

# Lecture 2: The ab initio many-body problem: from Hartree-Fock to wavefunction techniques

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# Outline

- Slater determinant, second quantization, 1e orbitals
- Hartree-Fock (HF) method and self-consistent field (SCF)
- Static and dynamic electronic correlations
- Configuration interaction (CI)
- Many-Body or Moller-Plesset (MP) perturbation theory, MP2
- Coupled cluster (CC), CCSD(T), EOM-CCSD
- Multiconfiguration SCF, CASSCF
- Composite methods, G4

# The Electronic Structure Problem

- A molecule composed from nuclei and electrons bound by Coulomb interactions
- Separate electronic (fast) from nuclei (slow) motion (adiabatic or Born-Oppenheimer approximation)
- Assign finite basis size (lattice) – Gaussian (Gaussian, Turbomole, Q-Chem, etc.) or plain waves (VASP, etc.) or Slater (ADF, etc.)
- Solve the Schrodinger equation for molecular electronic Hamiltonian:

$$\left[ -\frac{1}{2} \sum_i \nabla_i^2 - \sum_{iA} \frac{Z_A}{r_{iA}} + \sum_{i>j} \frac{1}{r_{ij}} \right] \psi_e(\mathbf{r}; \mathbf{R}) = E_e \psi_e(\mathbf{r}; \mathbf{R})$$

Exponentially hard  
with respect to N-  
electrons

<b>Method</b>	<b>Hamiltonian</b>	<b>Wavefunction</b>	<b>Cost</b>
<b>Ab initio</b> (e.g. HF, CAS-CI, CC-EOM)	<b>Exact</b>	<b>Approximate</b> (All electronic correlations)	<b>Large</b> (~10 atoms)
<b>Density Functional</b> (e.g. DFT, TDDFT)	<b>Approximate, <math>F(\rho)</math>,</b> (All electronic correlations)	<b>Fixed</b> (Kohn-Sham system, mean field)	<b>Significant</b> (~100 atoms)
<b>Semiempirical</b> (e.g. AM1, MNDO, INDO/S)	<b>Approximate,</b> (Some electronic correlations)	<b>Approximate</b> (Some electronic correlations)	<b>Low</b> (~1000 atoms)
<b>Tight-binding</b> (e.g. Huckel, Frenkel, SSH)	<b>Approximate,</b> (Min electronic correlations)	<b>Approximate</b> (Usually uncorrelated)	<b>Low</b> (~10,000 atoms)

# Electronic Hamiltonian in the second quantization form

*Using given basis set functions, the electronic Hamiltonian can be conveniently represented in a matrix form:*

$$\hat{H}_e = - \sum_i^N \frac{1}{2} \nabla_i^2 - \sum_i^N \sum_A^M \frac{Z_A}{r_{iA}} + \sum_{i>j}^N \frac{1}{r_{ij}}$$

$$\hat{H}_e = \sum_{mn}^K t_{mn} c_m^+ c_n + \frac{1}{2} \sum_{mnkl}^K V_{nm,kl} c_m^+ c_n^+ c_k c_l$$

One – electron integrals ( $t_{nm}$  or  $H_{nm}$ ),  $K \times K$  matrix

$$t_{nm} = \langle n | - \frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|} | m \rangle \equiv \int d\mathbf{r}_1 \psi_n^*(1) \left( \nabla_1^2 - \sum_A \frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|} \right) \psi_m(1)$$

Two – electron integrals (Coulomb electron-electron interaction), tetradic  $K \times K \times K \times K$  matrix

$$\langle nm | kl \rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_n^*(1) \psi_m^*(2) \frac{1}{r_{12}} \psi_k(1) \psi_l(2)$$

*Major problem: too many of them, V will not fit to the memory and needs to be calculated on-the-fly (direct method)*

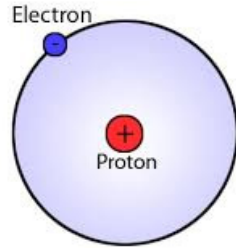
Other observables (generally described as  $K \times K$  matrices), such as dipole operator

$$\mu_{nm} = \langle n | \hat{\mu} | m \rangle \equiv \int d\mathbf{r}_1 \psi_n^*(1) \mathbf{r}_1 \psi_m(1) \quad \text{So interaction with electric field: } \mathcal{E}(t) \sum_{mn}^K \mu_{mn} c_m^+ c_n$$

# Pauli exclusion principle: electron spin

**Electrons are fermions with spin  $\frac{1}{2}$  obeying Pauli exclusion principle: no two electrons can occupy the same state (i.e., can be characterized by the same set of quantum numbers).**

For example, for electron in a hydrogen-like atom we have 4 numbers:  $n$  – principal quantum number ( $\sim$ average distance from the nuclei),  $l$  – azimuthal quantum number ( $\sim$ shape of the orbital),  $m$  – magnetic quantum number ( $\sim$ orientation of the orbital),  $m_s$  – spin quantum number ( $+1/2$  or  $-1/2$ , electron spin)



Spin degree of freedom lead to the introduction of spin orbitals:

$$\chi(\mathbf{x}) = \begin{cases} \psi(\mathbf{r})\alpha(\omega) \\ \text{or} \\ \psi(\mathbf{r})\beta(\omega) \end{cases}$$

One spatial single-electron orbital can be occupied up to 2 electrons

The Pauli exclusion principle: electronic wave functions must *change sign* whenever the coordinates of two electrons are interchanged, i.e., to be 'antisymmetric'.

$$\Psi[\mathbf{q}_1(1), \dots, \mathbf{q}_j(i), \dots, \mathbf{q}_i(j), \dots, \mathbf{q}_N(N)] = -\Psi[\mathbf{q}_1(1), \dots, \mathbf{q}_i(i), \dots, \mathbf{q}_j(j), \dots, \mathbf{q}_N(N)]$$

# Pauli exclusion principle: electron spin

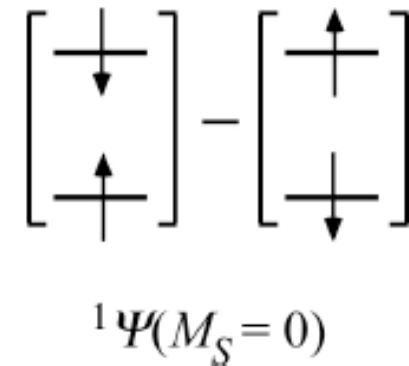
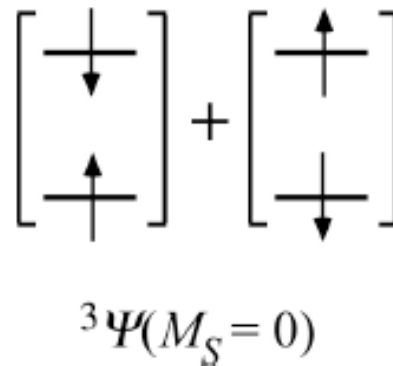
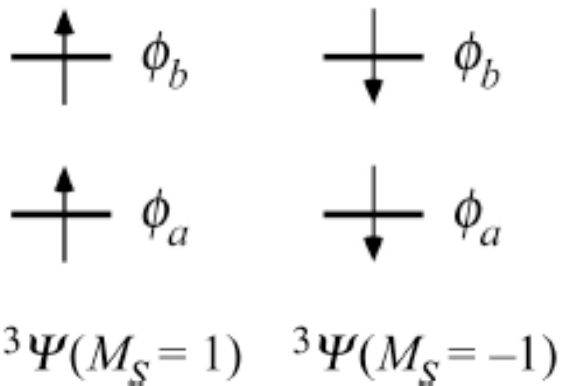
Example: singlet ( $S=0$ )  
and triplet ( $S=1$ ) states  
of 2 electrons.

$M_s = m_{s1} + m_{s2}$  are the  
z-components of the  
vector  $S$ .  $M_s$  takes  $(2S+1)$   
values, where  $(2S+1)$  is  
spin multiplicity

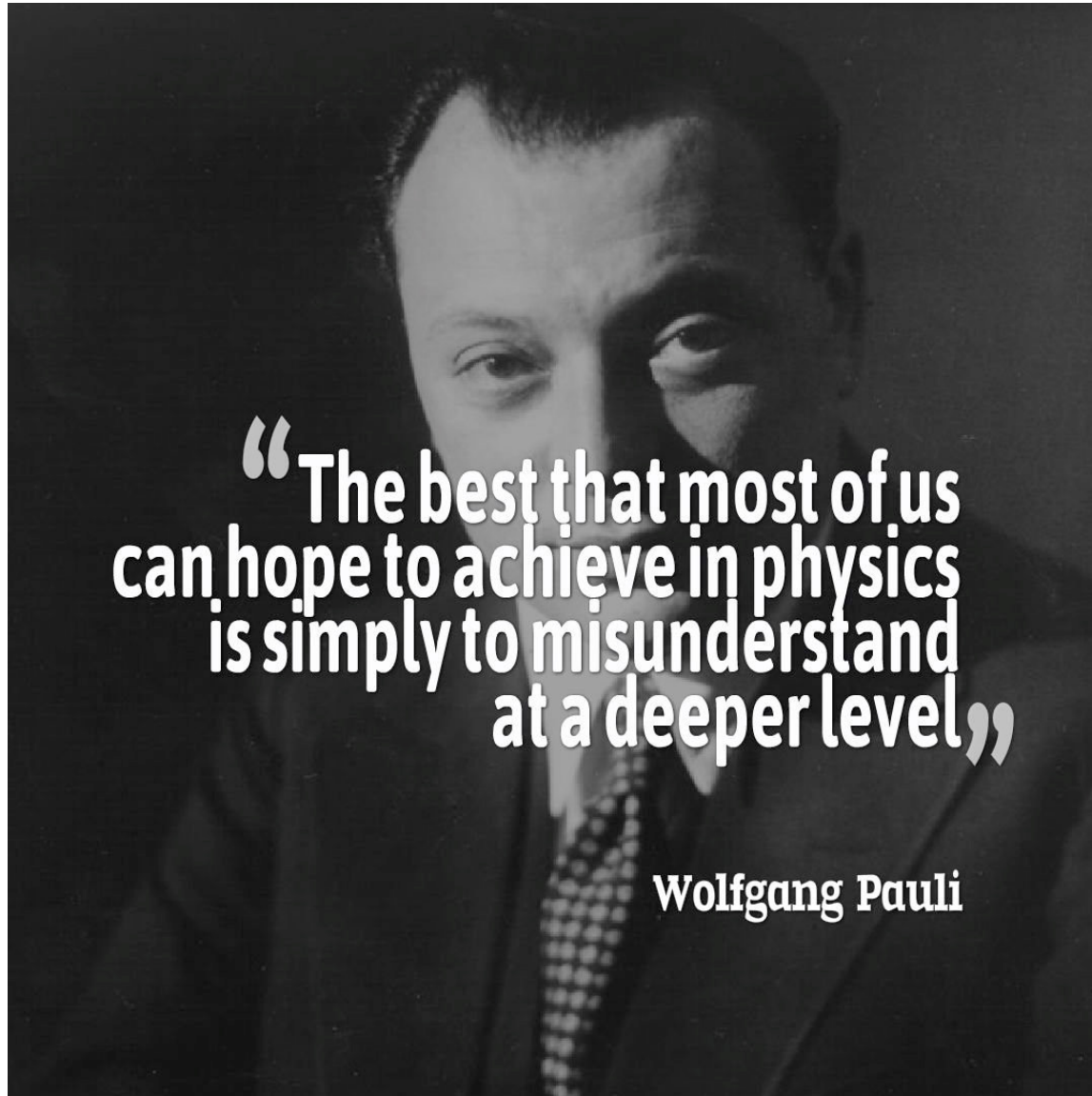
$${}^1\Psi = \overbrace{\frac{1}{\sqrt{2}}(\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2))}^{\text{Symmetric}} \times \overbrace{\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)}^{\text{Antisymmetric}} \quad \begin{matrix} M_S \\ 0 \end{matrix}$$

