REKS energy for several NO pairs can be easily derived

MF, T.J. Martínez, K. S. Kim, PCCP 18, 21040 (2016)
MF, F. Liu, K. S. Kim, T. J. Martínez, JCP 145, 244104 (2016)

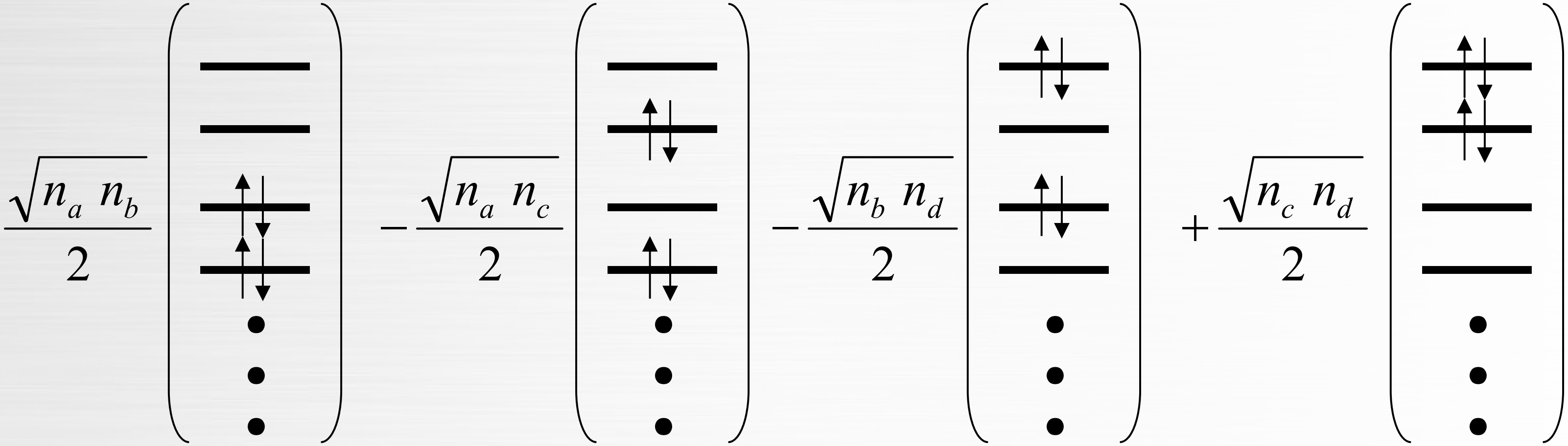
REKS(4,4)

REKS(4,4) employs perfectly spin-paired singlet (PPS) state

(a,d) and (b,c) GVB pairs

$$\Psi^{GVB-PP} = \hat{\mathcal{A}}\left[\cdots \Phi_0^{NO}(1,2)\,\Phi_0^{NO}(3,4)\cdots\right] \qquad \Phi_0^{NO}(1,2) = \sqrt{\frac{n_a}{2}}\left|\phi_a\bar{\phi}_a\right\rangle - \sqrt{\frac{n_b}{2}}\left|\phi_b\bar{\phi}_b\right\rangle$$

