

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

Variational (not response)
excited states

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

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

Part 1

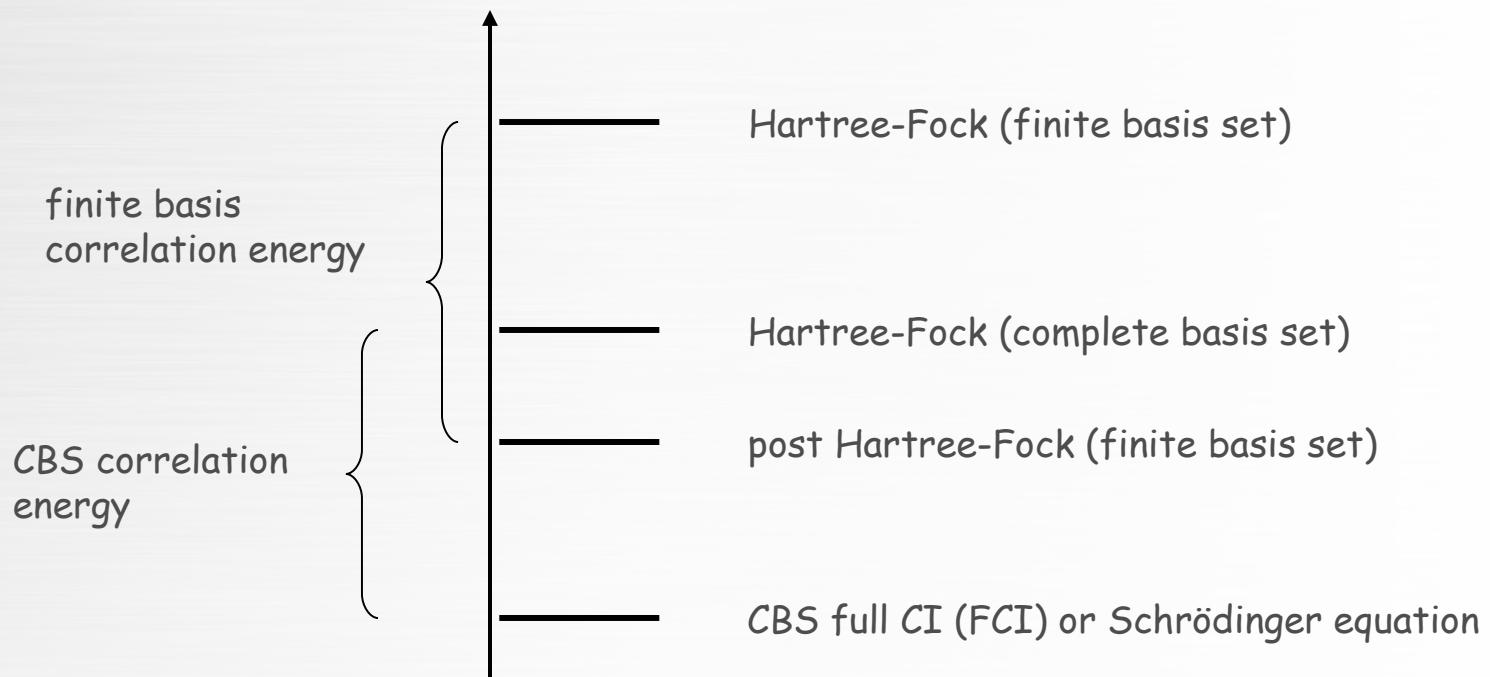
Ground States

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

introduced by P.-O. Löwdin in 1954

characterizes deviation from independent particles model



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

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(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 $\Omega_{\text{op}} = \mathcal{O}^\dagger \mathcal{H}_{\text{op}} \mathcal{O}$ 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.

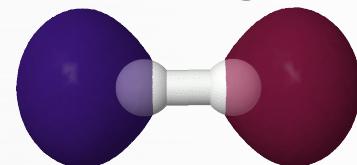
Hartree-Fock description of H₂

bonding MO



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

anti-bonding MO



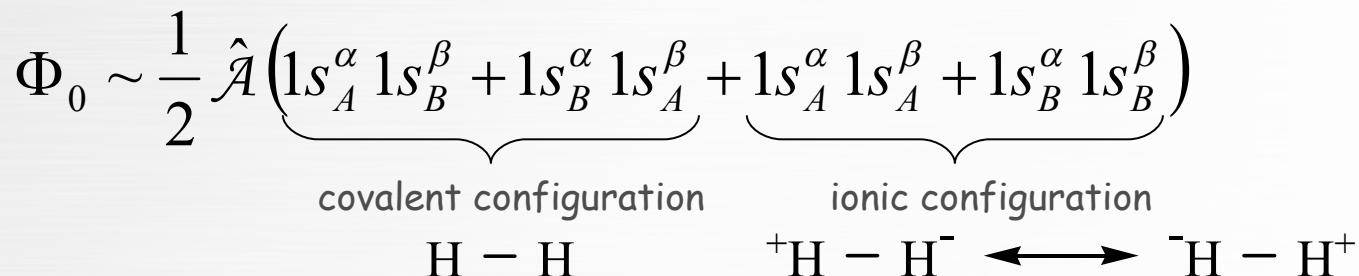
$$\sigma_u = \mathcal{N}_{\sigma_u} (\chi_A - \chi_B)$$

The ground state HF wave function:

$$\Phi_0 = \hat{\mathcal{A}} \sigma_g^\alpha(1) \sigma_g^\beta(2)$$

In the dissociation limit:

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



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

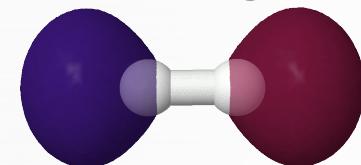
Doubly excited configuration of H₂

bonding MO



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

anti-bonding MO



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

The doubly excited wave function:

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

In the dissociation limit:

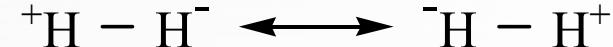
$$\chi_A \sim 1s_A, \chi_B \sim 1s_B, \mathcal{N}_{\sigma_u} = \frac{1}{\sqrt{2}}$$

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

covalent configuration



ionic configuration



covalent configuration enters with opposite sign

Configuration mixing in H₂

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:

$$\lambda = \frac{1}{\sqrt{2}}$$

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

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

Electron correlation in H₂

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 H₂

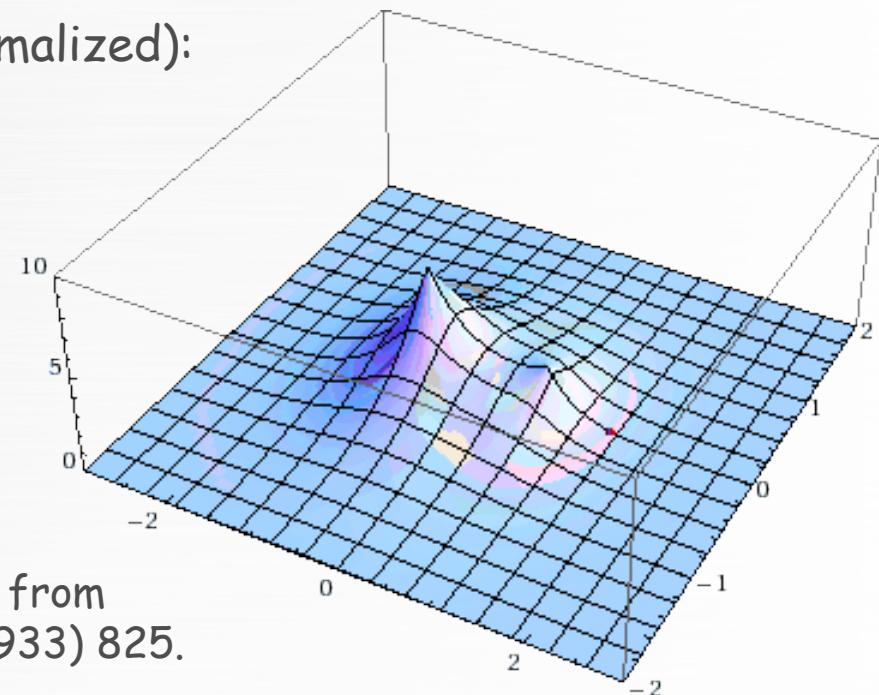
$$P(\vec{r}_1, \vec{r}_2) = |\Psi(\vec{r}_1, \vec{r}_2)|^2$$

Conditional probability (un-normalized):

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

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

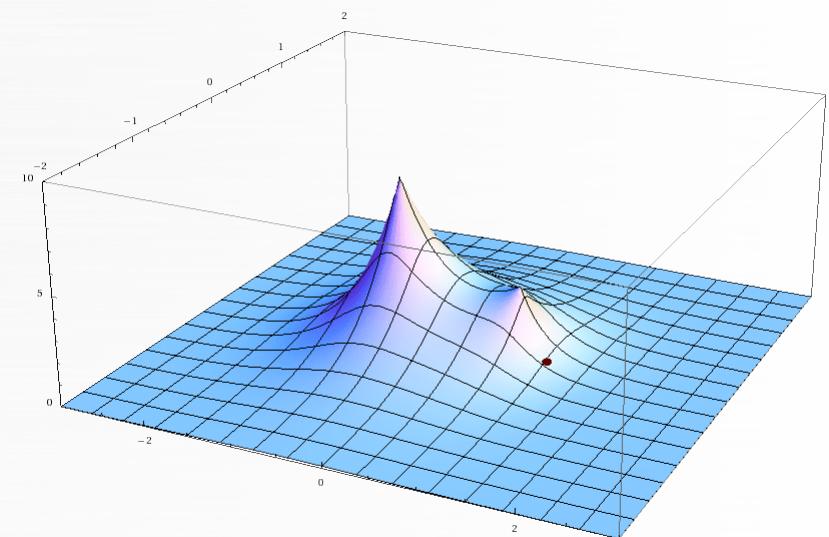
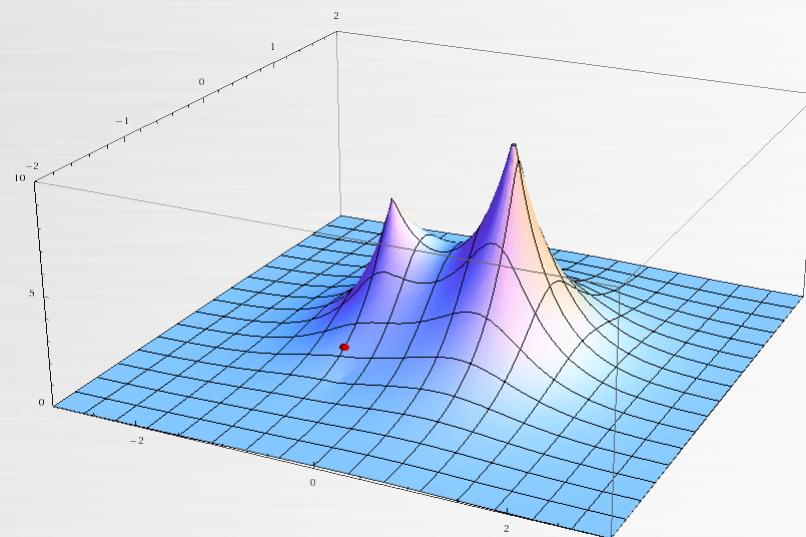
Explicitly correlated wave function from H. James and A. Coolidge, JCP, 1 (1933) 825.



Electron correlation in H₂

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

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



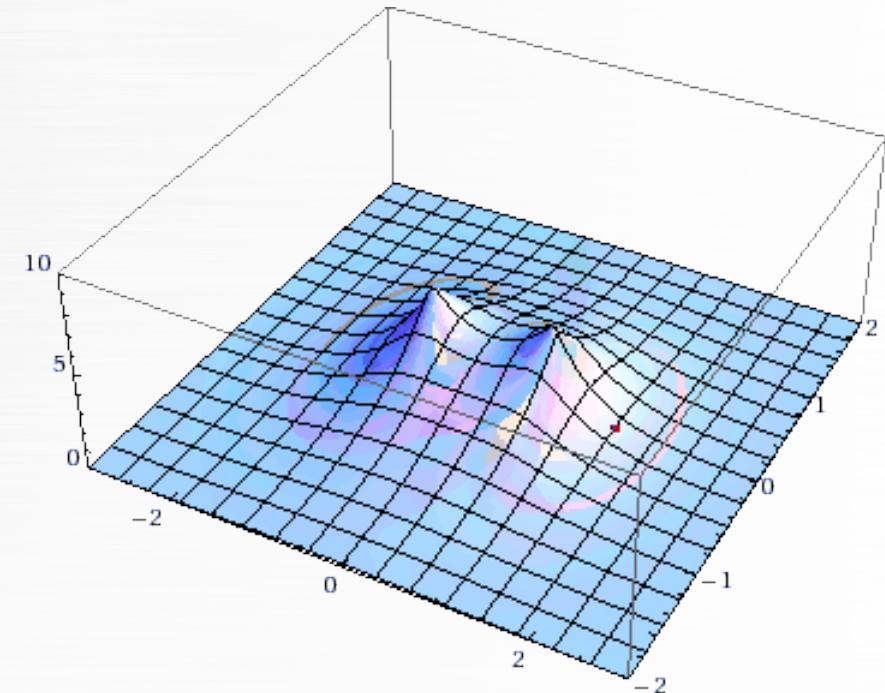
Explicitly correlated wave function from H. James and A. Coolidge, JCP, 1 (1933) 825.