$${}^3\Psi = \overbrace{\frac{1}{\sqrt{2}}(\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2))}^{\text{Antisymmetric}} \times \overbrace{\begin{cases} \alpha_1\alpha_2 & 1 \\ \frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2) & 0 \\ \beta_1\beta_2 & -1 \end{cases}}^{\text{Symmetric}}$$

*Or schematically:*



# Wolfgang Pauli: “It is not even wrong”



“The best that most of us  
can hope to achieve in physics  
is simply to misunderstand  
at a deeper level,”

Wolfgang Pauli

# Solving the many-body problem: Slater determinant

How to approach many-body wave-function  $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ ?

Use basis of symmetrized products on one-particle functions (orbitals)

$$\chi(\mathbf{x}) = \begin{cases} \psi(\mathbf{r})\alpha(\omega) \\ \text{or} \\ \psi(\mathbf{r})\beta(\omega) \end{cases}$$

**Two-electron case:**  $\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_2, \mathbf{x}_1)$

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \{ \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1) \} = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) \end{vmatrix}$$

Spin-orbitals

Electrons

**General form of Slater determinant for N-electrons**

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$

Alternative notations

$\equiv |\chi_1, \chi_2, \dots, \chi_N\rangle$

$\equiv |1, 2, \dots, N\rangle,$

**Basic properties:**

- Nonzero if spin-orbitals are linearly independent
- Invariant under unitary transformations
- Can always be considered orthonormalized



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# Hartree-Fock method (coordinate representation)

$$H = \sum_{k=1}^N H^{\text{1e}}(\xi_k) + \sum_{k<l} W(\xi_k, \xi_l), \quad H^{\text{1e}}(\xi) = -\frac{\hbar^2}{2m}\Delta + V(\xi).$$

Find “variationally-best” single Slater determinant approximation to the exact wave-function

$$E[\Psi] \equiv \langle \Psi | H | \Psi \rangle = \sum_{i=1}^N \langle \psi_i | H^{\text{1e}} | \psi_i \rangle + E^{\text{int}}$$

$$E^{\text{int}} = \frac{1}{2} \iint W(\xi, \eta) [\rho(\xi)\rho(\eta) - |\rho(\xi, \eta)|^2] d\xi d\eta \equiv \frac{1}{2} \int J(\xi)\rho(\xi) d\xi - \frac{1}{2} \iint K(\xi, \eta)\rho(\eta, \xi) d\xi d\eta$$

$$\rho(\xi, \eta) = \sum_{i=1} \psi_i(\xi)\bar{\psi}_i(\eta), \quad \rho(\xi, \xi) \equiv \rho(\xi) = \sum_i |\psi_i(\xi)|^2 \quad J(\xi) = \int W(\xi, \eta)\rho(\eta) d\eta, \quad K(\xi, \eta) = W(\xi, \eta)\rho(\xi, \eta)$$

$$(H^{\text{HF}}\psi)(\xi) = \left[ -\frac{\hbar^2}{2m}\Delta + V(\xi) + J(\xi) \right] \psi(\xi) - \int K(\xi, \eta)\psi(\eta) d\eta$$

$$\sum_{i=1}^N \langle \delta\psi_i | H^{\text{HF}}\psi_i \rangle = 0 \quad \forall \delta\psi : \langle \delta\psi_i | \psi_j \rangle + \langle \psi_i | \delta\psi_j \rangle = 0, \quad i, j = \overline{1, N}$$

$$H^{\text{HF}}\psi_i = \varepsilon_i\psi_i, \quad i = \overline{1, N}.$$

# Coulomb and exchange terms

*In the Slater determinant, every electron belongs to a specific spin orbital in the expansion: indistinguishability of quantum particles violated in the Hartree-product wave functions.*

Interelectronic repulsion for electrons of **opposite spins** includes Coulomb interaction only:

$$\Psi_{\text{SD}} = \frac{1}{\sqrt{2}}[\psi_a(1)\alpha(1)\psi_b(2)\beta(2) - \psi_a(2)\alpha(2)\psi_b(1)\beta(1)] \quad \begin{aligned} \langle \alpha | \alpha \rangle &= \langle \beta | \beta \rangle = 1 \\ \langle \alpha | \beta \rangle &= \langle \beta | \alpha \rangle = 0 \end{aligned}$$

$$\int \Psi_{\text{SD}} \frac{1}{r_{12}} \Psi_{\text{SD}} d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2 = \frac{1}{2} \left[ 2 \int |\psi_a(1)|^2 \frac{1}{r_{12}} |\psi_b(2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 - 2 \cdot 0 \right] = J_{ab}$$

Interelectronic repulsion for electrons of **the same spins** includes both Coulomb and exchange interactions:

$${}^3\Psi_{\text{SD}} = \frac{1}{\sqrt{2}}[\psi_a(1)\alpha(1)\psi_b(2)\alpha(2) - \psi_a(2)\alpha(2)\psi_b(1)\alpha(1)]$$

$$\int {}^3\Psi_{\text{SD}} \frac{1}{r_{12}} {}^3\Psi_{\text{SD}} d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2 = \frac{1}{2} \left( J_{ab} - 2 \int \psi_a(1)\psi_b(1) \frac{1}{r_{12}} \psi_a(2)\psi_b(2) d\mathbf{r}_1 d\mathbf{r}_2 + J_{ab} \right) = J_{ab} - K_{ab}$$

Exchange is a correlation effect *unique to electrons of the same spin*, i.e., the reduced probability of finding two electrons of the same spin close to one another, sometimes called 'Fermi hole' to surround each electron.

# The SCF (Hartree-Fock) method

*Hartree (1928) first introduced the notion of effective one-electron potential and self-consistent field (SCF) to compute it for a 'Hartree-product' wavefunction. Slater and Fock (1930) independently pointed to the necessity to use antisymmetric wavefunctions for electrons. Finally, Roothaan (1950) derived matrix algebraic equations for the problem*

- 1) HF is a wavefunction-based method (i.e., assumption that a wavefunction of the 'ground state' is a single determinant for a given basis set;
- 2) **Main idea:** replace complex potential of electron-electron interactions with a 'mean-field' average (i.e., each electron experiences an average field of all others)

$$\{\chi_n(\mathbf{r})\}, \quad n = 1, \dots, K$$

$$\chi(\mathbf{x}) = \begin{cases} \psi(\mathbf{r})\alpha(\omega) \\ \text{or} \\ \psi(\mathbf{r})\beta(\omega) \end{cases}$$

$$\hat{H}_{elec} = - \sum_i^N \frac{1}{2} \nabla_i^2 - \sum_i^N \sum_A^M \frac{Z_A}{r_{iA}} + \sum_{i>j}^N \frac{1}{r_{ij}} \quad \xrightarrow{\quad} \quad V_i^{HF}\{j\}$$

- 3) Energy of the Slater determinant:

$$E = \sum_{i=1}^{N_{elec}} h_i + \frac{1}{2} \sum_{i=1}^{N_{elec}} \sum_{j=1}^{N_{elec}} (J_{ij} - K_{ij}) + V_{nn}$$

- 4) Finally, idea for derivation of HF equation would be use of variational principle i.e. minimizing the respective **Lagrangian**:

$$\mathcal{L} = \langle \tilde{\Phi} | \mathcal{H} | \tilde{\Phi} \rangle - E(\langle \tilde{\Phi} | \tilde{\Phi} \rangle - 1)$$

# One- and two- electron integrals

*Assuming a given basis set,  $\{\chi_n(\mathbf{r})\}$ ,  $n = 1, \dots, K$   
 let evaluate matrix elements of the electronic Hamiltonian.  
 First of all, spin degrees of freedom can be factored out  
 leaving spatial functions only.*

$$\chi(\mathbf{x}) = \begin{cases} \psi(\mathbf{r})\alpha(\omega) \\ \text{or} \\ \psi(\mathbf{r})\beta(\omega) \end{cases}$$

$$\begin{aligned} \langle \alpha | \alpha \rangle &= \langle \beta | \beta \rangle = 1 \\ \langle \alpha | \beta \rangle &= \langle \beta | \alpha \rangle = 0 \end{aligned}$$

One – electron integrals ( $t_{nm}$  or  $H_{nm}$ ) describe both kinetic energy and nuclear attraction of an electron (i.e.  $KxK$  matrix)

$$t_{nm} = \langle n | -\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|} | m \rangle \equiv \int d\mathbf{r}_1 \psi_n^*(1) \left( \nabla_1^2 - \sum_A \frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|} \right) \psi_m(1)$$