size-consistent wavefunction

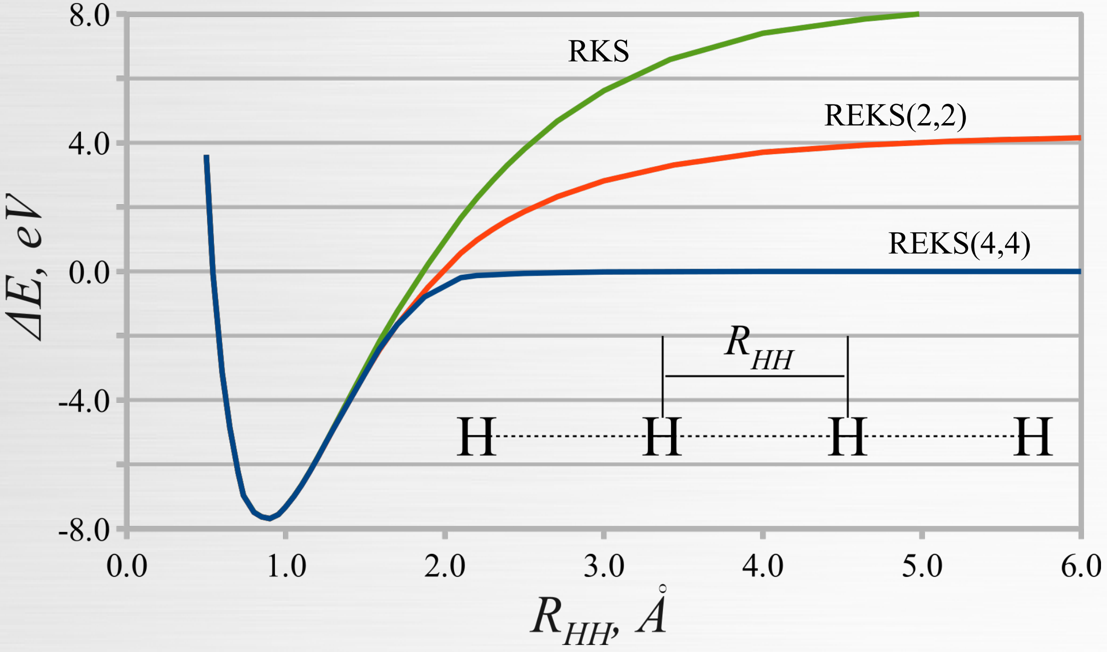


$$\frac{\sqrt{n_a\,n_b}}{2}\left(\cdots\right) - \frac{\sqrt{n_a\,n_c}}{2}\left(\cdots\right) - \frac{\sqrt{n_b\,n_d}}{2}\left(\cdots\right) + \frac{\sqrt{n_c\,n_d}}{2}\left(\cdots\right)$$

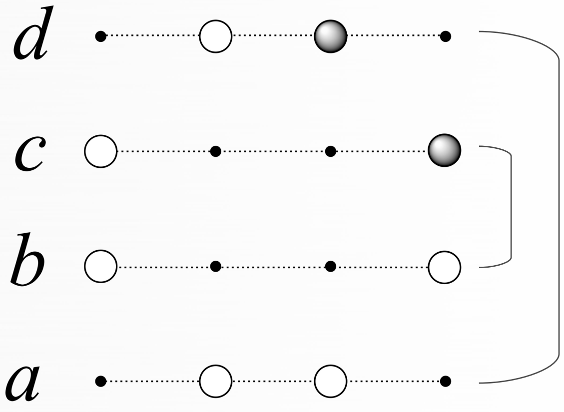
$$E^{(4,4)} = \frac{n_a\,n_b}{4}E_{a\bar{a}b\bar{b}} + \frac{n_a\,n_c}{4}E_{a\bar{a}c\bar{c}} + \frac{n_b\,n_d}{4}E_{b\bar{b}d\bar{d}} + \frac{n_c\,n_d}{4}E^{\lambda}_{c\bar{c}d\bar{d}} - \left(n_a\,n_d\right)^{1/2}\Delta_{ad} - \left(n_b\,n_c\right)^{1/2}\Delta_{bc}$$