Probability distribution from HF wave function

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

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 H₂

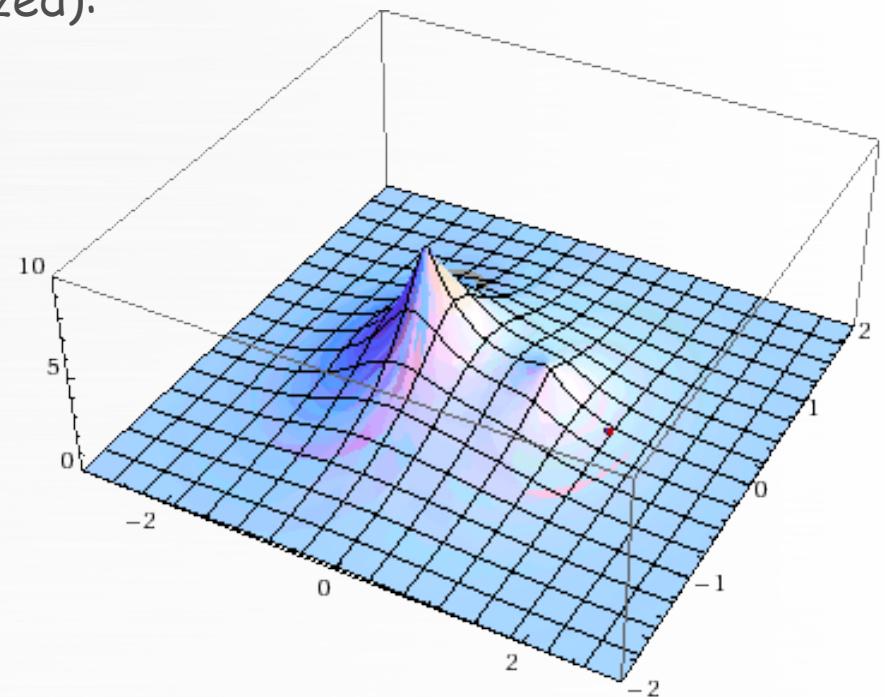
GVB-PP (2-config.) wave function:

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

Conditional probability (un-normalized):

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

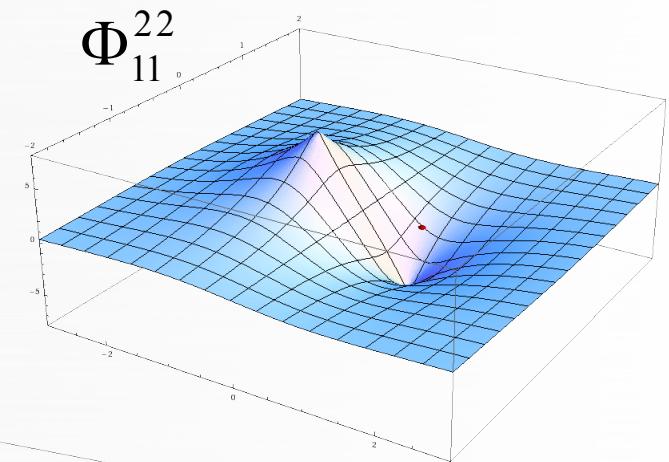
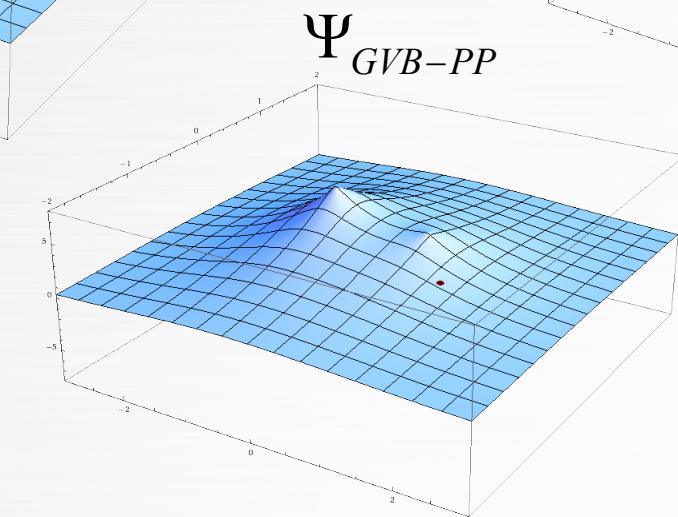
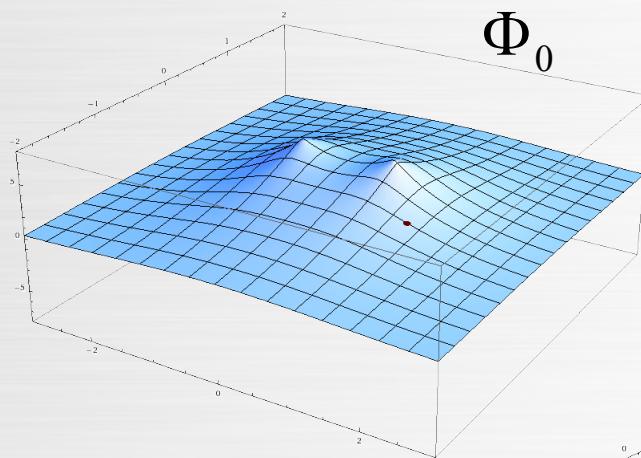
Configuration mixing brings
in the electron correlation!



Configuration mixing in H₂

GVB-PP wave function:

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



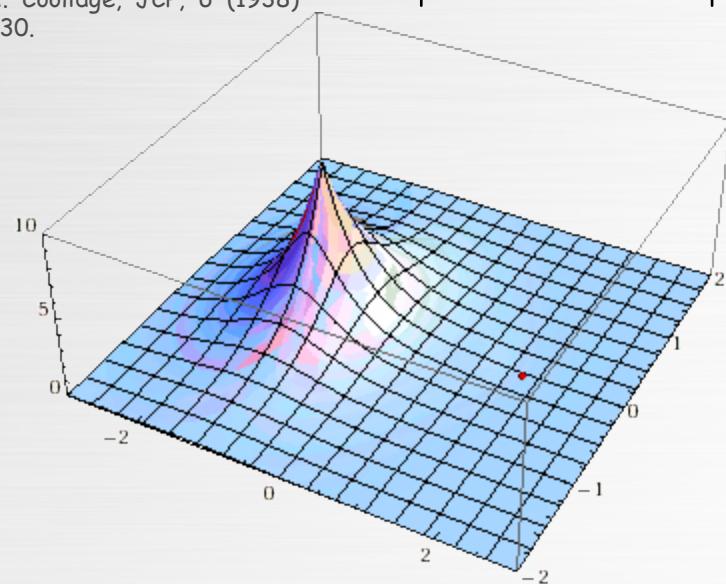
Fermi correlation in open shell wave functions

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

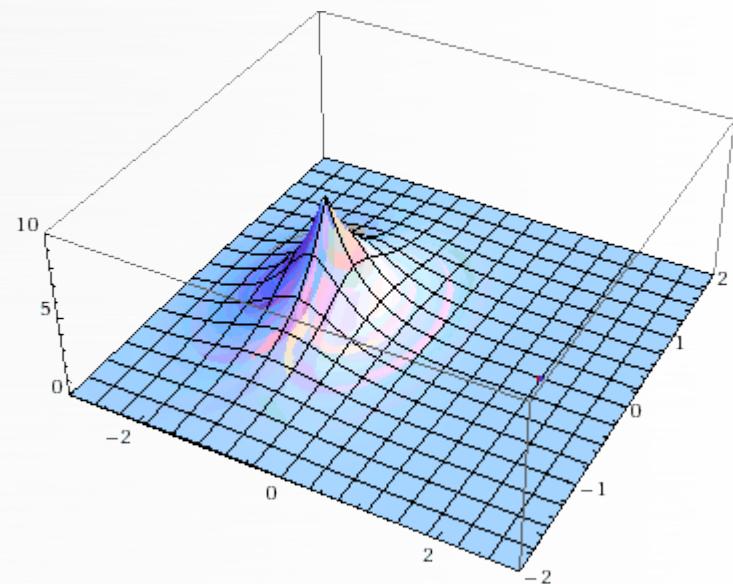
Motion of the same-spin electrons is correlated at the HF level.

Example: Triplet state of H_2

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



$$\left| \Phi_{HF}^T(\vec{R}, \vec{r}_2) \right|^2 = \left| \hat{\mathcal{A}} \sigma_g^\alpha(1) \sigma_u^\alpha(2) \right|^2$$



Fermi correlation in open shell wave functions

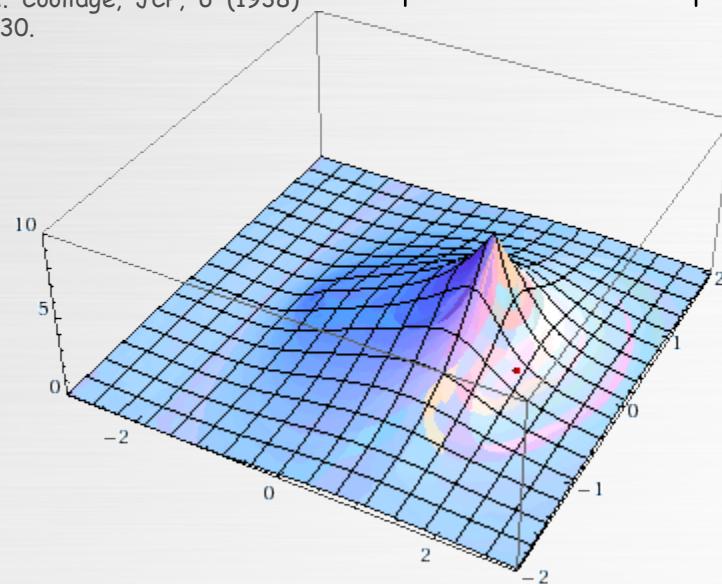
Fermi correlation: Correlation due to the Pauli principle (w.f. antisymmetry).