Two – electron integrals ( $\langle nm | kl \rangle$  or  $(nk | ml)$ ) describe Coulomb electron-electron interaction

$$\langle nm | kl \rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_n^*(1) \psi_m^*(2) \frac{1}{r_{12}} \psi_k(1) \psi_l(2) \quad \text{Tetradic } KxKxKxK \text{ matrix}^*$$

Overlap integrals ( $S_{nm}$ ) describe non-orthogonality of spatial basis functions

$$S_{nm} = \langle n | m \rangle \equiv \int d\mathbf{r}_1 \psi_n^*(1) \psi_m(1)$$

Other observables can be generally described via  $KxK$  matrices, such as dipole operator

$$\mu_{nm} = \langle n | \hat{\mu} | m \rangle \equiv \int d\mathbf{r}_1 \psi_n^*(1) \mathbf{r}_1 \psi_m(1)$$

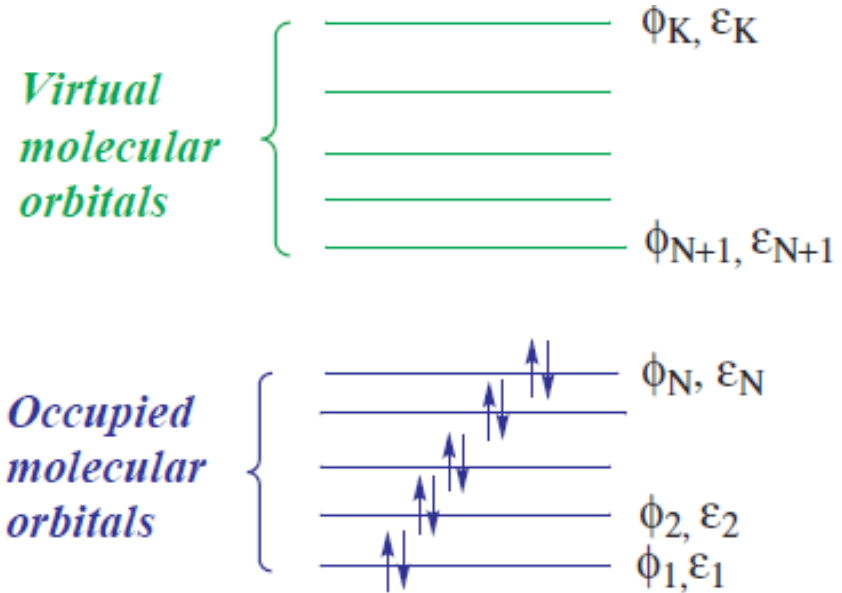
\*More common conventions:  $\langle aa' | bb' \rangle = \int \int \varphi_a(r_1) \varphi_{a'}(r_1) \varphi_b(r_2) \varphi_{b'}(r_2) r_{12}^{-1} dr_1 dr_2$

# Hartree-Fock procedure

For simplicity, assume an even number of electrons (closed shell) and an orthogonal basis set

Looking for a solution of electronic problem,  
 $H_e \Psi = E \Psi$  where the wavefunction is a single Slater determinant  $\Psi = |\phi_1 \dots \phi_N\rangle$  built on the (unknown) molecular orbitals

$$\phi_i(\mathbf{r}) = \sum_j^K C_{ij} \psi_j(\mathbf{r})$$



Ground state one-electron density matrix

$$\bar{\rho}_{nm} = 2 \sum_a^{occ} C_{na} C_{ma}^*$$

The Fock operator

$$F(\bar{\rho})_{nm} = t_{nm} + V(\bar{\rho})_{nm}$$

The Coulomb operator (V or G  $\sim 2J-K$ )

$$V(\bar{\rho})_{mn} = \sum_{k,l}^K \bar{\rho}_{kl} [\langle mk|nl\rangle - \frac{1}{2} \langle mn|kl\rangle]$$

The eigenvalue problem (secular equation)

$$\underline{FC = SC\epsilon}$$

Ground state energy  $E = Tr(\bar{\rho}(F + t))$

The total energy  $E + \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}$

**Nonlinear integro-differential equations, needs to be solved iteratively to achieve self-consistency!**

# Koopman's theorems

The meaning of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) in the frozen orbital approximation

Ionization potential (IP) or 'yanking out' an electron from the molecule, is simply **-HOMO energy**:

$$\text{IP} = {}^{N-1}E_c - {}^N E_0 = -\varepsilon_c$$

$${}^N E_0 = \langle {}^N \Psi_0 | \mathcal{H} | {}^N \Psi_0 \rangle$$

$${}^{N-1} E_c = \langle {}^{N-1} \Psi_c | \mathcal{H} | {}^{N-1} \Psi_c \rangle$$

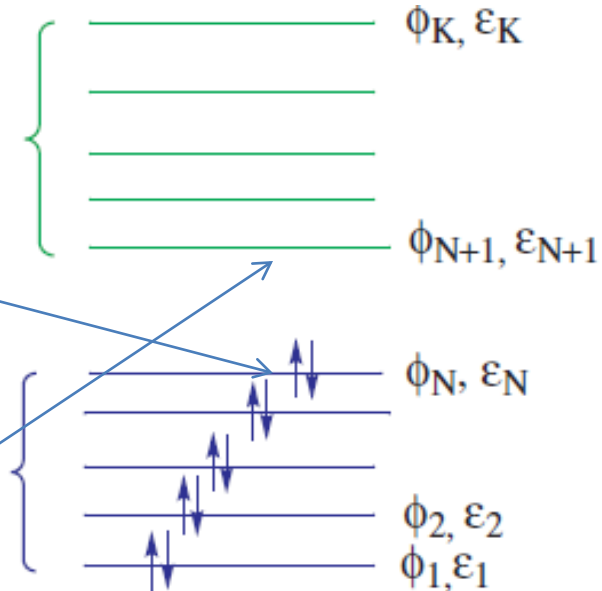
Electron Affinity (EA) or 'adding' an electron from the molecule, is simply **-LUMO energy**:

$$\text{EA} = {}^N E_0 - {}^{N+1} E^r = -\varepsilon_r$$

$${}^{N+1} E^r = \langle {}^{N+1} \Psi^r | \mathcal{H} | {}^{N+1} \Psi^r \rangle$$

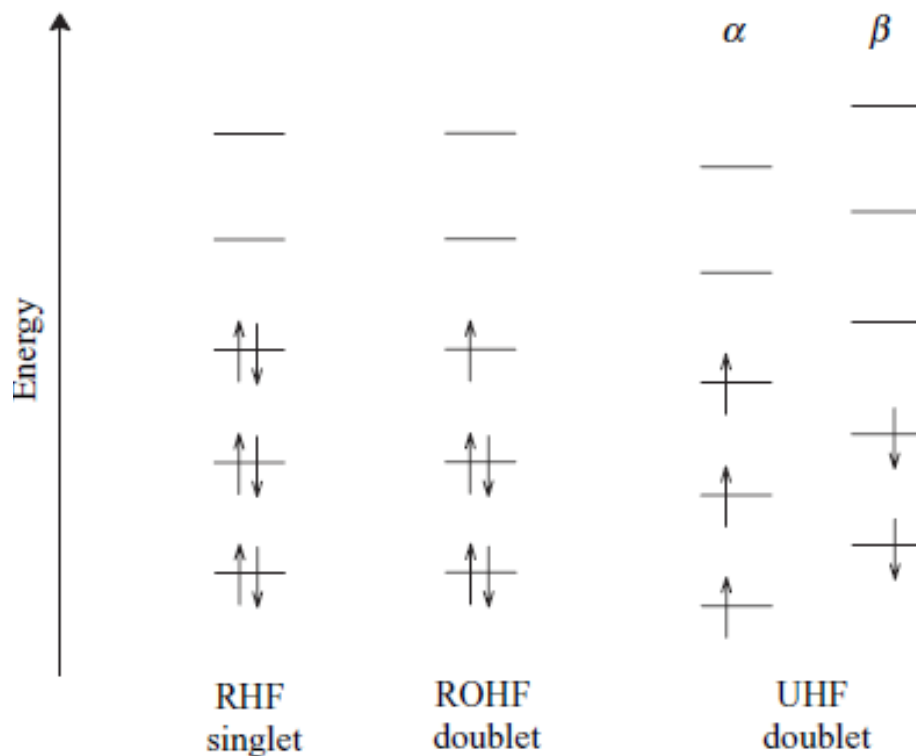
*Virtual molecular orbitals*

*Occupied molecular orbitals*



# What about spin states?

- **Closed shell singlet state: restricted HF approach, most stable**
- **Open shell: restricted open-shell HF approach (however, the wavefunction is not uniquely defined and the energy may not be the lowest)**
- **Open shell: unrestricted open-shell HF approach (however, beware of spin contamination from the higher spin states since the wavefunction is not an eigenfunction of  $S^2$ )**
- **ROHF and spin-constrained UHF are rarely used (require human guidance)**



**Figure 3.4 (from Jensen)** Illustrating an RHF singlet, and ROHF and UHF doublet states

$\Delta$ SCF technique can be considered as optimizations subject to spin constraints  $\rightarrow$  Voorhis's constrained DFT (CDFT) for evaluating energies of charge-transfer states.