REKS(4,4): Dissociation of several single bonds

uniform stretching of linear H chain; RE(4,4)-BH&HLYP/6-31G**



active orbitals

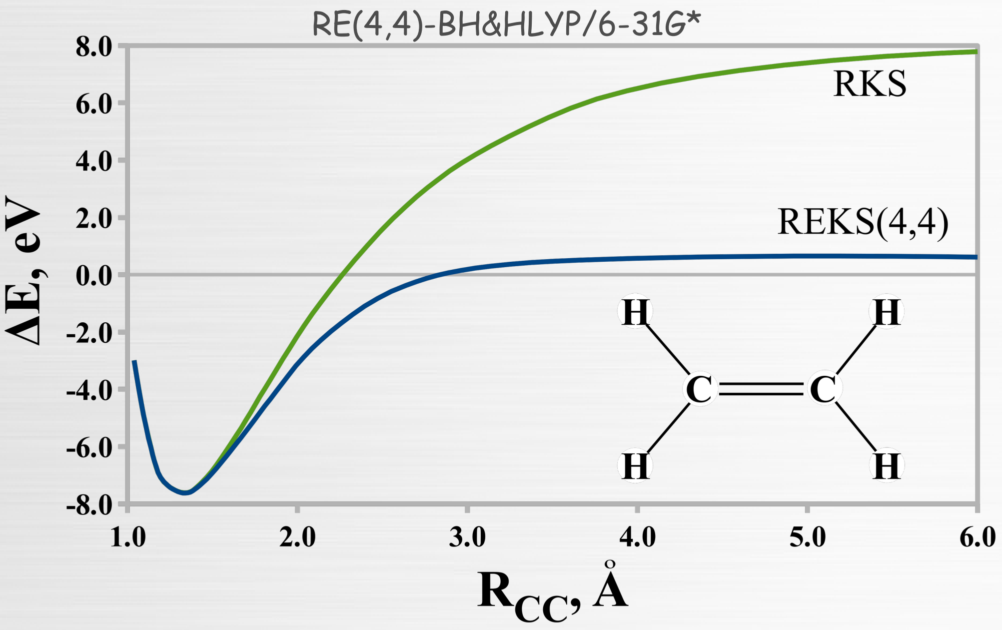


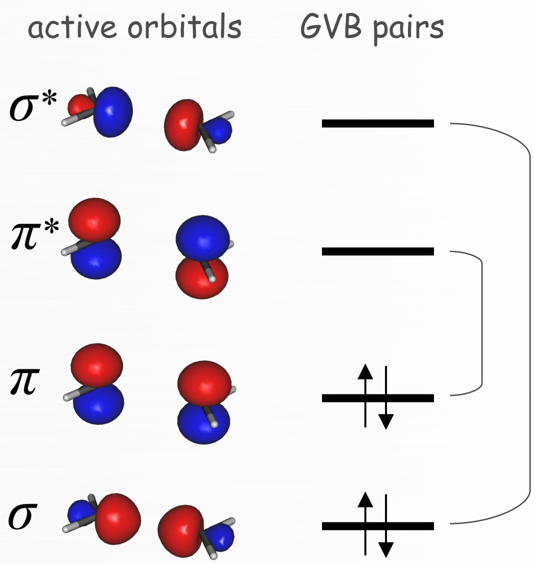
size-consistent when dissociating into individual atoms (spin centers)

$$E^{(4,4)}(H_4)\Big|_{R\to\infty} = 4\,E(H)$$

MF, T.J. Martínez, K. S. Kim, PCCP 18, 21040 (2016)
MF, F. Liu, K. S. Kim, T. J. Martínez, JCP 145, 244104 (2016)

REKS(4,4): Double Bond Dissociation





dissociation into open-shell fragments;

$$E^{(4,4)}\left(C_2H_4\right)\Big|_{R_{CC}\to\infty} \neq 2\,E\left({}^3CH_2\right)$$

spin re-coupling on the fragments – requires open-shell configurations

corrected by SSR(4,4); see below.

MF, T.J. Martínez, K. S. Kim, PCCP 18, 21040 (2016)
MF, F. Liu, K. S. Kim, T. J. Martínez, JCP 145, 244104 (2016)

REKS method for ground states: Summary

- Provides accurate symmetry adapted description of biradicals, bond-breaking, magnetic coupling *etc*.
- Avoids problems with spin contamination and false $\langle S^2 \rangle$ values
- Can be used in connection with any density functional
- Mean-field computational cost (no steep scaling of MRCI or response methods)
- Current implementation – REKS(2,2), REKS(4,4); further extensions are under way...

That's it for today