Another example: Open-Shell Singlet (OSS) $^1\Sigma_u^+$ state of H_2

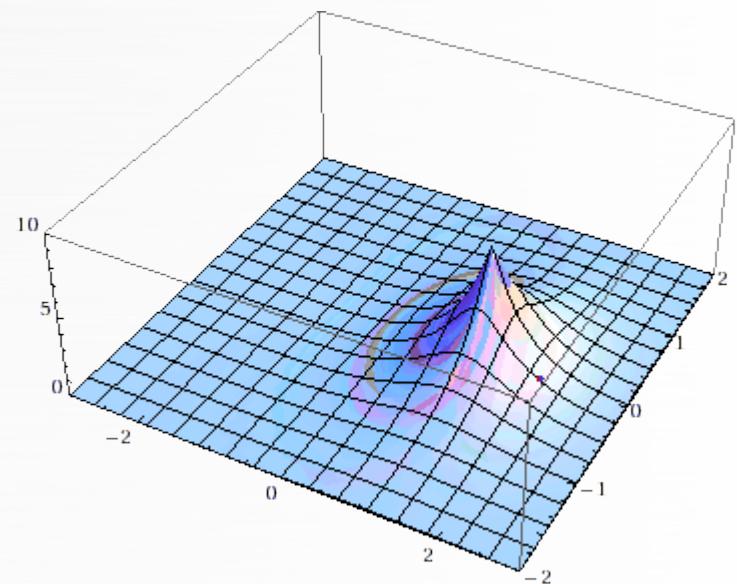
Two-configurational wave function

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

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



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



Electron correlation

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

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

correlation energy

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

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

all single excitations
are absorbed in Φ_{HF}

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

pairwise interactions in H;
only pair correlations survive

Dynamic and non-dynamic electron correlation

dynamic correlation

non-dynamic (static) correlation

single reference wavefunction

multi reference wavefunction

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

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

$$C_0 \approx C_1 \approx C_p$$

RS perturbation theory is valid

RS perturbation theory is not valid

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

(near) zero denominators

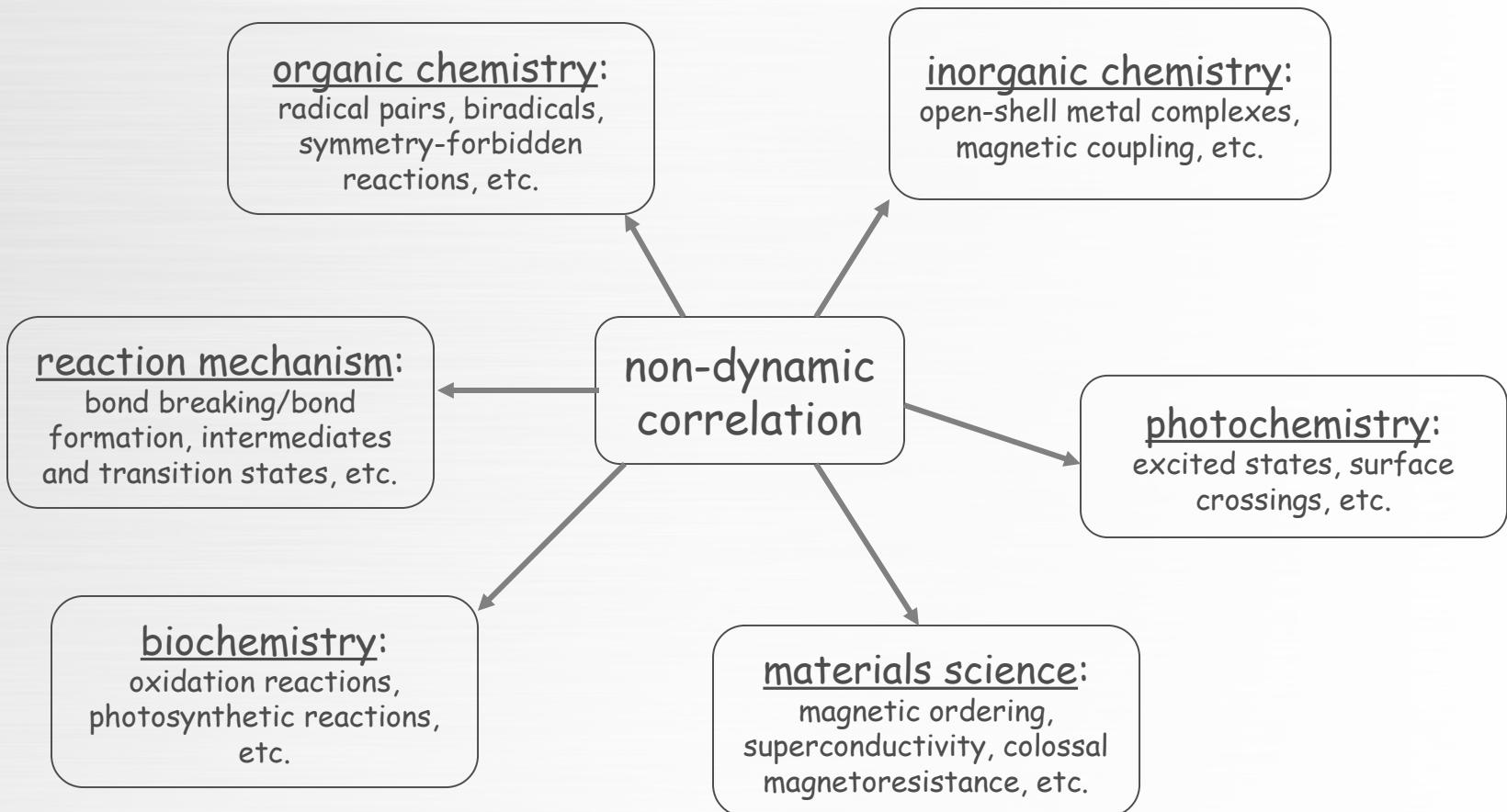
$$E_0 \approx E_1 \approx E_p$$

divergent PT series

Non-dynamic electron correlation

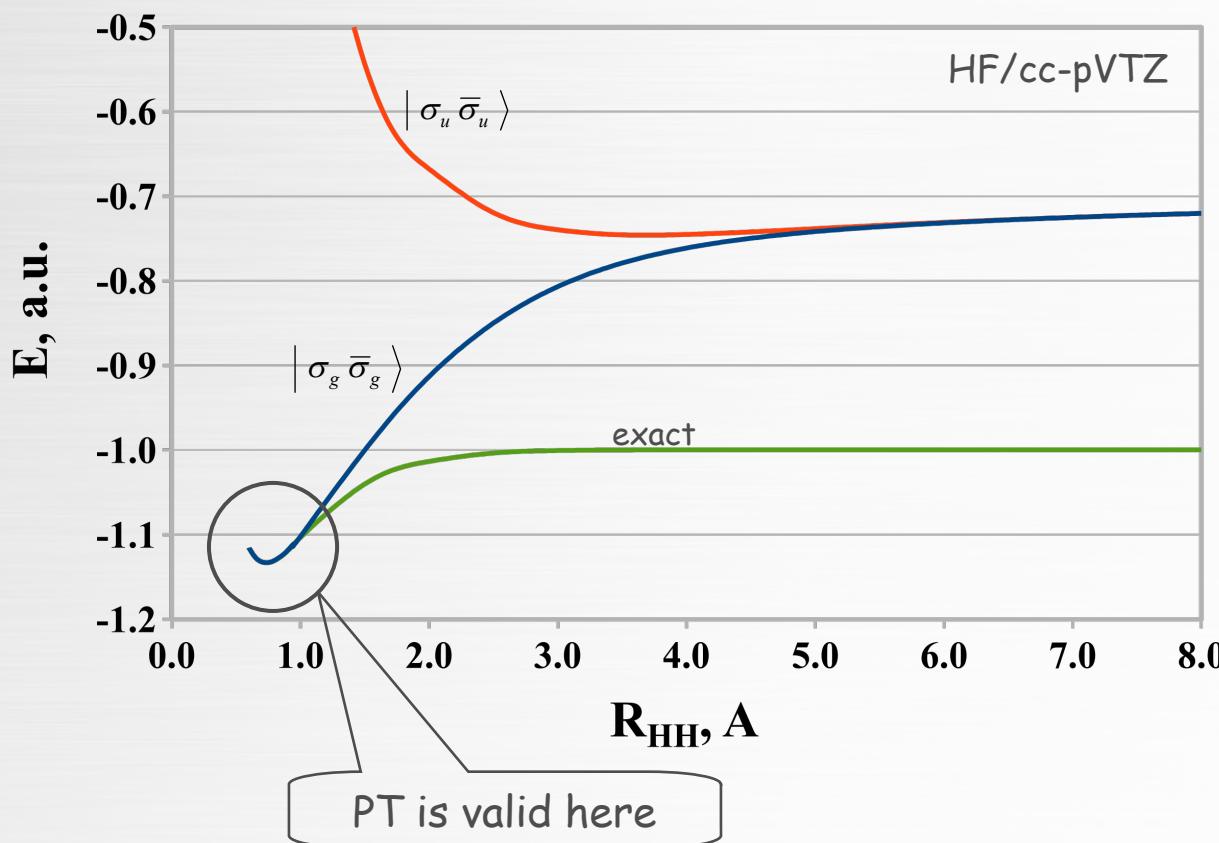
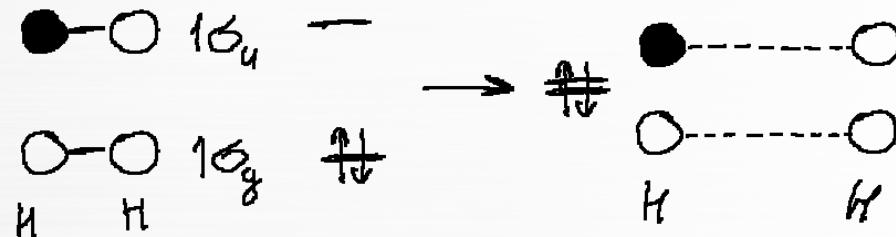
Electron correlation - deviation from mean-field approximation

Non-dynamic correlation - multi-reference wavefunction...



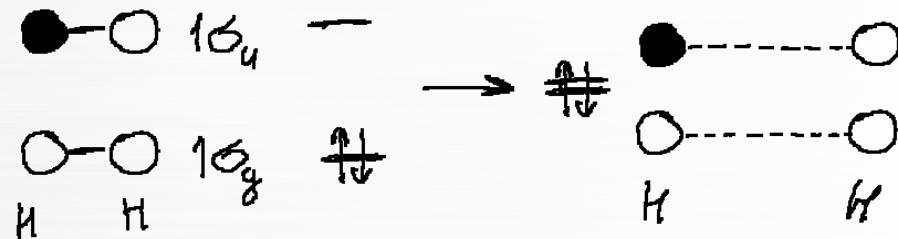
Examples of non-dynamic electron correlation

Bond breaking in H_2



Examples of non-dynamic electron correlation

Bond breaking in H_2



second order correlation energy:

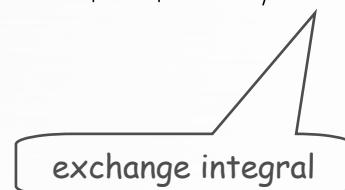
$$E_{corr}^{(2)} = \sum_{\substack{i < j \\ a < b}} \frac{\left| \left\langle \Phi_{HF} \left| \hat{H} - E_{HF} \right| \Phi_{ij}^{ab} \right\rangle \right|^2}{E_{HF} - E_{ij}^{ab}}$$

expectation values:

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

coupling term:

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



Slater-Condon rules

vacuum state:

$$\Phi_0 = \hat{\mathcal{A}}(\phi_1^{\sigma_1} \phi_2^{\sigma_2} \dots \phi_i^{\sigma_i} \dots \phi_j^{\sigma_j} \dots)$$

single substitution:

$$\Phi_i^a = \hat{\mathcal{A}}(\phi_1^{\sigma_1} \phi_2^{\sigma_2} \dots \phi_a^{\sigma_a} \dots \phi_j^{\sigma_j} \dots)$$

double substitution:

$$\Phi_{ij}^{ab} = \hat{\mathcal{A}}(\phi_1^{\sigma_1} \phi_2^{\sigma_2} \dots \phi_a^{\sigma_a} \dots \phi_b^{\sigma_b} \dots)$$

Hamiltonian:

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

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

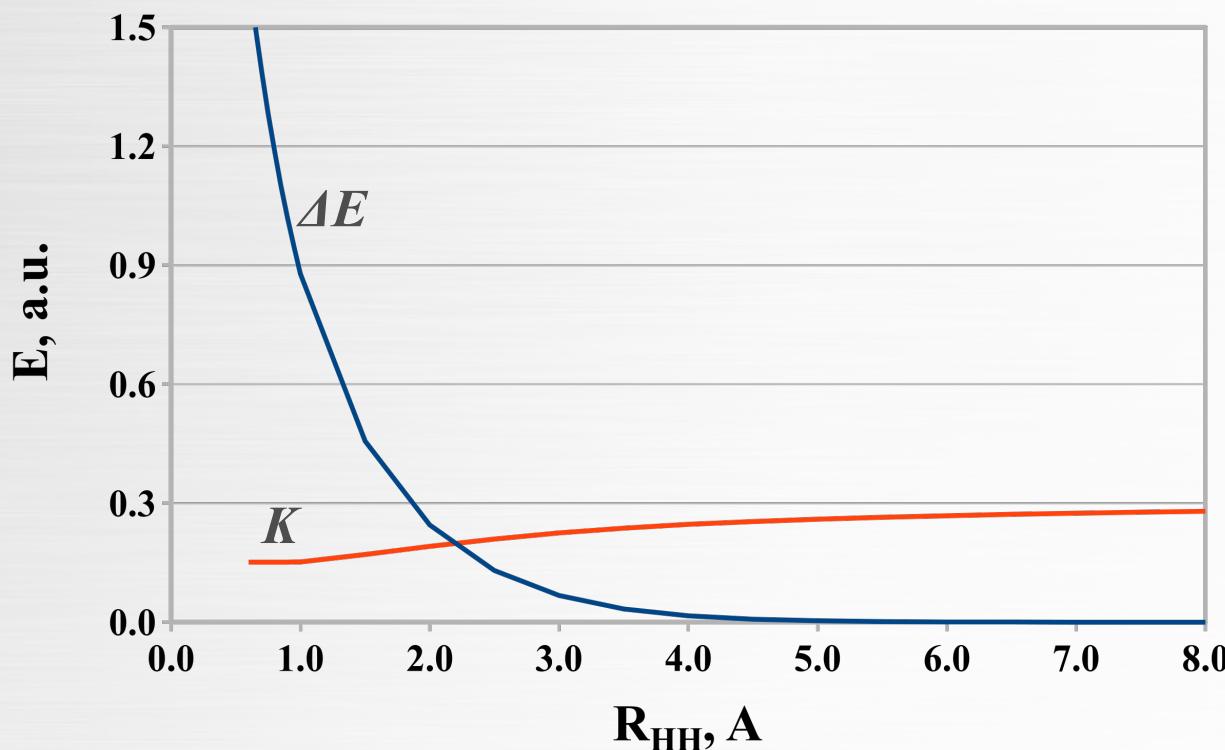
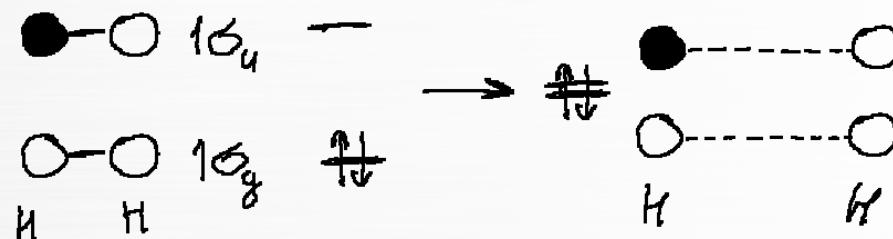
$$\langle \Phi_0 | \hat{H} | \Phi_i^a \rangle = h_{ia} + \sum_k^{occ} (\langle i k | a k \rangle - \langle i k | k a \rangle) = \langle i | \hat{F} | a \rangle$$

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

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

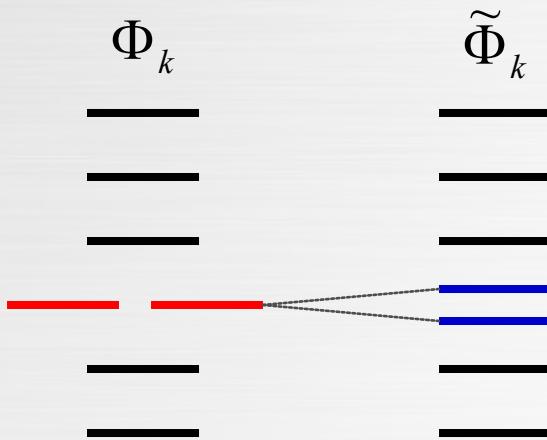
Quasi-degenerate perturbation theory

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

and $\hat{H}_0 \Phi_k = E_k \Phi_k, \Phi_k, \Phi_{k'}, \dots \in \mathcal{H}_d, E_k = E_{k'} = \dots$

where \mathcal{H}_d is a d -fold degenerate subspace

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



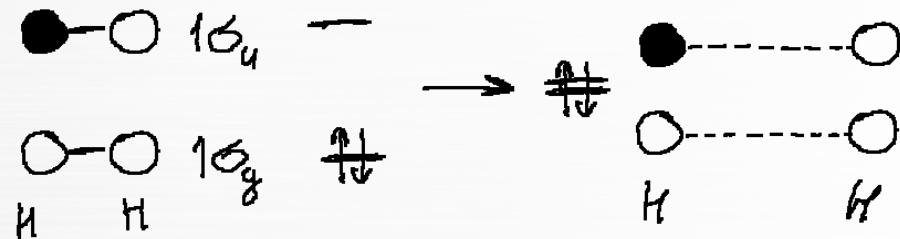
degeneracy lifted \rightarrow NDPT is good again
NDPT uses renormalized perturbation