Notably, calculation of spin states within HF approach is quite accurate way for evaluating some electronic excitations (so-called  $\Delta$ SCF technique). For example:

- $IP = E(\text{cation}) - E(\text{neutral})$
- $EA = E(\text{neutral}) - E(\text{anion})$
- $\Delta E(\text{Singlet-triplet}) = E(\text{triplet}) - E(\text{singlet})$



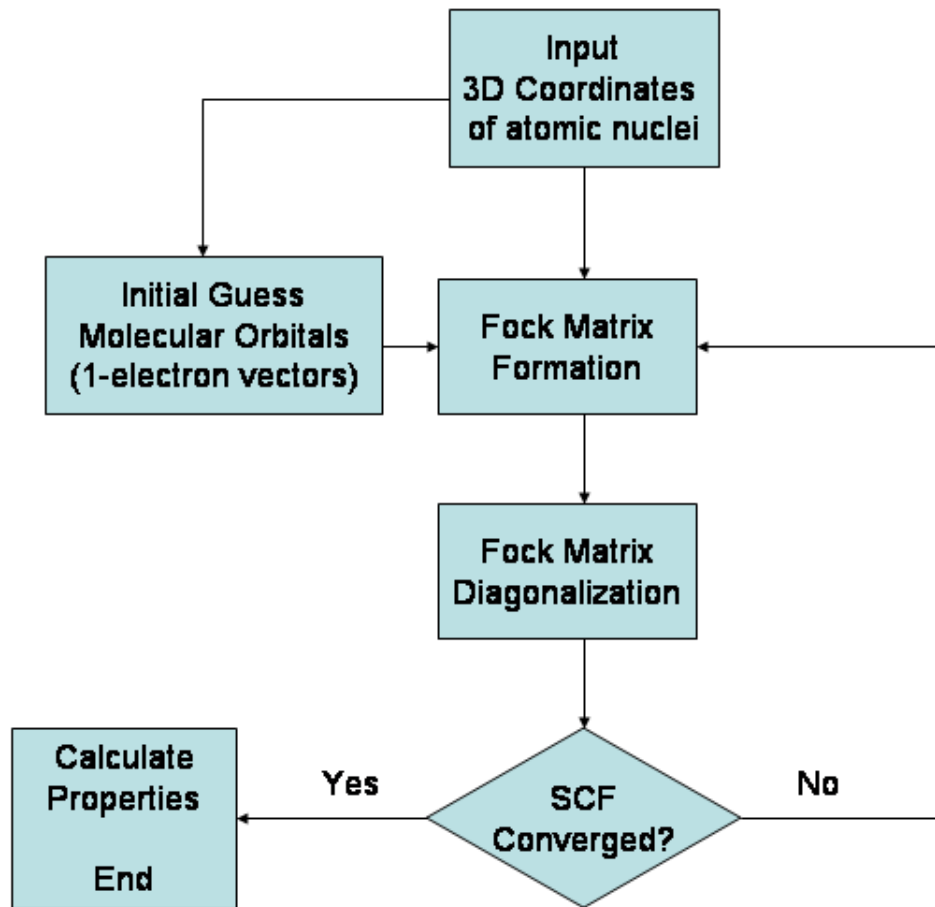
# The SCF algorithm

*A typical 'mean-field' iterative procedure!*

Guess of molecular orbitals = essentially guess of the ground state density matrix. When using atomic orbital (AO) basis set type, assumption of uniform charge distribution is a good one (i.e. diagonal  $\rho_{ij}$ )

Fock-matrix formation is calculations of one- and two- electron integrals. The latter are numerically expensive and are computed 'on-the-fly' (direct method). Using various cut-off procedure (e.g., FMM), expense is  $\sim K^{2-3}$

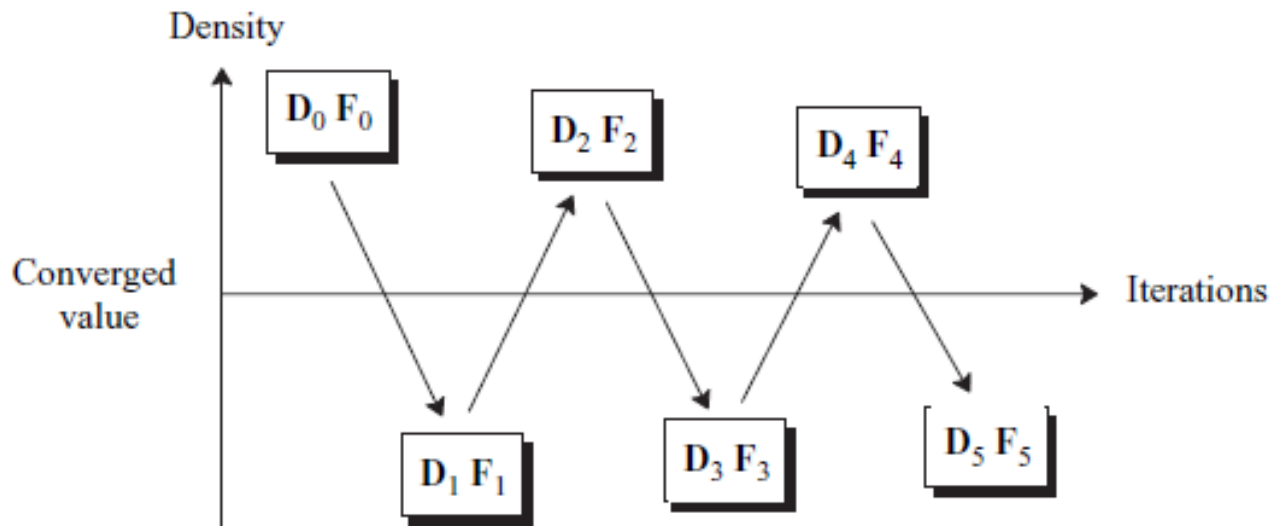
Fock-matrix diagonalization has  $\sim K^3$  expense. For 'general' basis set one need to check for over-completeness and orthogonalize the basis (e.g. Lowdin's symmetric orthogonalization)



$$\begin{array}{lll} \mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon} & \mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{1} & \mathbf{X} \equiv \mathbf{S}^{-1/2} \\ \mathbf{C}' = \mathbf{X}^{-1} \mathbf{C} & \mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X} & \mathbf{F}' \mathbf{C}' = \mathbf{C}' \boldsymbol{\varepsilon} \end{array}$$

# SCF convergence

**The truth is that iterative procedure DOES NOT converge by itself due to 'density slushing'. Similar to geometry optimization, special algorithms need to be used to ensure SCF convergence!**



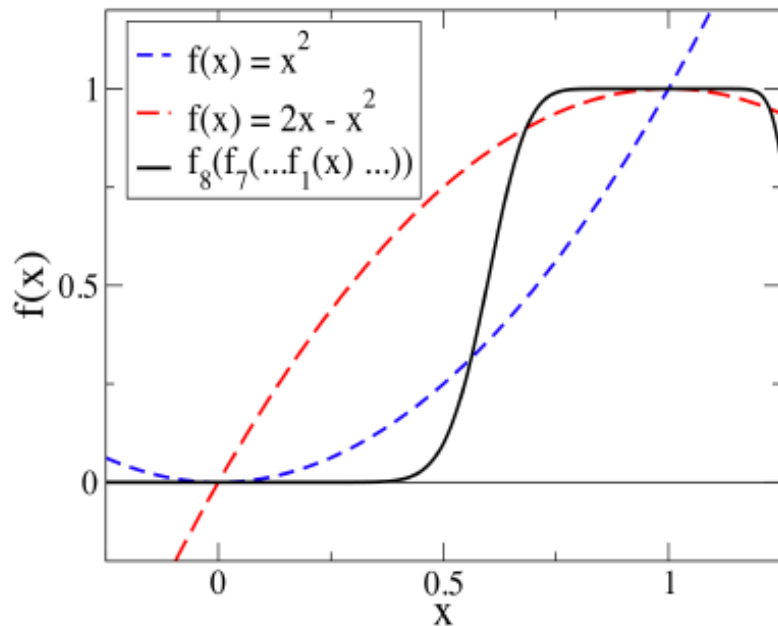
**Figure 3.5 (from Jansen)** An oscillating SCF procedure

- *Extrapolation*: Use several previous density matrices to calculate the next one;
- *Damping*: Use linear combination with previous step density matrix:  $\mathbf{D}'_{n+1} = \omega \mathbf{D}_n + (1 - \omega) \mathbf{D}_{n+1}$ .
- *Level shifting*: Shift energies of virtual orbitals up to increase the gap
- *Direct inversion in the iterative subspace (DIIS)*: Extrapolation procedure by P. Pulay constructing the new density matrix from sequence  $(\mathbf{F}_0, \mathbf{F}_1, \mathbf{F}_2, \dots)$  and  $(\mathbf{D}_0, \mathbf{D}_1, \mathbf{D}_2, \dots)$  ( $\mathbf{E}_0, \mathbf{E}_1, \mathbf{E}_2, \dots$ )
- “Direct minimization” techniques: optimize MO coefficients to minimize the energy (optimization problem, conjugated gradient, steepest descent, Newton-Raphson, etc.)
- Metals are gap-less and difficult. Damp density depending on k:  $k/(k+\Delta)$  (e.g. VASP)
- Multi-step SCF calculations, from smaller basis to larger set with re-use of density matrix

# Bypassing SCF, SP2 linear scaling algorithm for E and P

Recursive Fermi operator expansion

$$\mathbf{P} = \theta(\mu\mathbf{I} - \mathbf{H}) = \lim_{n \rightarrow \infty} f_n(f_{n-1}(\dots f_0(\mathbf{H}) \dots))$$



$$\mathbf{X}_0 = f_0(\mathbf{H}) = \frac{\varepsilon_{\max}\mathbf{I} - \mathbf{H}}{\varepsilon_{\max} - \varepsilon_{\min}}$$

$$\mathbf{X}_{n+1} = \mathbf{X}_n^2 \quad \text{if } \text{Tr}[\mathbf{X}_n] > N_{occ}$$