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

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

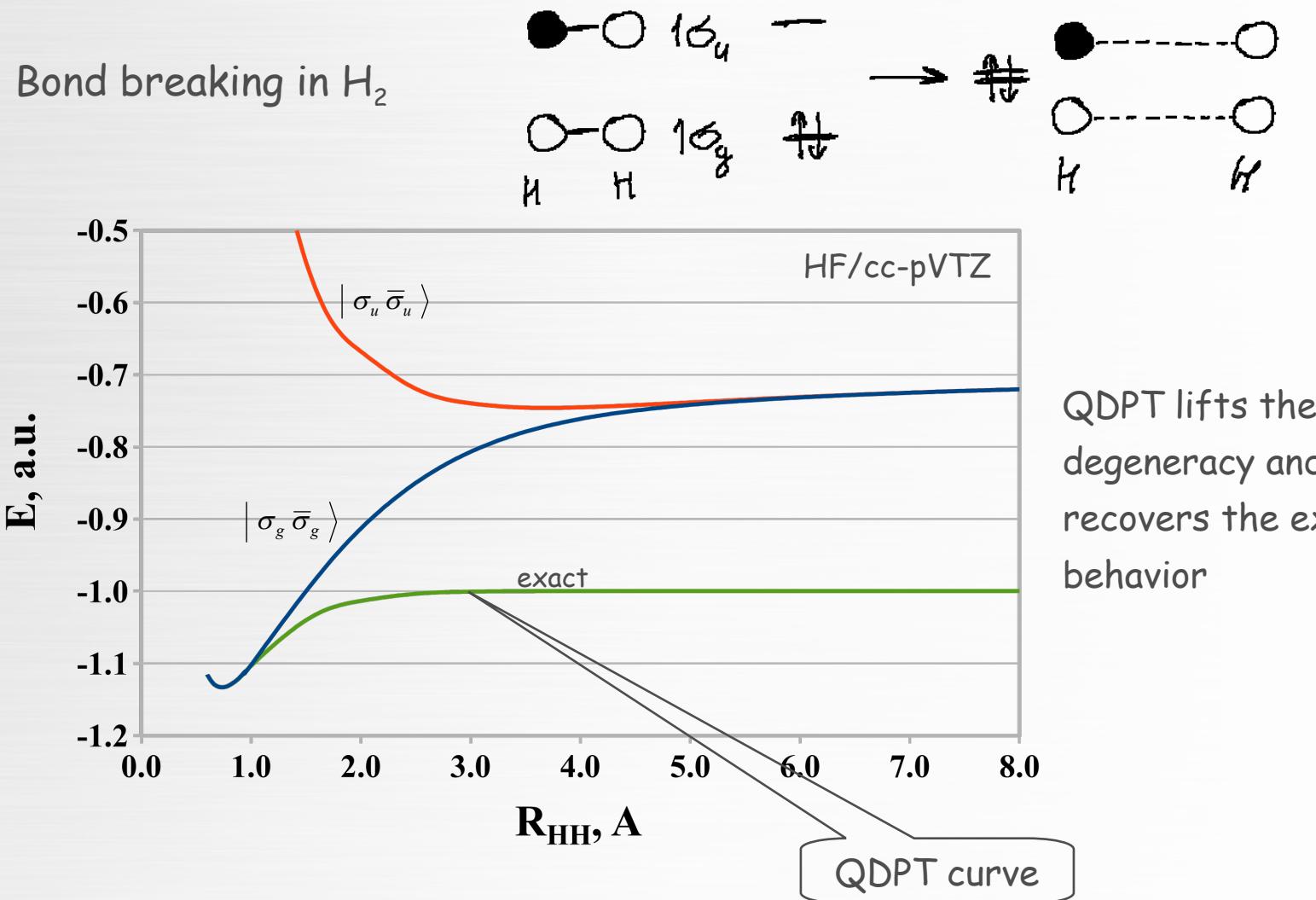
$$\begin{pmatrix} E_{HF} & K_{gu} \\ K_{gu} & E_{ij}^{ab} \end{pmatrix} \begin{pmatrix} \tilde{\Phi}_0 \\ \tilde{\Phi}_2 \end{pmatrix} = \begin{pmatrix} E_0 & 0 \\ 0 & E_2 \end{pmatrix} \begin{pmatrix} \tilde{\Phi}_0 \\ \tilde{\Phi}_2 \end{pmatrix}$$

Eigenvalues:

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

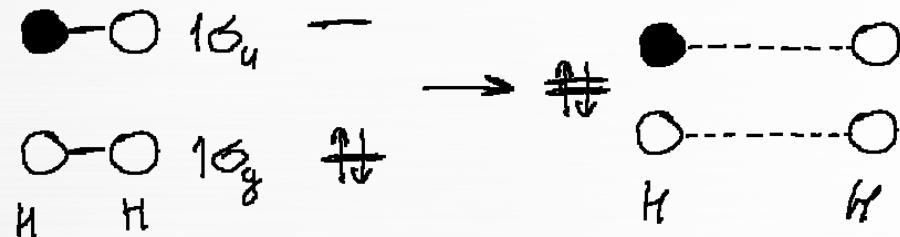
Non-linear in energies and couplings

Examples of non-dynamic electron correlation



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 combinations of old functions

$$\tilde{\Phi}_0 = C_{00} \Phi_{HF} + C_{20} \Phi_{ij}^{ab}$$

$$\tilde{\Phi}_2 = C_{02} \Phi_{HF} + C_{22} \Phi_{ij}^{ab}$$

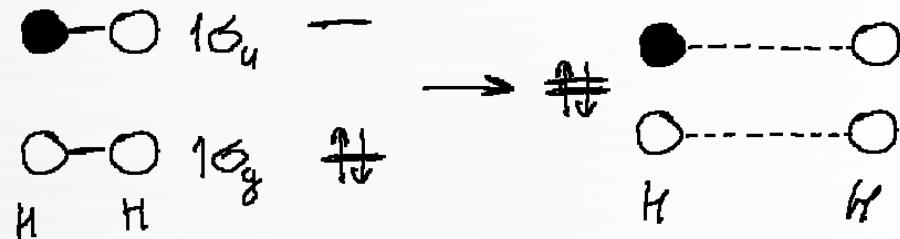
then $E_0 = C_{00}^2 E_{HF} + C_{20}^2 E_{ij}^{ab} + 2C_{00} C_{20} K_{gu}; \quad C_{00} > 0; C_{20} < 0$

because $\Phi_{HF} = |\sigma_g \bar{\sigma}_g\rangle \quad \Phi_{ij}^{ab} = |\sigma_u \bar{\sigma}_u\rangle \quad \rightarrow \quad 2C_{00}^2 = n_g \quad 2C_{20}^2 = n_u$

$$E_0 = \frac{n_g}{2} E_{HF} + \frac{n_u}{2} E_{ij}^{ab} - (n_g n_u)^{1/2} K_{gu} \quad \text{energy is a function of orbital's fractional occupation numbers (FONs)}$$

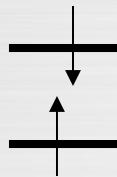
Examples of non-dynamic electron correlation

Bond breaking in H_2

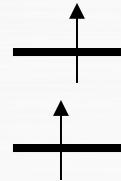


energies and coupling terms:

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



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



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

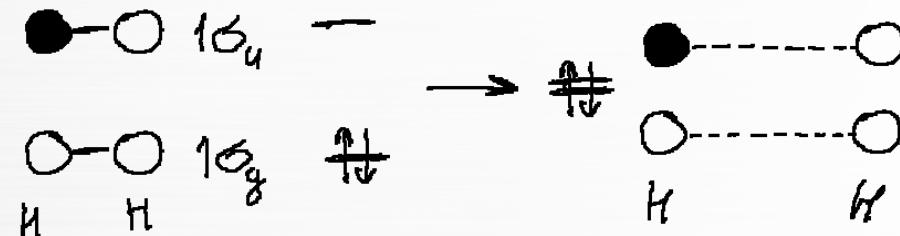
$$K_{gu} = E_{bs-u} - E_T$$

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

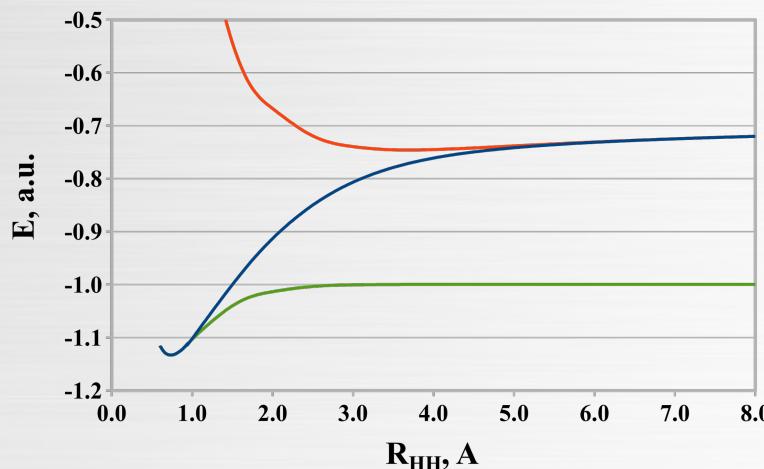
linear in energies only

Examples of non-dynamic electron correlation

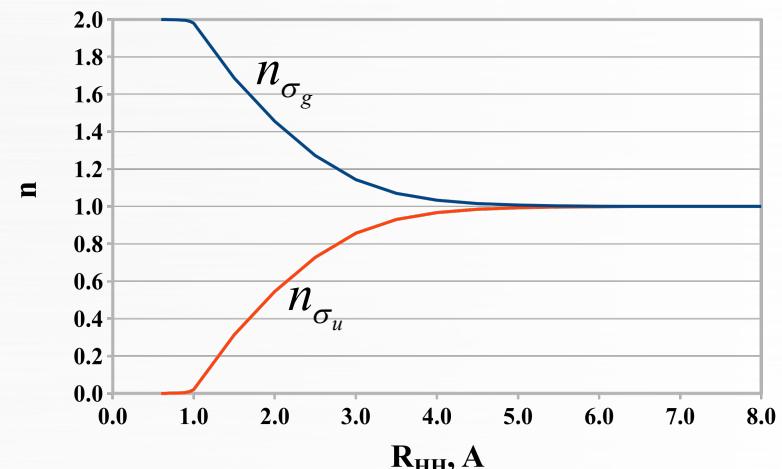
Bond breaking in H_2



energies



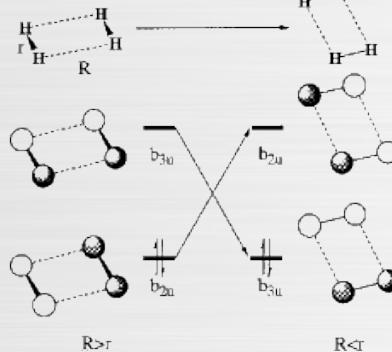
FONs in the exact energy



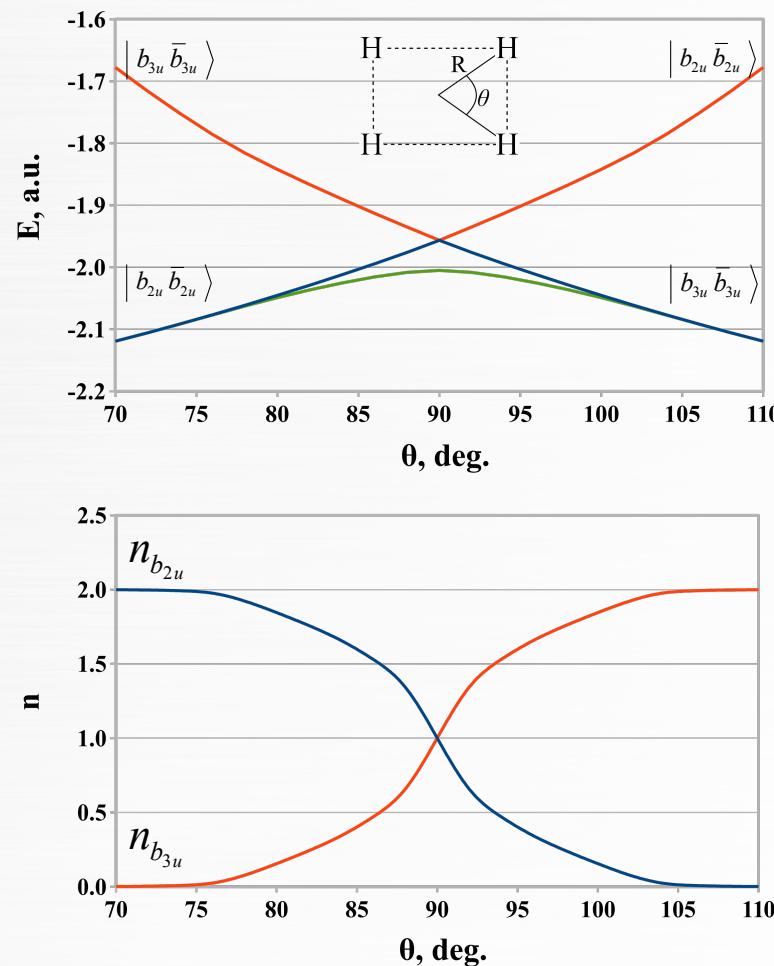
As bond breaks, FONs rapidly deviate from 2 and 0; converge at 1

Examples of non-dynamic electron correlation

Symmetry forbidden reaction: Automerization of rectangular H_4

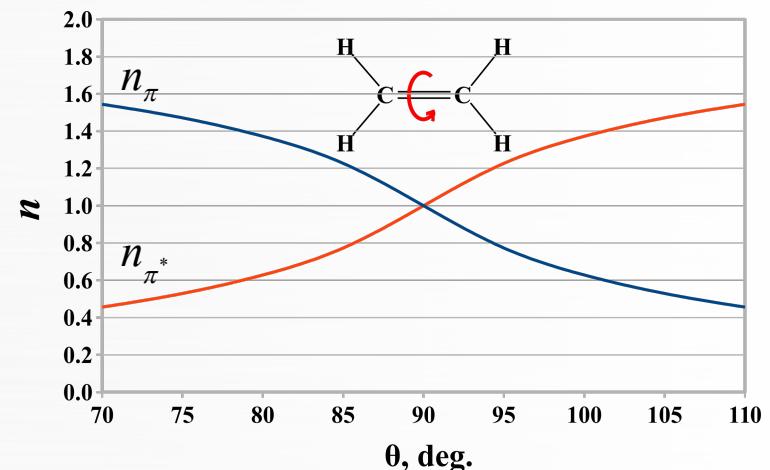
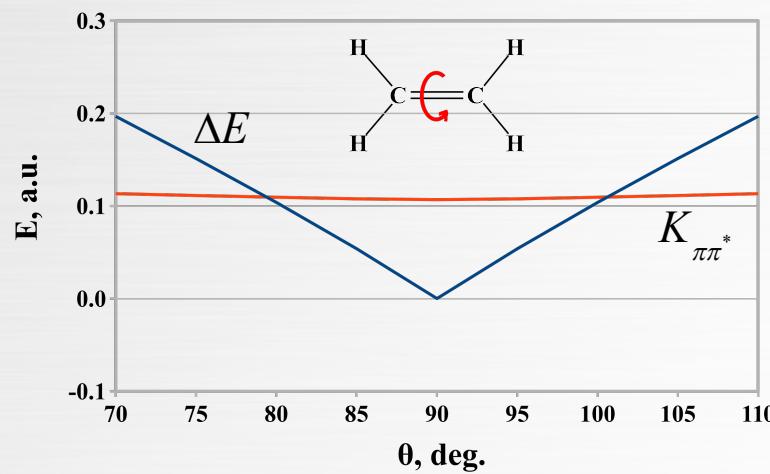
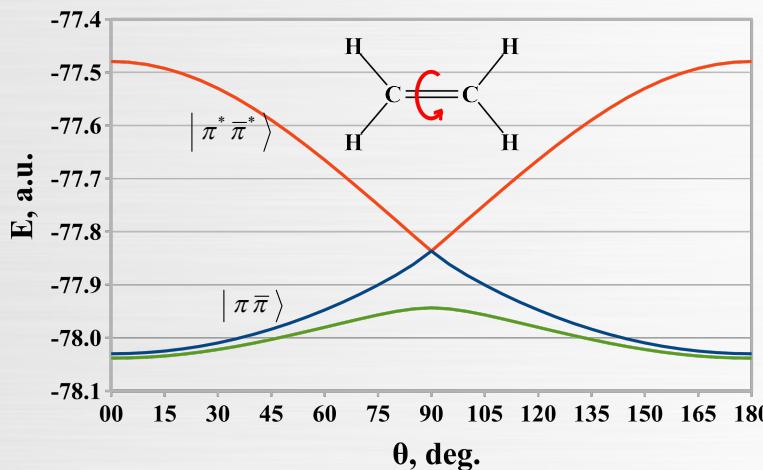


non-dynamic correlation
sets in long before the
degeneracy occurs



Examples of non-dynamic electron correlation

Double bond torsion of C_2H_4



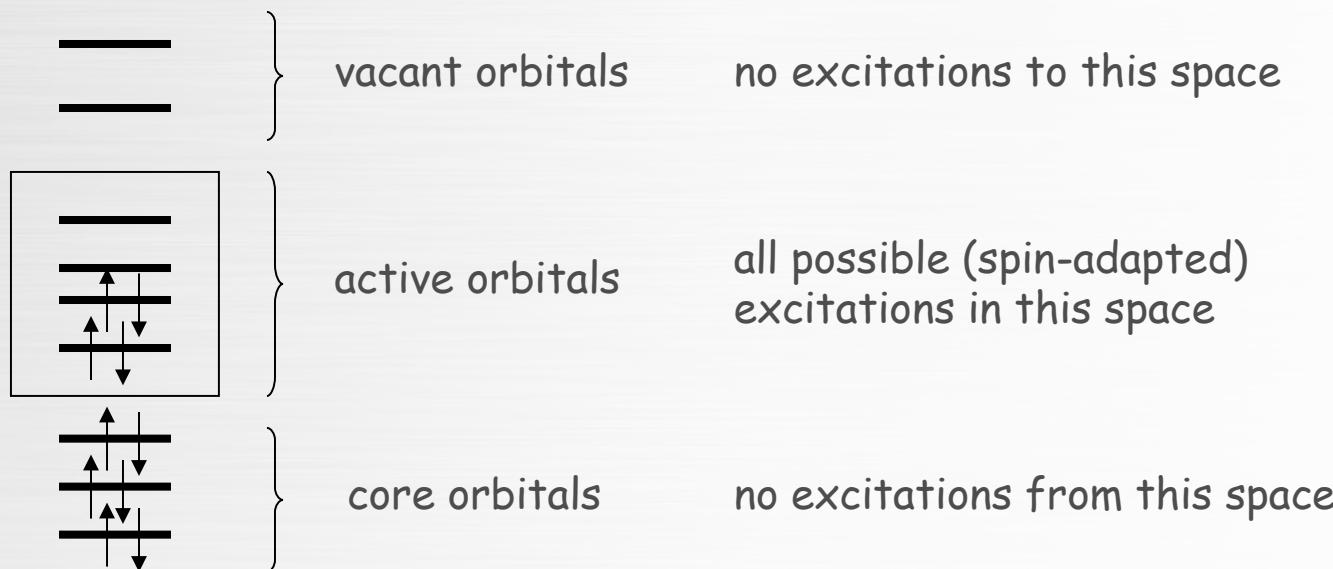
Multi-configurational wavefunction methods

complete-active
space wavefunction

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

excitation operators
(spin-symmetry adapted)

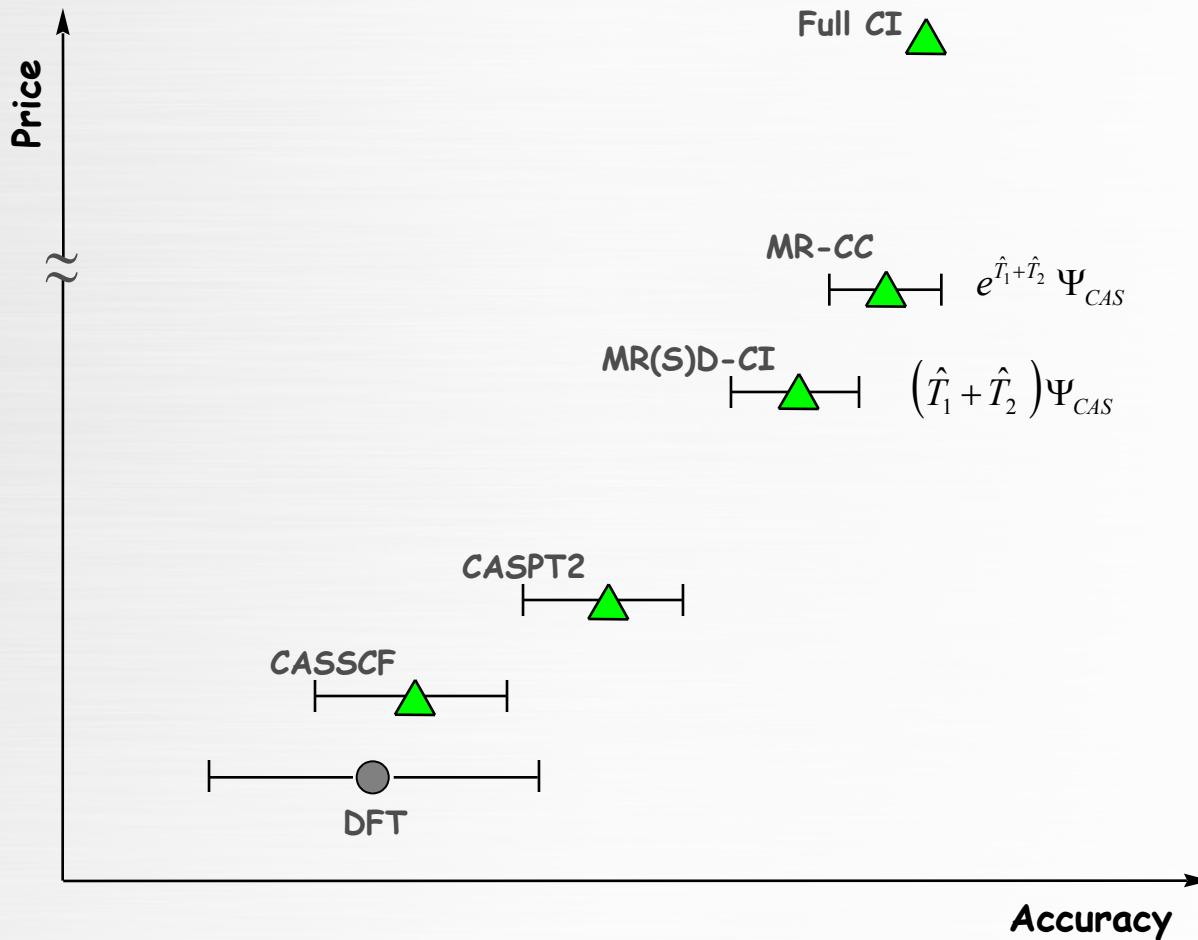
$$\hat{E}_I^A; \quad I \in \{i, ij, ijk, \dots\}; A \in \{a, ab, abc, \dots\}$$



$$E_{CAS} = \left\langle \Psi_{CAS} \left| \hat{H} \right| \Psi_{CAS} \right\rangle$$

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 ρ

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

Kohn-Sham method:

Assumes that any ρ can be mapped onto the ground state (single Slater determinant) of a non-interacting system (KS reference system)

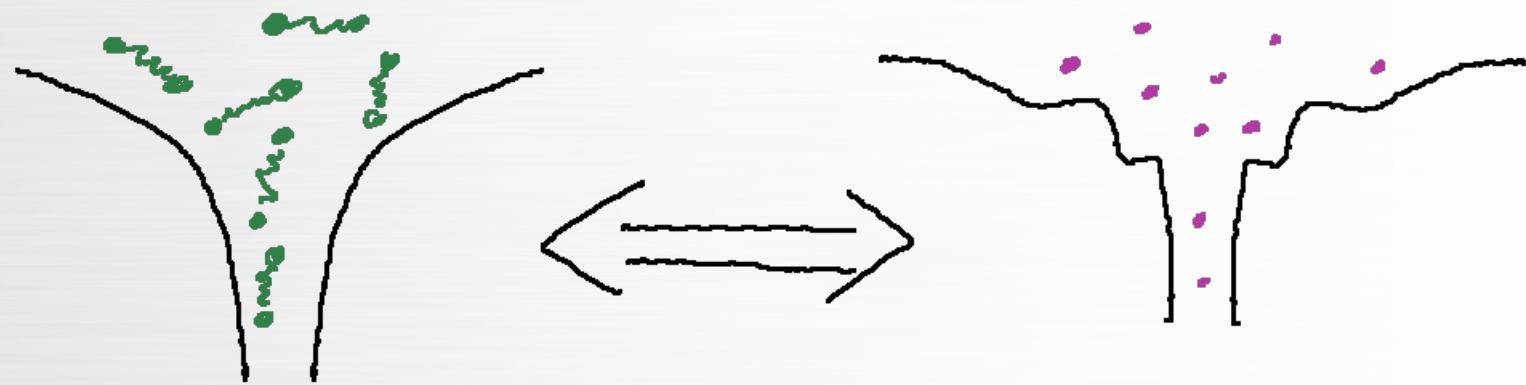
$$\rho \Leftrightarrow \rho_s$$

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



$$\lambda = 1$$

$$\lambda \cdot V_{ee}$$

$$\lambda = 0$$

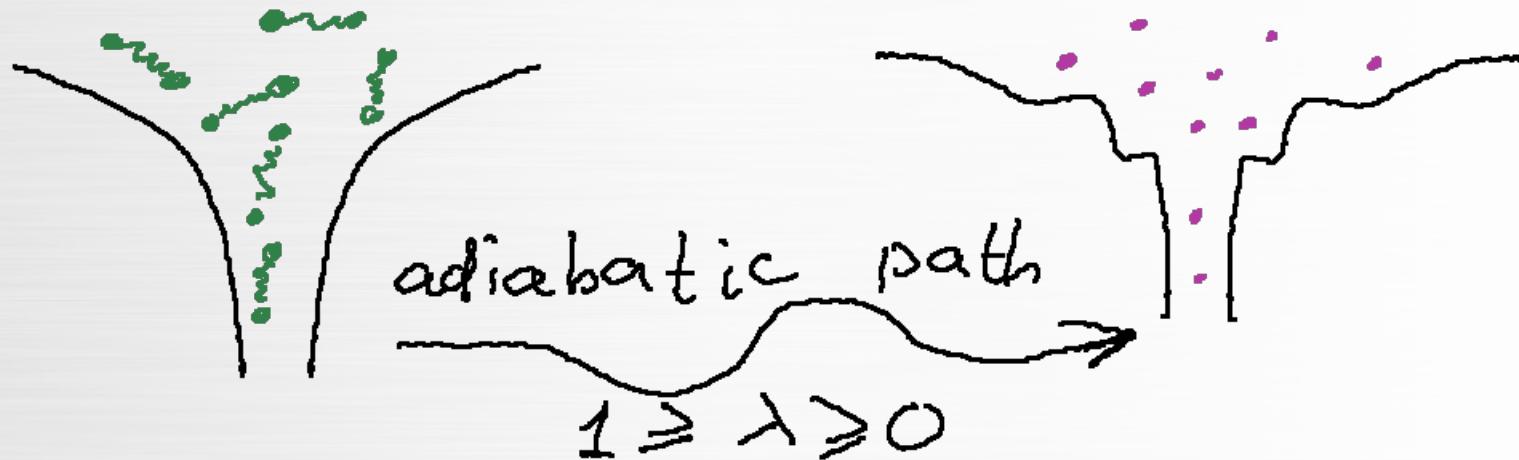
$$V_{ext}$$

$$\rho_0$$

$$V_s$$

$$\rho_s$$

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

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

$$\lambda = 1$$

$$\lambda \cdot V_{ee}$$

$$\lambda = 0$$

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

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

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

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

$$E_{Hxc} = \int_0^1 \frac{dE_\lambda}{d\lambda} d\lambda - \int (V_{ext}(\vec{r}) - V_s(\vec{r})) \rho(\vec{r}) d\vec{r} \quad \text{can be obtained from adiabatic connection}$$

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:	breaks symmetry and/or wrong	doesn't break symmetry

Ensemble DFT (eDFT)

Ground states:

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):

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

Excited states:

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

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

basis for variational DFT for excited states

Basic ideas of eDFT

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

The most important work:

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

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

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

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

E.-J. Baerends et al., (1998):

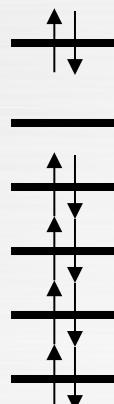
molecular systems H_2+H_2 , C_2 , CH_2

R. C. Morrison (2002):

Be-like atomic systems

not a ground state!!!

holes below
the Fermi level

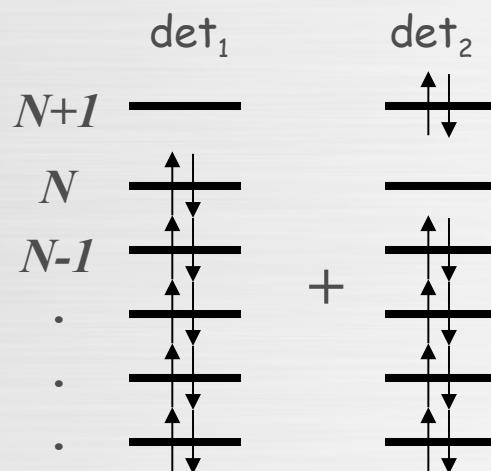


OR

Fractional Occupation Numbers
only a few KS orbitals with FONs

FONs in eDFT

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



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

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

$$\rho_{\text{ens}}(\vec{r}) = \lambda_1 \rho_1(\vec{r}) + \lambda_2 \rho_2(\vec{r})$$

$$= \sum_{i=1}^{N-1} 2|\phi_i(\vec{r})|^2 + 2\lambda_1 |\phi_N(\vec{r})|^2 + 2\lambda_2 |\phi_{N+1}(\vec{r})|^2$$