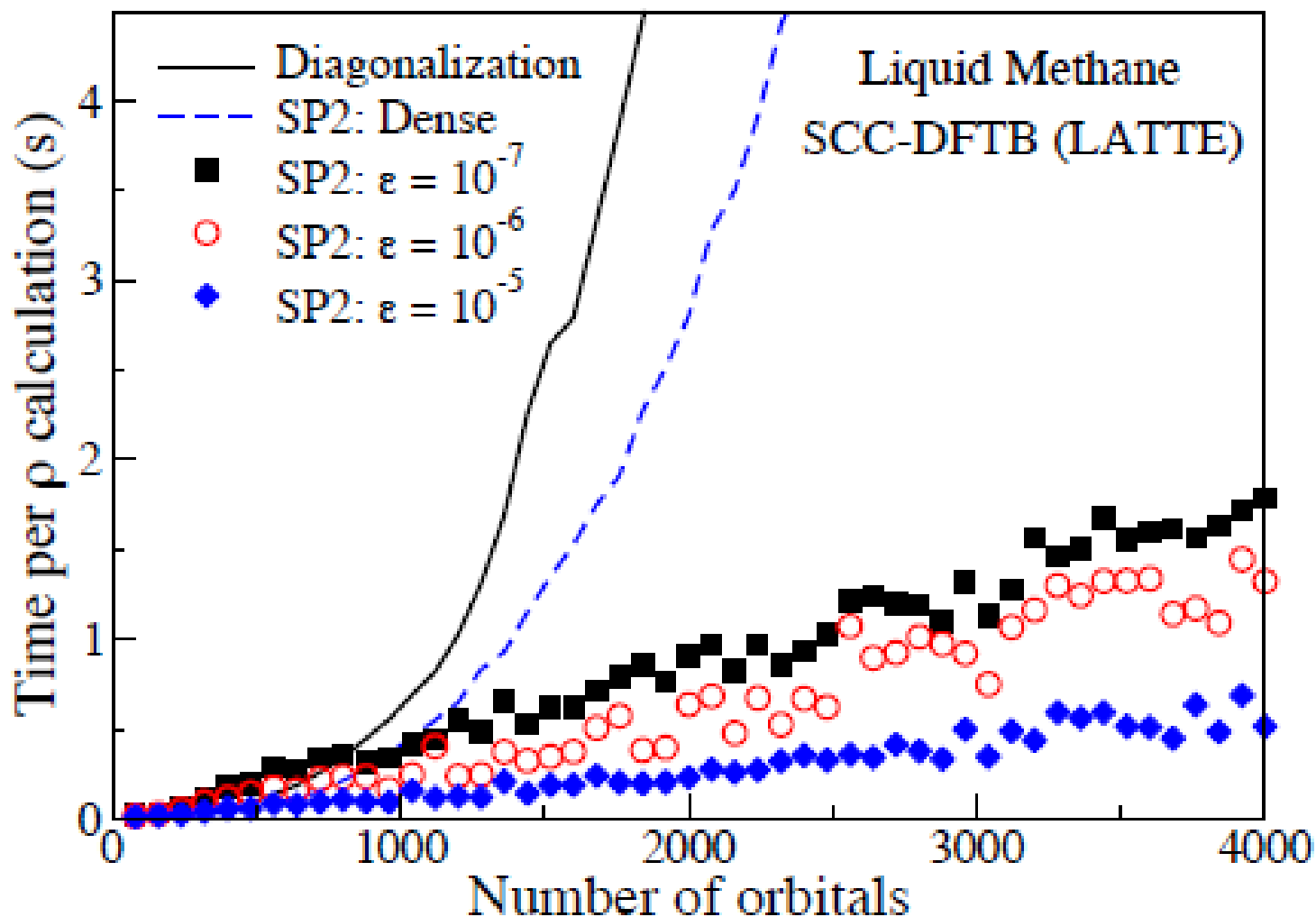
$$\mathbf{X}_{n+1} = 2\mathbf{X}_n - \mathbf{X}_n^2 \quad \text{else}$$

$$\mathbf{P} = \lim_{n \rightarrow \infty} \mathbf{X}_n \quad T_e = 0$$

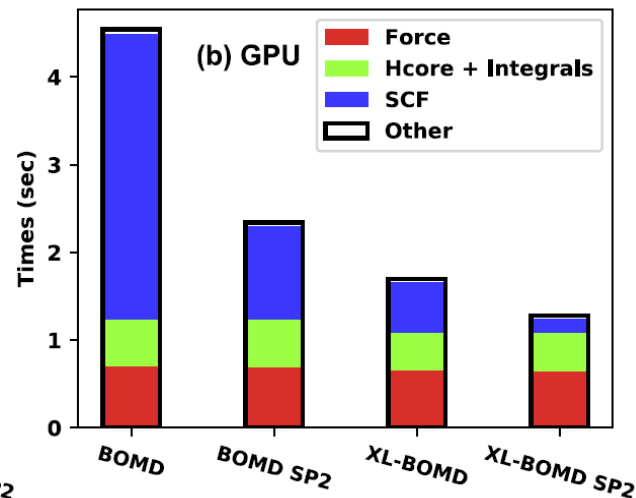
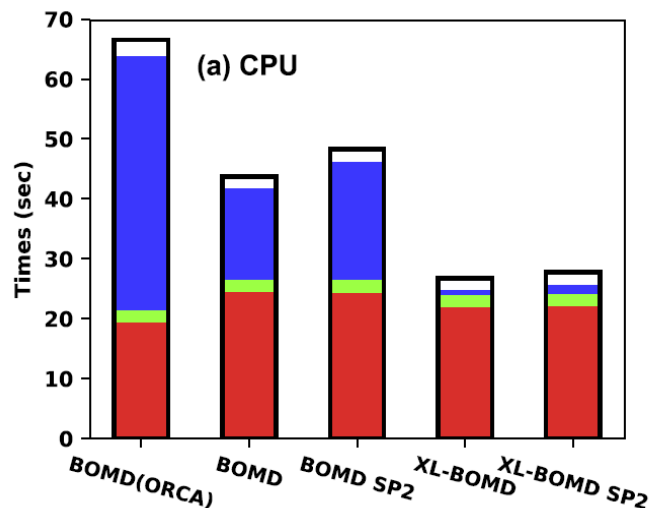
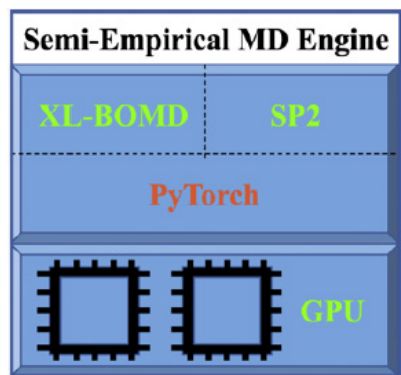
30 multiplications gives an expansion order > 1 Billion!  
No Gibbs oscillations!

# SP2 example

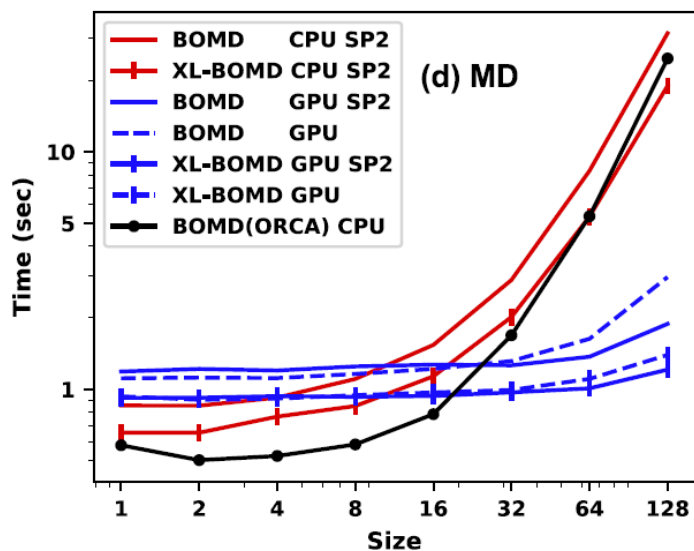
Cawkwell and Niklasson (2011)



# PyTorch semiempirical quantum mechanics(PySQM)



molecules  $H-(C_7H_4)_n-H$  with size  $n = 1, 2, \dots, 128$



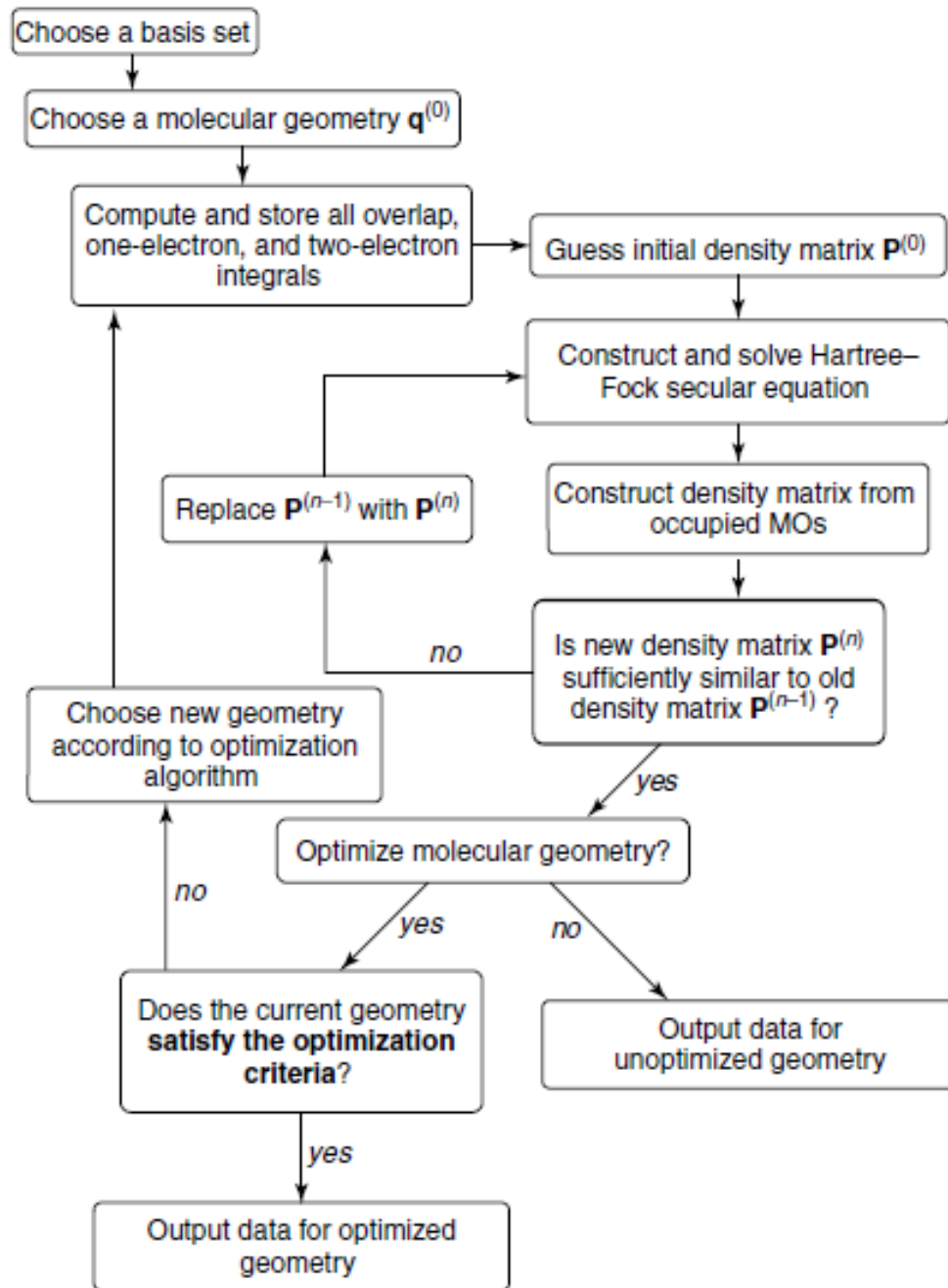
- PyTorch = native interface to machine learning;
- Natively CPU and GPU compatible, parallel;
- Common semiempirical models AM1, PM3... now PM6 (d-functions, metals)
- SP2 linear + XL Born-Oppenheimer ground state dynamics