FONs result from *ensemble* of KS densities

$$\rho_{\text{ens}} = \sum_k \lambda_k \rho_k \longrightarrow \rho_{\text{ens}} = \sum_i^{\text{occ}} n_i |\phi_i|^2$$

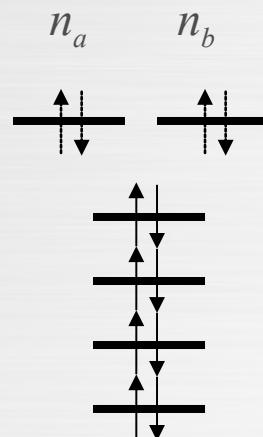
KS orbitals in eDFT

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

$$\varepsilon_k = \mu + \frac{\partial E}{\partial n_k}$$

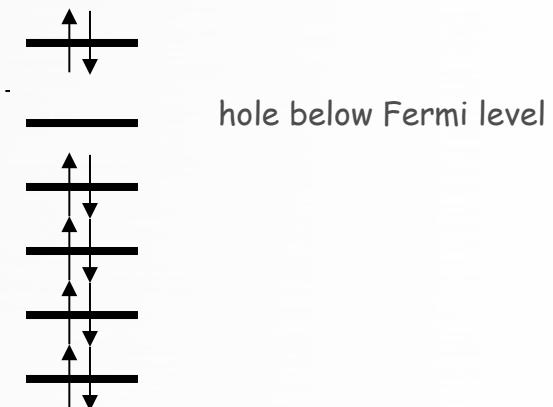
$$\frac{\partial E}{\partial n_k} = 0; \quad 0 < n_k < 2$$

ensemble KS state



$$\varepsilon_F \quad E_s^{\text{EV}} < E_s^{\text{PSV}}$$

pure KS state



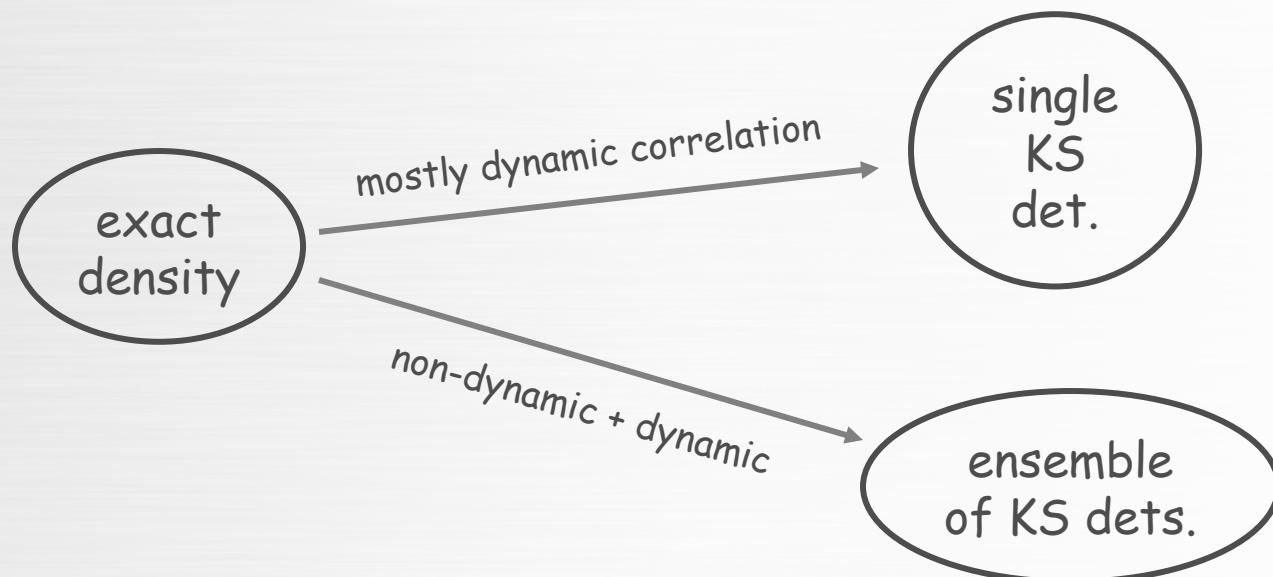
$$\rho_s^{\text{EV}} = \rho$$

$$\rho_s^{\text{PSV}} \approx \rho$$

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

then
$$\begin{aligned} J[\rho_{ens}] &= \frac{1}{2} \int d\vec{r}_1 d\vec{r}_2 r_{12}^{-1} \rho_{ens}(\vec{r}_1) \rho_{ens}(\vec{r}_2) \\ &= \frac{\lambda_a^2}{2} \int \frac{\rho_a(\vec{r}_1) \rho_a(\vec{r}_2)}{r_{12}} d\vec{r}_2 d\vec{r}_1 + \dots + \frac{\lambda_a \lambda_b}{2} \int \frac{\rho_a(\vec{r}_1) \rho_b(\vec{r}_2)}{r_{12}} d\vec{r}_2 d\vec{r}_1 + \dots \end{aligned}$$

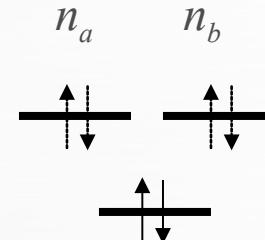
cross terms (ghost terms, Gross et al, 2002) - should not appear in ensemble energy

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

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 ($\lambda \approx 0$):

$$\begin{vmatrix} E_{a\bar{a}}^\lambda & \Delta_{ab}^\lambda \\ \Delta_{ab}^\lambda & E_{b\bar{b}}^\lambda \end{vmatrix}$$

$$\Delta_{ab}^\lambda = \lambda \langle aa | bb \rangle = (E_{a\bar{b}}^\lambda - E_{a\bar{b}}^\lambda)$$

exchange integral as energy difference

lowest root at $\lambda \approx 0$:

$$E = \frac{n_a^\lambda}{2} E_{a\bar{a}}^\lambda + \frac{n_b^\lambda}{2} E_{b\bar{b}}^\lambda - (n_a^\lambda n_b^\lambda)^{\nu_2} (E_{a\bar{b}}^\lambda - E_{a\bar{b}}^\lambda)$$

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

$$E = \frac{n_a}{2} E_{a\bar{a}}^{DFT} + \frac{n_b}{2} E_{b\bar{b}}^{DFT} - (n_a n_b)^{\nu_2} (E_{a\bar{b}}^{DFT} - E_{a\bar{b}}^{DFT})$$

λ -Integration of eDFT energy

Hamiltonian:

$$\hat{H}^\lambda = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i V_{ext}^\lambda(\vec{r}_i) + \lambda \sum_{i < j} r_{ij}^{-1}$$

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

Derivative w.r.t. λ :

$$\frac{dE_{a\bar{a}}^\lambda}{d\lambda} = \int d\vec{r} \rho(\vec{r}) \frac{dV_{ext}^\lambda}{d\lambda} + \frac{dE_{Hxc}^\lambda}{d\lambda}$$

Expand the secular matrix:

$$\begin{pmatrix} E_{a\bar{a}}^\lambda & \Delta_{ab}^\lambda \\ \Delta_{ab}^\lambda & E_{b\bar{b}}^\lambda \end{pmatrix} = \begin{pmatrix} E_{a\bar{a}}^0 & 0 \\ 0 & E_{b\bar{b}}^0 \end{pmatrix} + \lambda \begin{pmatrix} \frac{dE_{a\bar{a}}^\lambda}{d\lambda} & \frac{d\Delta_{ab}^\lambda}{d\lambda} \\ \frac{d\Delta_{ab}^\lambda}{d\lambda} & \frac{dE_{b\bar{b}}^\lambda}{d\lambda} \end{pmatrix} + O(\lambda^2)$$

Lowest root (expansion):

$$E^\lambda = \frac{n_a^\lambda}{2} E_{a\bar{a}}^0 + \frac{n_b^\lambda}{2} E_{b\bar{b}}^0 + \lambda \left(\frac{n_a^\lambda}{2} \frac{dE_{a\bar{a}}^\lambda}{d\lambda} + \frac{n_b^\lambda}{2} \frac{dE_{b\bar{b}}^\lambda}{d\lambda} - (n_a^\lambda n_b^\lambda)^{\frac{1}{2}} \frac{d\Delta_{ab}^\lambda}{d\lambda} \right)$$

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

$$= \int d\vec{r} \rho_{ens}(\vec{r}) \left(V_{ext}^1(\vec{r}) - V_{ext}^0(\vec{r}) \right) + \frac{n_a}{2} E_{Hxc}^1[a\bar{a}] + \frac{n_b}{2} E_{Hxc}^1[b\bar{b}] - (n_a n_b)^{\frac{1}{2}} \Delta_{ab}^1$$

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

$$\rho_{ens}(\vec{r}) = \frac{n_a}{2} \rho_a(\vec{r}) + \frac{n_b}{2} \rho_b(\vec{r}) \quad E_{a\bar{a}}^0 = -\frac{1}{2} \sum_k \left\langle \phi_k \left| \nabla^2 \right| \phi_k \right\rangle + \int d\vec{r} \rho(\vec{r}) V_{ext}^0(\vec{r})$$

$$\begin{aligned} E^1 &= \frac{n_a}{2} \left[\left(E_{a\bar{a}}^0 - \int d\vec{r} \rho_a(\vec{r}) V_{ext}^0(\vec{r}) \right) + \int d\vec{r} \rho_a(\vec{r}) V_{ext}^1(\vec{r}) + E_{Hxc}^1[a\bar{a}] \right] \\ &\quad + \frac{n_a}{2} \left[\left(E_{b\bar{b}}^0 - \int d\vec{r} \rho_b(\vec{r}) V_{ext}^0(\vec{r}) \right) + \int d\vec{r} \rho_b(\vec{r}) V_{ext}^1(\vec{r}) + E_{Hxc}^1[b\bar{b}] \right] - (n_a n_b)^{\frac{1}{2}} \Delta_{ab}^1 \\ &= \frac{n_a}{2} E_{a\bar{a}}^1 + \frac{n_b}{2} E_{b\bar{b}}^1 - (n_a n_b)^{\frac{1}{2}} \Delta_{ab}^1 \quad (\text{final expression}) \end{aligned}$$

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

strong correlation

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

2×2

$$\begin{vmatrix} E_{aa} & \Delta_{ab} \\ \Delta_{ab} & E_{bb} \end{vmatrix}$$

$n_a \sim n_b \sim 1$

$$E = \frac{n_a}{2} E_{aa} + \frac{n_b}{2} E_{bb} - \sqrt{n_a n_b} \Delta_{ab}$$

weak correlation

$$\frac{1}{b}$$

$$\frac{1}{a}$$

interpolation

$$f(n_a, n_b)$$

$$E_{aa}$$

$n_a \sim 2, n_b \sim 0$

$$E = \frac{n_a}{2} E_{aa} + \frac{n_b}{2} E_{bb} - (n_a n_b) \Delta_{ab}$$

Interpolation between strong and weak correlation

Inspect the usual KS DFT energy

with the ensemble density

XC part is inseparable,
so only an approximation

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

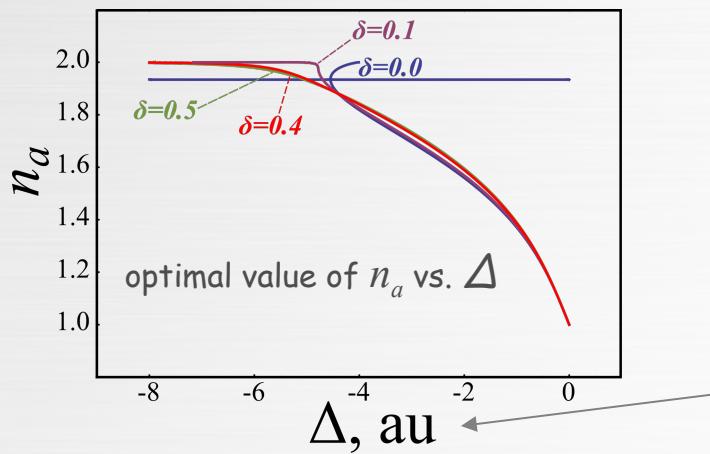
$$\rho_{ens} = \frac{n_a}{2} |\phi_a|^2 + \frac{n_b}{2} |\phi_b|^2$$

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

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:

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



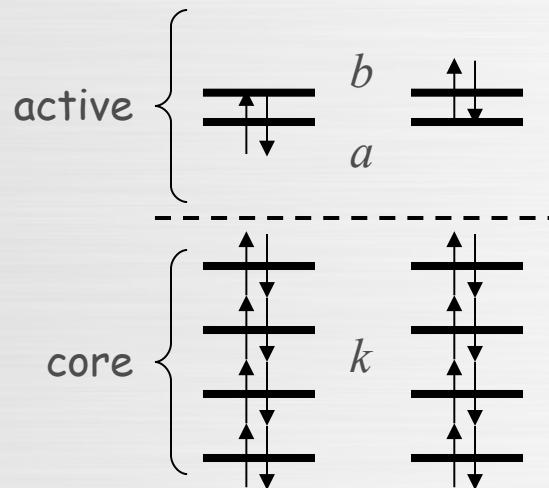
$\delta = 0.4$ - smooth transition btw single det. and ensemble

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

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

spin-Restricted Ensemble-referenced KS (REKS) method

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



Energy is optimized w.r.t.

- KS orbitals
- fractional occupation numbers

Density:

$$\begin{aligned}\rho(\mathbf{r}) &= \frac{n_a}{2} \rho_a(\mathbf{r}) + \frac{n_b}{2} \rho_b(\mathbf{r}) \\ &= \sum_k^{\text{core}} 2 |\phi_k(\mathbf{r})|^2 + n_a |\phi_a(\mathbf{r})|^2 + n_b |\phi_b(\mathbf{r})|^2\end{aligned}$$

Energy:

$$E = \frac{n_a}{2} E[\rho_{a\bar{a}}] + \frac{n_b}{2} E[\rho_{b\bar{b}}] - f(n_a, n_b) (E[\rho_{a\bar{b}}] + E[\rho_{\bar{a}b}] - E[\rho_{ab}] - E[\rho_{\bar{a}\bar{b}}])$$

all approximations
are here

REKS technology: orbital optimization

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

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

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

$$\varepsilon_{pq} = \varepsilon_{qp}^* \quad \text{Hermiticity of } \varepsilon - \text{variational condition}$$

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

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

$$\hat{F}_q = \sum_L w_L \frac{n_{q,L}^\alpha \hat{F}_L^\alpha + n_{q,L}^\beta \hat{F}_L^\beta}{n_q}$$

combined "Fock" operator (diagonalizable)

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

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

$$\rho = \sum_k^n \omega_k \rho_k \quad E = \sum_k^n \omega_k E[\rho_k]$$

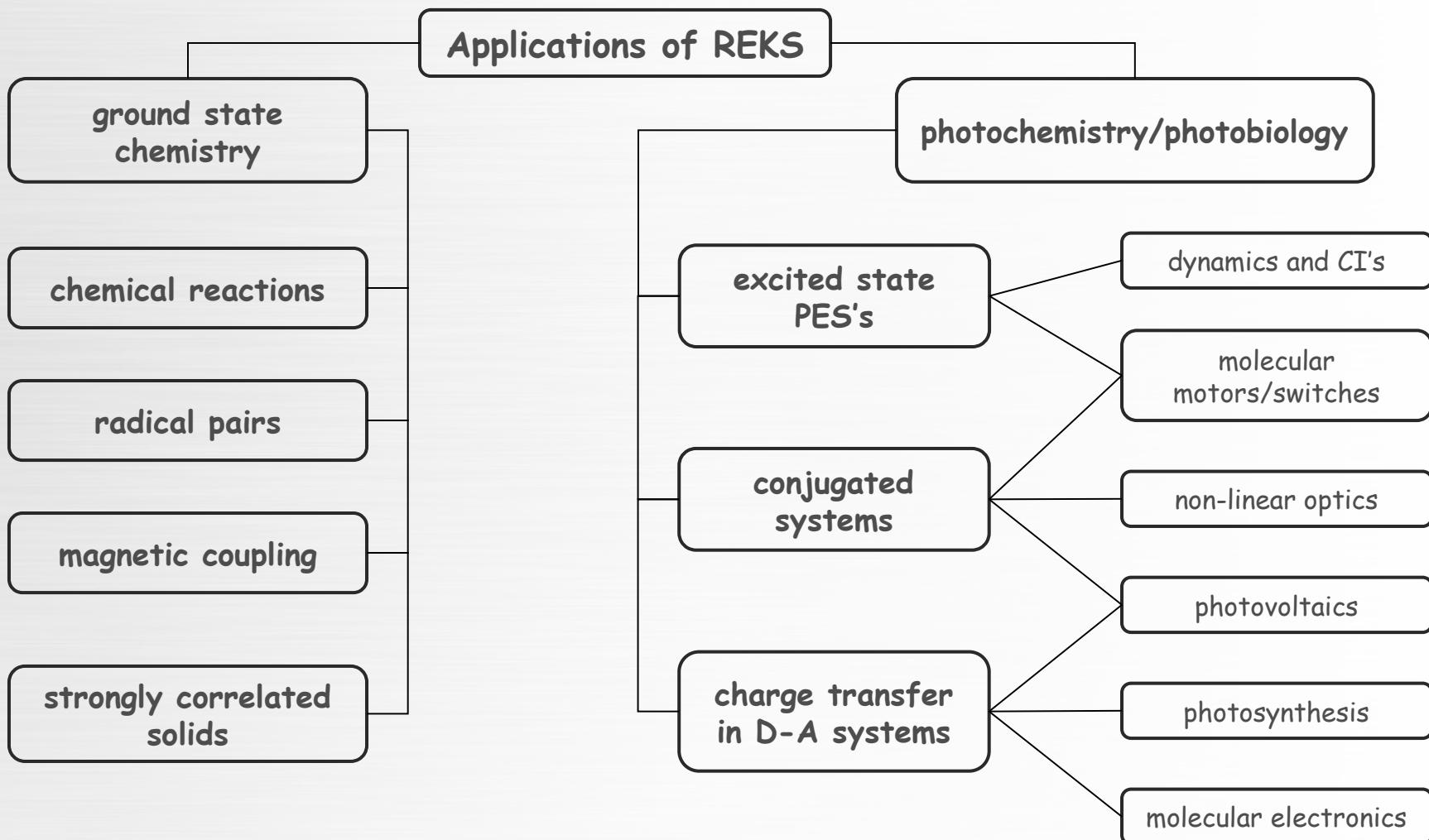
Designed to describe strong (static) correlation

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

Can be used with any approximate density functional

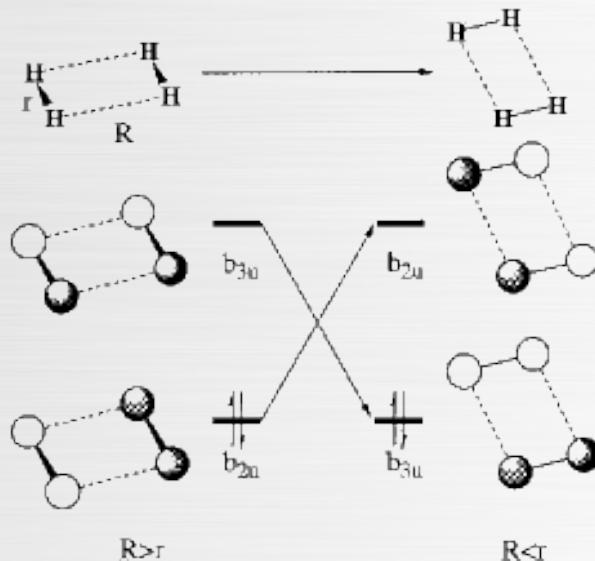
Computational cost: mean-field cost (similar to the usual DFT)

Applications of REKS methodology



Benchmarking REKS vs. exact eDFT

Model system: $\text{H}_2 + \text{H}_2$ (D_{2h})
 [2+2] cycloaddition; symmetry forbidden

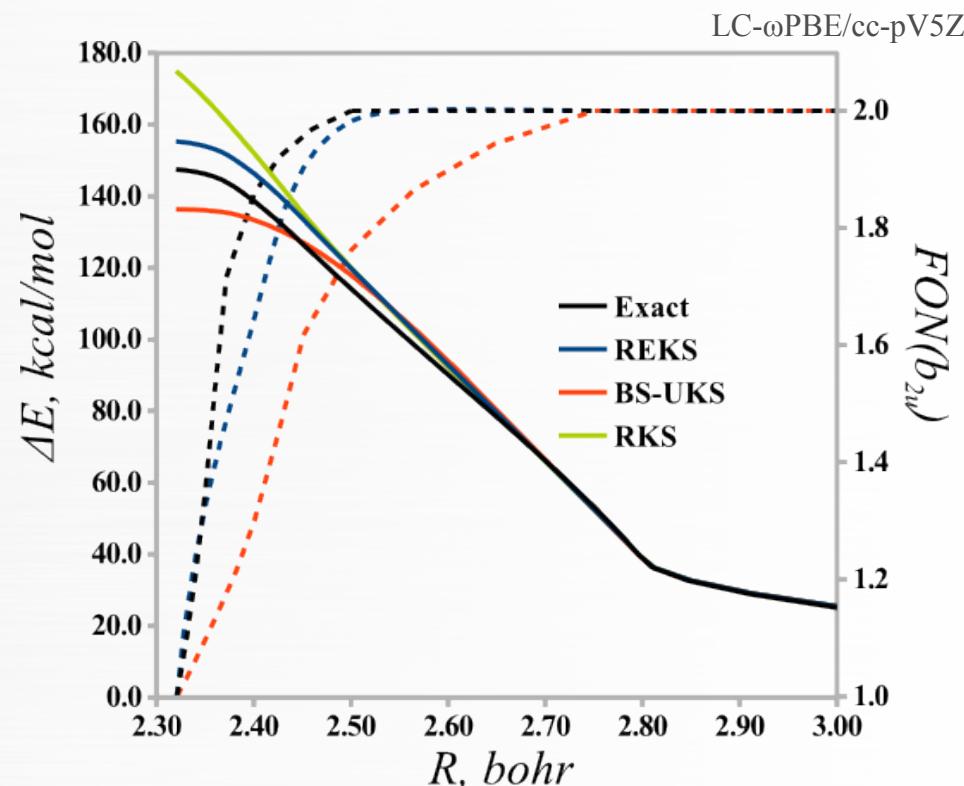


Exact KS DFT:

REKS:

BS-UKS:

Standard RKS:



fractional orbital occupations (ensemble)

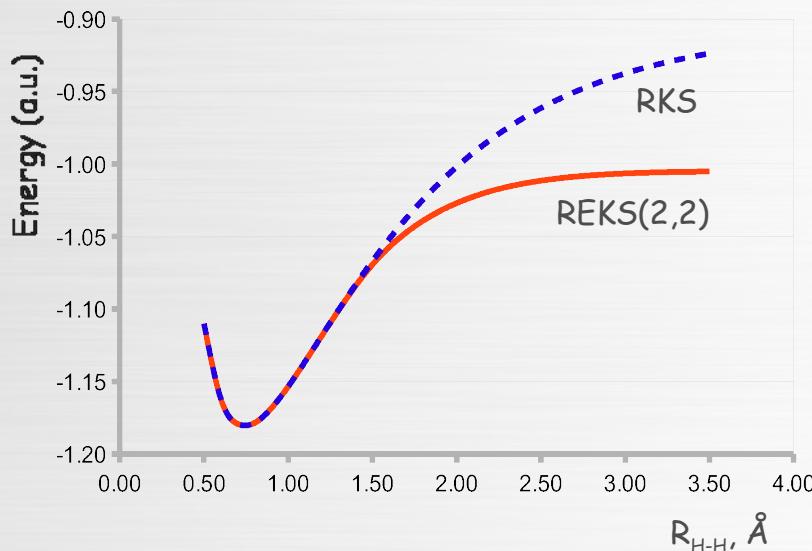
accurate PES and orbital occupations

underestimates barrier, overestimates static correlation

fails completely

Applications of REKS: Bond dissociation

Bond stretching in H_2



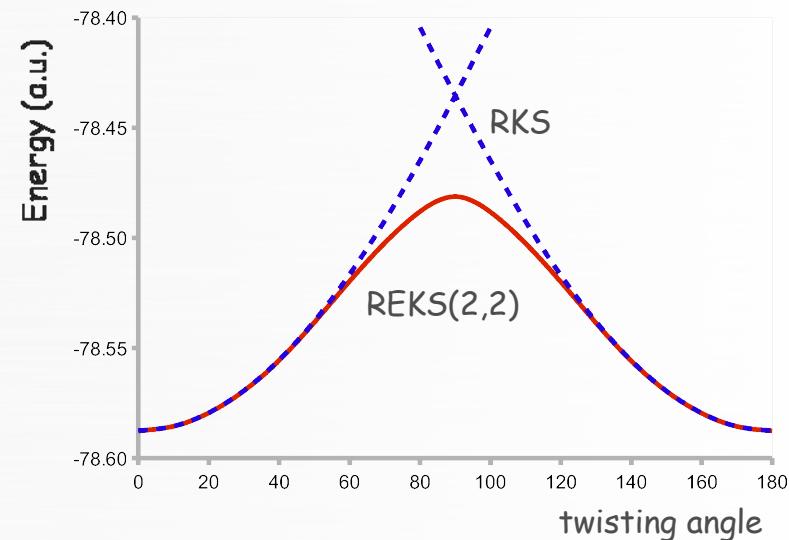
Total energy at R_{H-H} = 0.741 Å

$$E^{\text{RKS}} = -1.1786 \text{ a.u.}$$

$$E^{\text{REKS}} = -1.1786 \text{ a.u.}$$

B3LYP/aug-cc-pVQZ

Twisting about double bond in C₂H₄



Total energy of planar ethylene

$$E^{\text{RKS}} = -78.5874 \text{ a.u.}$$

$$E^{\text{REKS}} = -78.5874 \text{ a.u.}$$

B3LYP/6-31G*

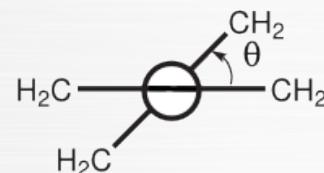
Applications of REKS: Tetramethyleneethane diradical

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

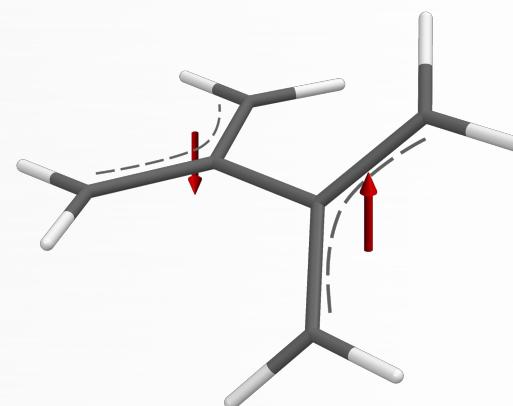
resonance structures



frontier orbitals

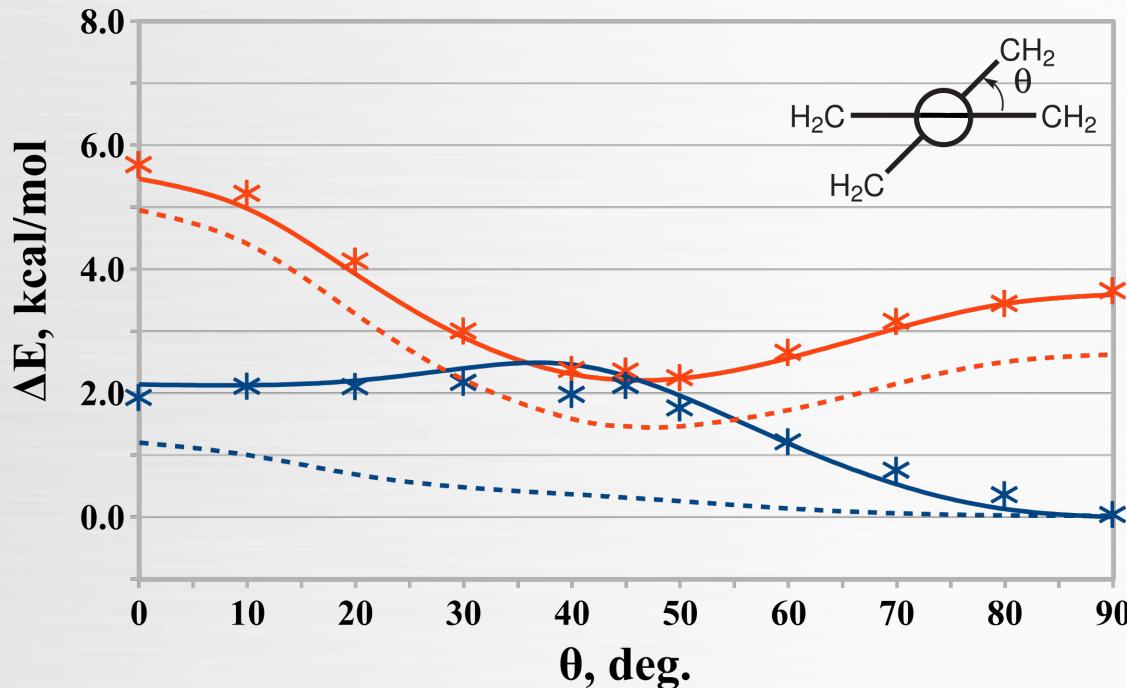


TME: singlet or triplet?