<https://github.com/lanl/PYSEQM>

G. Zhou, B. Nebgen, N. Lubbers, A. M. N. Niklasson, S. Tretiak, "GPU-Accelerated Semi-Empirical Born Oppenheimer Molecular Dynamics using PyTorch" *J. Chem. Theory Comput.* **16**, 4951 (2020).

# HF geometry optimization (from Cramer)

Contains 2 loops: SCF interactions and geometry optimization



# Gradients for HF geometry optimization

To optimize geometry, we need derivatives of the energy with respect to nuclei coordinates:

$$\mathbf{g} = \frac{\partial E_{HF}}{\partial X_i}$$

HF ground-state energy

$$E_{HF} = \text{Tr}(\bar{\rho}(F(\rho) + t)) = \text{Tr}(\bar{\rho}(V(\rho) + 2t))$$

$$V(\bar{\rho})_{mn} = \sum_{k,l} \bar{\rho}_{kl} [\langle mk|nl\rangle - \frac{1}{2} \langle mn|kl\rangle]$$

1) Numerical gradients (inaccurate and numerically demanding): increase computational cost  $\times N$

$$\mathbf{g} = E_{HF}^X = \frac{E_{HF}(X_i + \Delta) - E_{HF}(X_i - \Delta)}{2\Delta}$$

2) Analytic gradients (very accurate and numerically easy). **Idea:** express derivative of the energy in terms of derivatives of the Hamiltonian matrix elements:  $t_{nm}^X, V_{nm,kl}^X$

$$\rho_{nm}^X = \left( \sum_a^{\text{occ}} C_{na} C_{ma}^* \right)^X = 0$$

So that:  $E_{HF}^X = \text{Tr}(\bar{\rho}(V^X(\rho) + 2t^X))$

$$V(\bar{\rho})_{mn}^X = \sum_{k,l} \bar{\rho}_{kl} [\langle mk|nl\rangle^X - \frac{1}{2} \langle mn|kl\rangle^X]$$

**Semiempirical HF:** take derivatives of the matrix elements numerically;

**Ab initio HF:** express derivatives of the matrix elements via derivatives of the basis functions

# Discussion

1. By looking at the electronic Hamiltonian, which term represents the complexity of many-body (i.e. many-electron) problem?
2. Question to all: write on the chat expression for a simple tight-binding Hamiltonian in the second quantization term.
3. How accurate are assumptions that HOMO and LUMO represent IP and EA?
4. Does geometry optimization guarantees you the molecular geometry that has the lowest energy? Why?



# Hartree-Fock procedure

For simplicity, assume an even number of electrons (closed shell)

Looking for a solution of electronic problem,  
 $H_e \Psi = E \Psi$  where the wavefunction is a single  
 Slater determinant  $\Psi = |\phi_1 \dots \phi_N\rangle$  built on the  
 (unknown) molecular orbitals

$$\phi_i(\mathbf{r}) = \sum_j^K C_{ij} \psi_j(\mathbf{r})$$

Ground state one-electron density matrix

$$\bar{\rho}_{nm} = 2 \sum_a^{occ} C_{na} C_{ma}^*$$

The Fock operator

$$F(\bar{\rho})_{nm} = t_{nm} + V(\bar{\rho})_{nm}$$

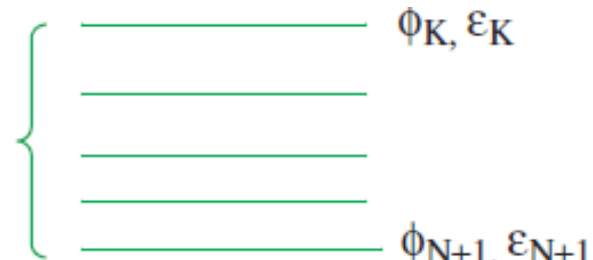
The Coulomb operator (V or G  $\sim 2J-K$ )

$$V(\bar{\rho})_{mn} = \sum_{k,l}^K \bar{\rho}_{kl} [\langle mk|nl\rangle - \frac{1}{2} \langle mn|kl\rangle]$$

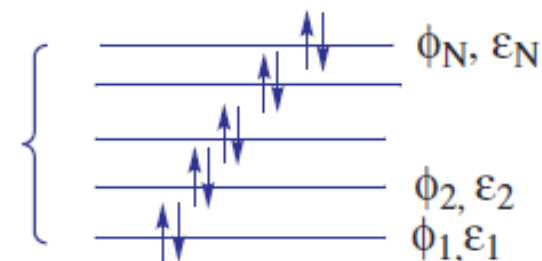
The eigenvalue problem (secular equation)

$$\underline{FC = SC\varepsilon}$$

*Virtual  
molecular  
orbitals*



*Occupied  
molecular  
orbitals*



Ground state energy  $E = Tr(\bar{\rho}(F + t))$

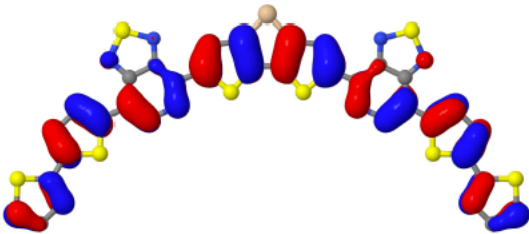
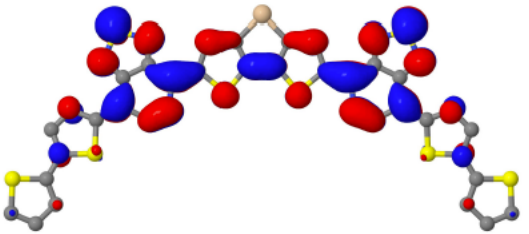
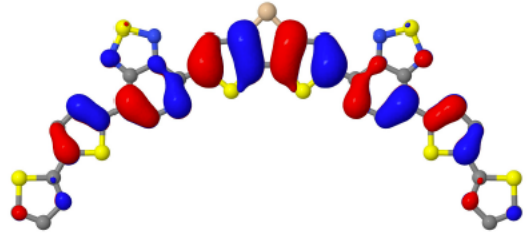
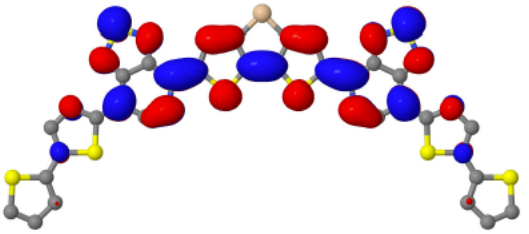
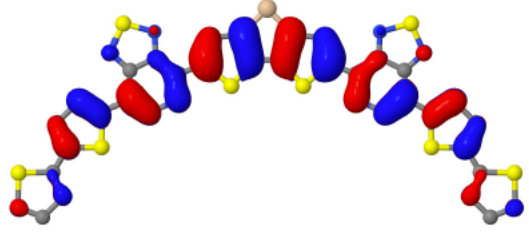
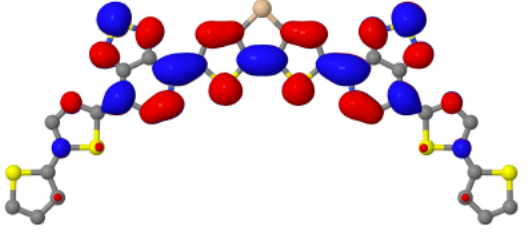
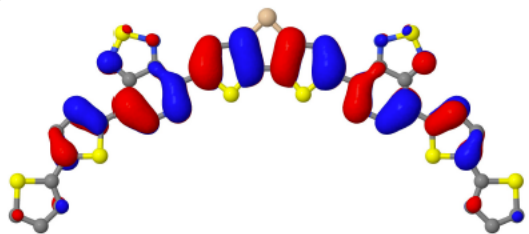
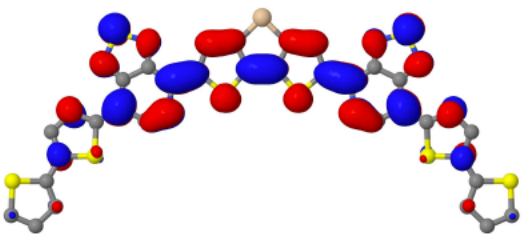
The total energy  $E + \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}$

**Nonlinear integro-differential equations,  
needs to be solved iteratively to achieve  
self-consistency!**

# One-electron orbitals

- molecular orbitals (MO) – eigenfunctions of one-electron Hamiltonian (HF/DFT)
- localized molecular orbitals (LMO) – a rotation of MOs localizing each orbital in space
- natural orbitals (NO) – eigenfunctions of one-electron density matrix  $\rho_{\Psi}^{1e}(\xi; \eta) = N \int \Psi(\xi, \zeta_2, \dots, \zeta_N) \bar{\Psi}(\eta, \zeta_2, \dots, \zeta_N) d\zeta$
- natural transition orbitals (NTO) – the same for transition density matrix  $\rho_{\Psi\Phi}^{1e}(\xi; \eta) = N \int \Psi(\xi, \zeta_2, \dots, \zeta_N) \bar{\Phi}(\eta, \zeta_2, \dots, \zeta_N) d\zeta$

# Examples: MO vs NO

	HOMO	LUMO
ground state $n_h = 2$ $n_e = 0$		
	hole NO	electron NO
cation/anion $n_{h/e} = 1$ $\Delta n_2 = .07/.06$		
singlet exciton $n_h = 1 + .12$ $n_e = 1 - .12$		
triplet exciton $n_h = 1 + .17$ $n_e = 1 - .18$		

# Examples: NO vs NTO

	hole NTO/NO	electron NTO/NO
singlet exciton $n_h = 1 + .12$ $n_e = 1 - .12$		
singlet transition $n_{h/e} = 1 \pm .17$		
triplet exciton $n_h = 1 + .17$ $n_e = 1 - .18$		
triplet transition $n_{h/e} = 1 \pm .25$		

# Accuracy of Hartree-Fock

Property	Accuracy
Bond lengths	$\pm 0.02 \text{ \AA}$
Bond angles	$\pm 2^\circ$
Vibrational frequencies	$\pm 11\%$
Dipole moments	$\pm 0.3 \text{ D}$
Relative energy	$\pm 25\text{-}40 \text{ kcal/mol}$ for dissociation energies

*What is wrong with Hartree-Fock? Electrons interact beyond 'average' potential or 'mean field', i.e. there are electronic correlations (frequently separated into 'dynamic' and 'static').*

**A chemical accuracy ( $\sim 1\text{kcal/mol} \sim 50\text{meV}$ ) is needed for realistic chemical problems!**

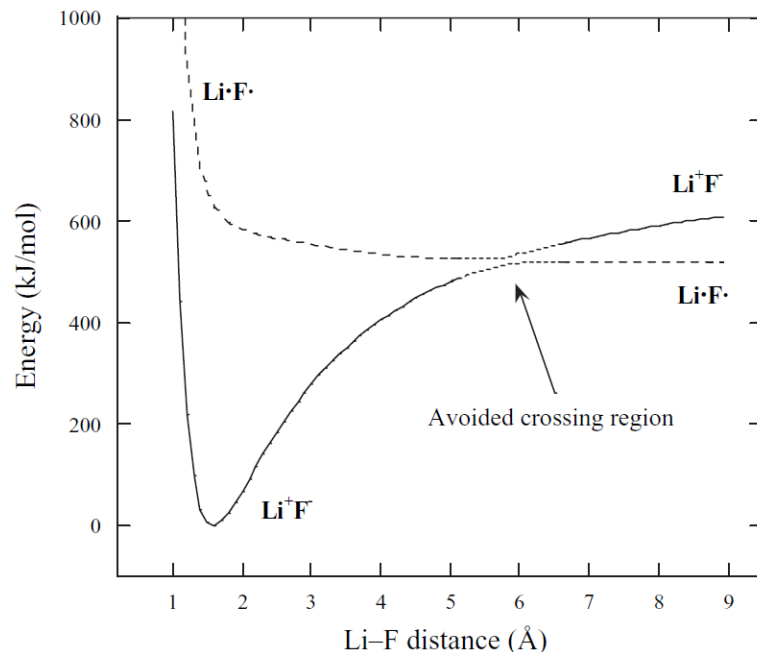
# Static and dynamic electronic correlations

- Dynamical correlations: the electrons get too close to each other in Hartree-Fock.*
- Static correlations: a single determinant variational class is inaccurate (but SCF with fractional occupations can handle static correlations, see AMM course)*

Basis Set Correlation for H<sub>2</sub>O with a DZ Basis

Geometry	$E_{\text{corr}}$ (hartree) <sup>a</sup>
$R_e$	-0.148028
$1.5 R_e$	-0.210992
$2.0 R_e$	-0.310067

<sup>a</sup>Data from Harrison, 1983.



“Dynamical” correlation, electrons instantaneously avoiding each other, should become less important at stretched geometries, since the electrons are further apart. However, the correlation energy increases with stretching! This is signature of “static” or “nondynamical” correlation.

# Electronic correlations



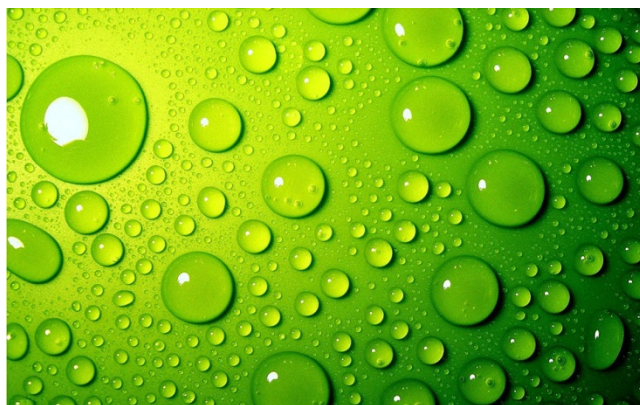
## Metals

“Stable” density of states at Fermi level  
Fermi liquid or homogeneous electron gas  
Strong dynamic correlations  
Wave-function is too complicated  
Electron density is smooth and predictable  
DFT-like mean field and Fermi liquid theory



## Strongly correlated systems

Nonlocal static correlations  
Often frustrated  
Usually no mean field, no perturbation theory



## Insulators

Small number of states near Fermi level  
Electrons are paired into molecular orbitals  
Wave function is a single Slater determinant  
Some amount of static/dynamic correlations  
HF-like mean field and molecular orbital theory

# Static correlations: examples

- Static correlations always originate from exact or approximate degeneracy of electronic states (spin multiplicity is not considered).
- In the ground state any degeneracy is almost always removed by molecular deformation or charge/spin redistribution (often with symmetry breaking).
- In the former case the static correlations are removed as well.

## Examples – molecular deformation

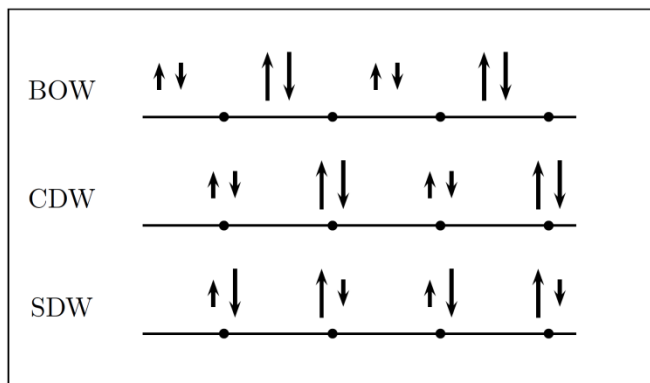
- Jahn-Teller effect
  - Octahedral transition metal sites in oxides are often deformed
  - Huckel's rule – no fully symmetric cyclic  $\pi$ -conjugated  $C_{4n}H_{4n}$  molecules
  - Low symmetry of small metal clusters, e.g.  $Na_4$
- Peierls transition – dimerization of trans-polyacetylene
- Peierls transition in 3D (weak) – layered structure of pnictogens



# Static correlations: examples

## Examples – charge/spin redistribution

- Charge redistribution (atomic charges)
  - Charge density wave in extended Hubbard model at high  $V$
- Charge redistribution (bond orders)
  - Fully symmetric planar  $C_4H_4$
  - Bond order wave in extended Hubbard model at  $U \approx 2V$
  - Undimerized trans-polyacetylene is Mott insulator
- Spin redistribution
  - Ground state of  $O_2$  molecule is triplet
  - Spin density wave in extended Hubbard model at high  $U$



# Wavefunction approach: a systematic way to seek an exact answer

*The wavefunction for our 'exact' Hamiltonian should be more complex than a single Slater determinant*

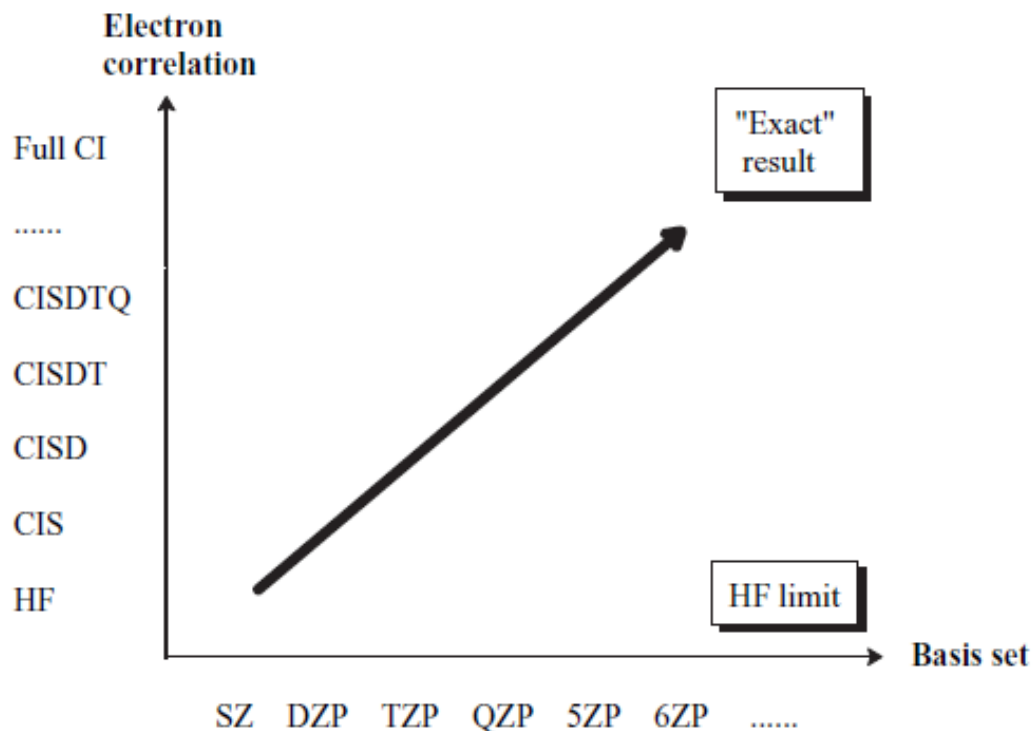
A better wavefunction will give lower ground state energy respecting variational principle:

$$\Psi = a_0 \Phi_{\text{HF}} + \sum_{i=1} a_i \Phi_i$$

Correlation energy:  $E_C^{\text{trad}} = E - E^{\text{HF}}$

atom	$E^{\text{HF}}$	$E$	$E_C$
He	-2.862	-2.904	-0.042
Be	-14.571	-14.667	-0.096
Ne	-128.555	-128.938	-0.383