- | | | |
|--|---|-------------------------|
| Matrix isolated TME: | <u>triplet</u> EPR signal; linear CW plot | (Dowd, 1970, 1986) |
| NIPE spectroscopy ($\text{TME}^{\cdot-}$): | <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

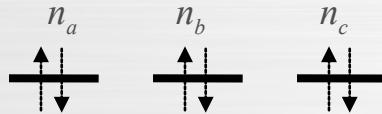
Triplet is meta-stable at intermediate θ (trapping, slow relaxation)

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 $\lambda \approx 0$:

$$\begin{vmatrix} E_{a\bar{a}}^\lambda & \Delta_{ab}^\lambda & \Delta_{ac}^\lambda \\ \Delta_{ab}^\lambda & E_{b\bar{b}}^\lambda & \Delta_{bc}^\lambda \\ \Delta_{ac}^\lambda & \Delta_{bc}^\lambda & E_{c\bar{c}}^\lambda \end{vmatrix}$$

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

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

carry out λ -integration:

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

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

optimize:

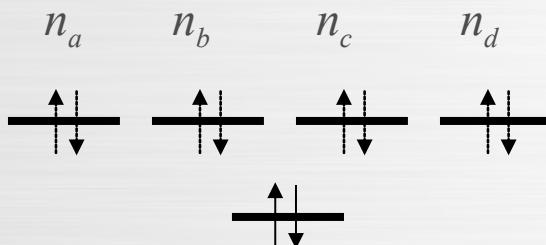
the orbitals and FONs;
enjoy;

}

Extending REKS to larger active spaces

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

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

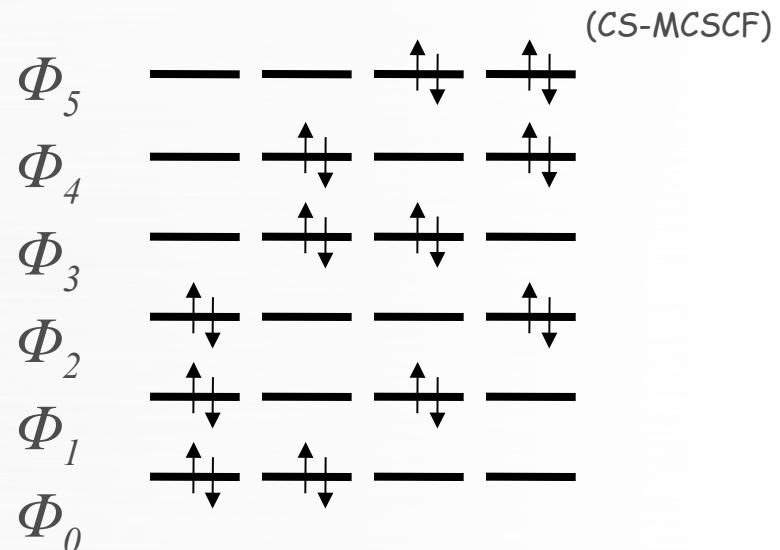


6x6 secular problem;
only 4 FON's;
no unique mapping of C's on FONs

Idea: use GVB to reduce the problem

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

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



only pairs of natural orbitals
(geminals) are needed

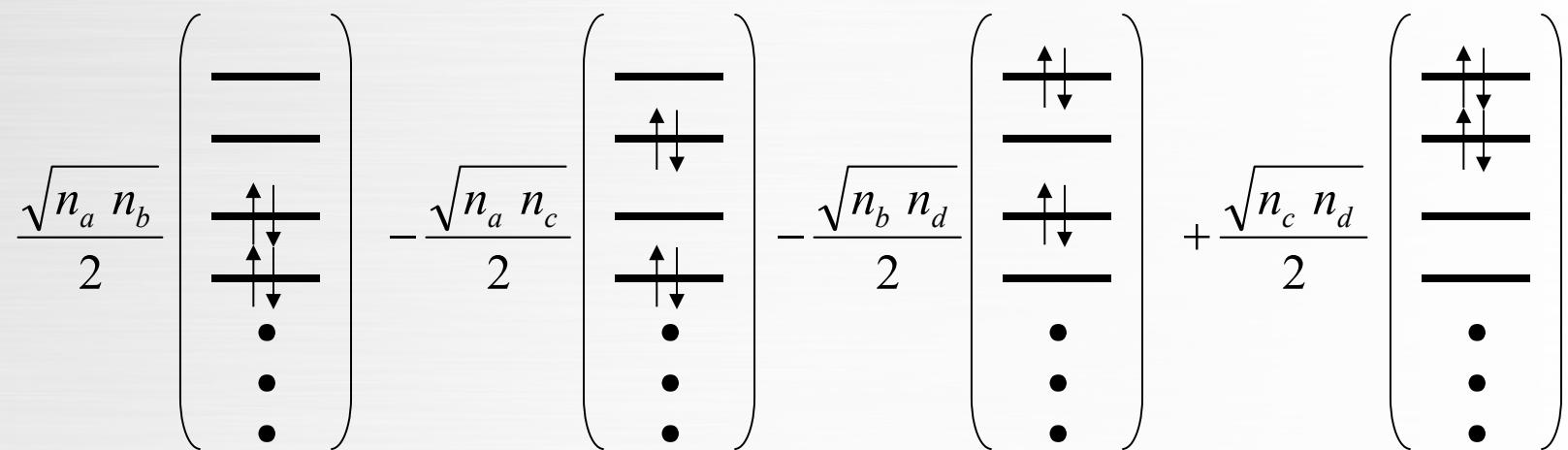
REKS energy for several NO pairs can be easily derived

REKS(4,4)

REKS(4,4) employs perfectly spin-paired singlet (PPS) state (a,d) and (b,c) GVB pairs

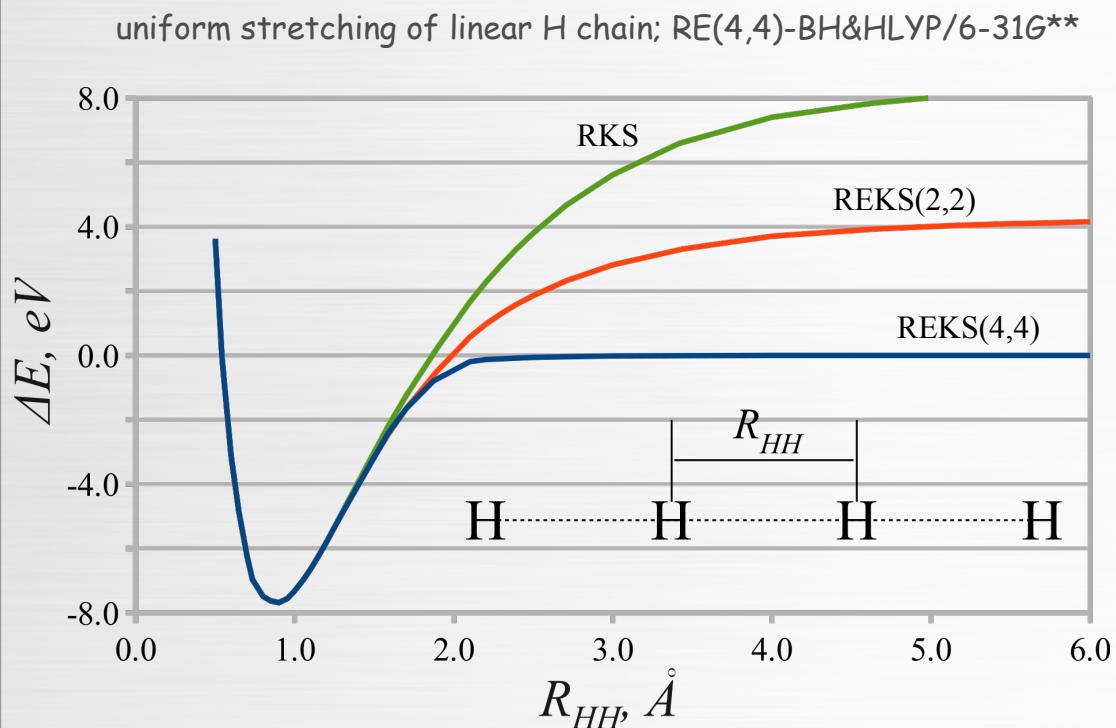
$$\Psi^{GVB-PP} = \hat{\mathcal{A}}[\dots \Phi_0^{NO}(1,2)\Phi_0^{NO}(3,4)\dots] \quad \quad \Phi_0^{NO}(1,2) = \sqrt{\frac{n_a}{2}}|\phi_a \bar{\phi}_a\rangle - \sqrt{\frac{n_b}{2}}|\phi_b \bar{\phi}_b\rangle$$

size-consistent wavefunction



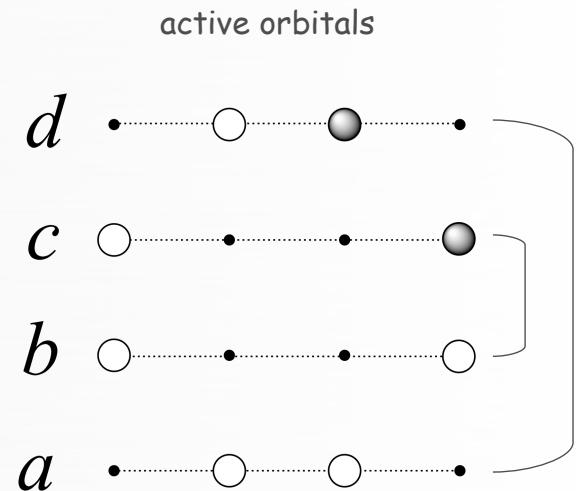
$$E^{(4,4)} = \frac{n_a n_b}{4} E_{a\bar{a}b\bar{b}} + \frac{n_a n_c}{4} E_{a\bar{a}c\bar{c}} + \frac{n_b n_d}{4} E_{b\bar{b}d\bar{d}} + \frac{n_c n_d}{4} E_{c\bar{c}d\bar{d}} - (n_a n_d)^{\frac{1}{2}} \Delta_{ad} - (n_b n_c)^{\frac{1}{2}} \Delta_{bc}$$

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

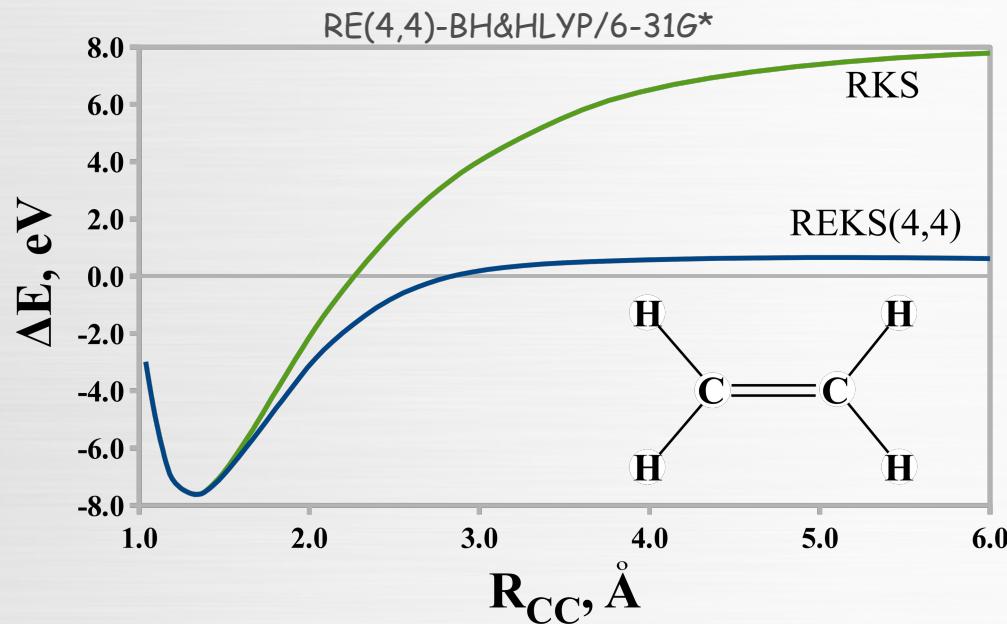


size-consistent when dissociating into individual atoms (spin centers)

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



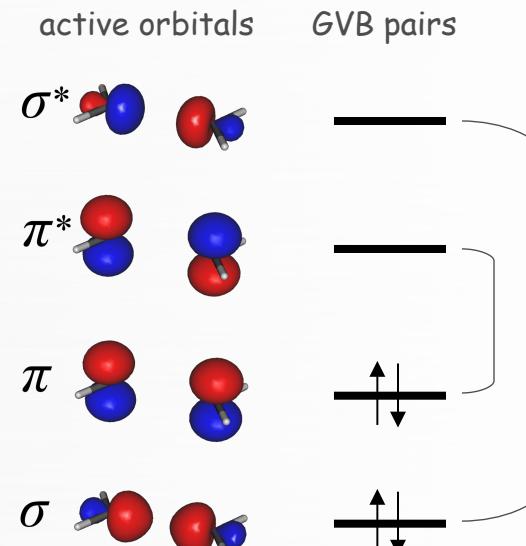
REKS(4,4): Double Bond Dissociation



dissociation into open-shell fragments;

$$E^{(4,4)}(\text{C}_2\text{H}_4) \Big|_{R_{CC} \rightarrow \infty} \neq 2 E(^3\text{CH}_2)$$

spin re-coupling on the fragments - requires open-shell configurations corrected by SSR(4,4); see below.



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