Example: correlations energies for noble gas atoms (in Hartrees)



**Figure 4.3 (from Jensen)**  
Convergence to the exact solution

# Configuration interaction (CI)

## Both static and dynamic correlations

$$\chi \rightarrow \phi \rightarrow \Phi \rightarrow \Psi$$

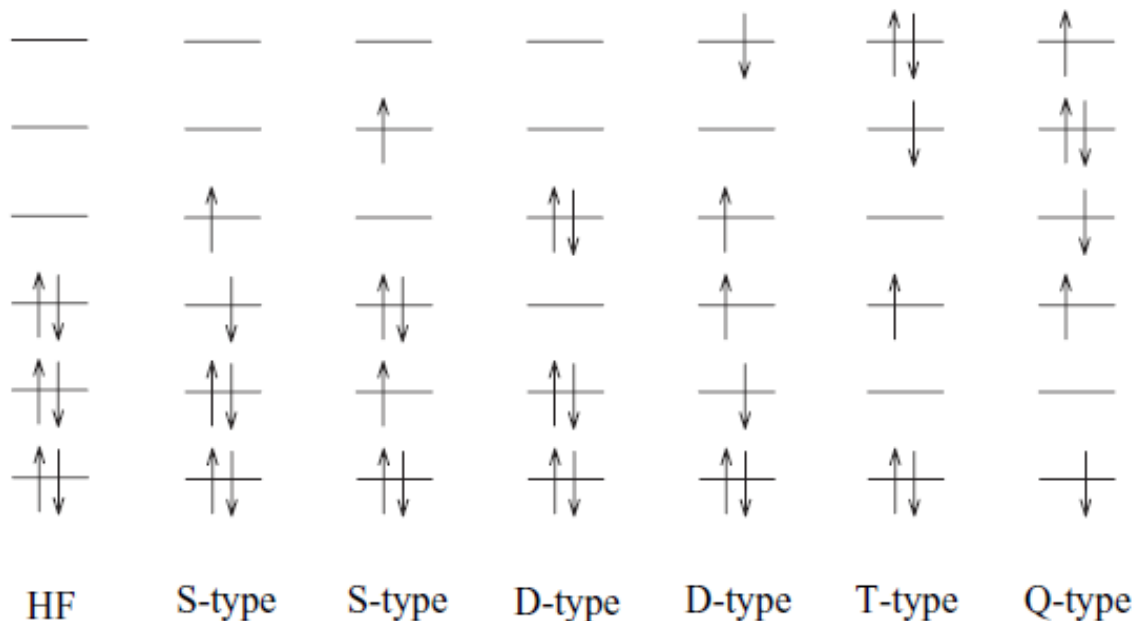
$$\text{AO} \rightarrow \text{MO} \rightarrow \text{SD} \rightarrow \text{ME}$$

$$\phi = \sum_{\alpha=1} c_{\alpha} \chi_{\alpha}$$

$$\Psi = \sum_{i=1} a_i \Phi_i$$

**Figure 4.1 (from Jensen)**

Progression from atomic orbitals (AO) (basis functions), to molecular orbitals (MO), to Slater determinants (SD) and to a many-electron (ME) wave function



**Figure 4.2 (from Jensen)** Excited Slater determinants generated from an HF reference

**The CI wavefunction:**

$$\Psi_{\text{CI}} = a_0 \Phi_{\text{HF}} + \sum_{\text{S}} a_{\text{S}} \Phi_{\text{S}} + \sum_{\text{D}} a_{\text{D}} \Phi_{\text{D}} + \sum_{\text{T}} a_{\text{T}} \Phi_{\text{T}} + \dots = \sum_{i=0} a_i \Phi_i$$

Slater determinants are the proper N-electron basis functions for CI expansion!

# The CI matrix and secular equation

How to get expansion coefficients? Variationally!  
Need to minimize the Lagrangian

$$L = \langle \Psi_{\text{CI}} | \mathbf{H} | \Psi_{\text{CI}} \rangle - \lambda (\langle \Psi_{\text{CI}} | \Psi_{\text{CI}} \rangle - 1)$$

$$\Psi_{\text{CI}} = \sum_{i=0} a_i \Phi_i$$

$$\frac{\partial L}{\partial a_i} = 2 \sum_j a_j \langle \Phi_i | \mathbf{H} | \Phi_j \rangle - 2\lambda a_i = 0$$

$$a_i(E_i - \lambda) + \sum_{j \neq 0} a_j \langle \Phi_i | \mathbf{H} | \Phi_j \rangle = 0$$

*Of course, secular equation & eigenproblem!*

$$(\mathbf{H} - E\mathbf{I})\mathbf{a} = \mathbf{0}$$

$$\mathbf{H}\mathbf{a} = E\mathbf{a}$$

$$\begin{pmatrix} H_{00} - E & H_{01} & \cdots & H_{0j} & \cdots \\ H_{10} & H_{11} - E & \cdots & H_{1j} & \cdots \\ \vdots & \vdots & \ddots & \vdots & \cdots \\ H_{j0} & \vdots & \cdots & H_{jj} - E & \cdots \\ \vdots & \vdots & \cdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_0 \\ a_1 \\ \vdots \\ a_j \\ \vdots \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ \vdots \end{pmatrix}$$

$$\frac{\int \Phi H \Phi d\mathbf{r}}{\int \Phi^2 d\mathbf{r}} \geq E_0$$

Note: not all matrix elements are non-zero. For example, Brillouin's theorem states that ground state Slater is orthogonal to singly excited Slaters.

$$\begin{pmatrix} \Phi_{\text{HF}} & \Phi_{\text{S}} & \Phi_{\text{D}} & \Phi_{\text{T}} & \Phi_{\text{Q}} & \Phi_{\text{S}} & \cdots \end{pmatrix} \begin{pmatrix} E_{\text{HF}} & 0 & x & 0 & 0 & 0 & 0 \\ 0 & E_{\text{S}} & x & x & 0 & 0 & 0 \\ x & x & E_{\text{D}} & x & x & 0 & 0 \\ 0 & x & x & E_{\text{T}} & x & x & 0 \\ 0 & 0 & x & x & E_{\text{Q}} & x & x \\ 0 & 0 & 0 & x & x & E_{\text{S}} & x \\ \vdots & 0 & 0 & 0 & x & x & \ddots \end{pmatrix}$$

Figure 4.5 (from Jensen) Structure of the CI matrix

# What can we calculate with CI?

1) We can include about 10-100 billion determinants into Full CI computations. This requires highly optimized computer code!

2) Full CI matrix size for N-electrons on M-orbitals is

$$\text{Number of CSFs} = \frac{M!(M+1)!}{\left(\frac{N}{2}\right)! \left(\frac{N}{2}+1\right)! \left(M-\frac{N}{2}\right)! \left(M-\frac{N}{2}+1\right)!}$$

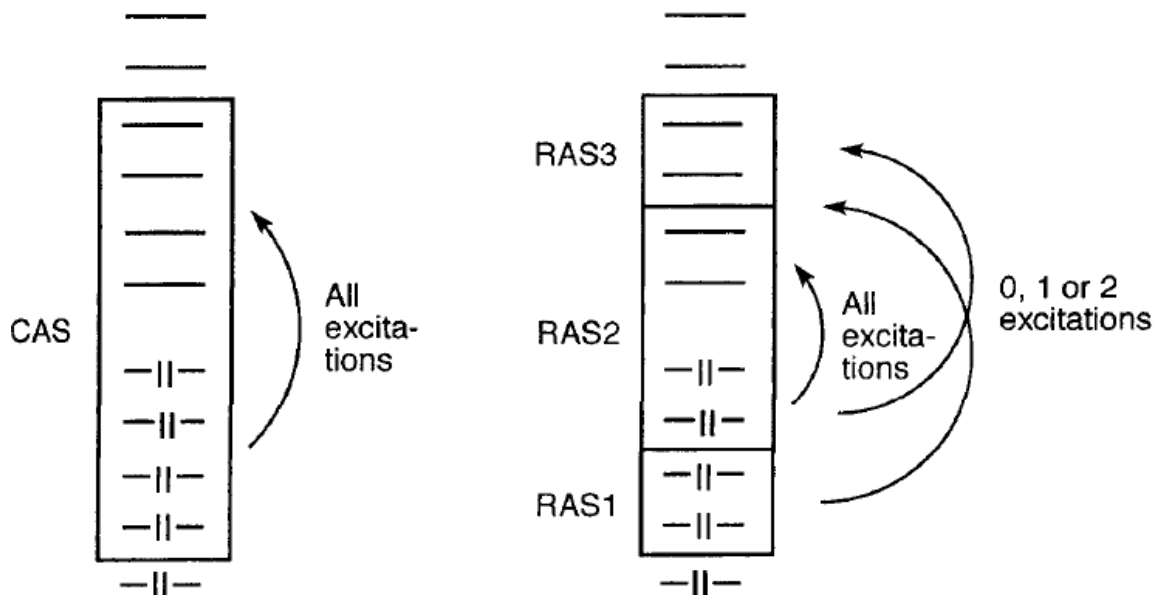
3) For a determinant basis, this means about

14 electrons in 20 orbitals, or 10 electrons in 40 orbitals: diatomics and triatomics.

4) Practical recipe: separation of the “more important” determinants from the “less important” ones (example MRCI).

5) A common way: truncate CI expansion according to excitation level: CIS ( $O(N^4)$ ), CISD ( $O(N^6)$ ), CISDT ( $O(N^8)$ ).

6) Another approach is to impose so-called active space limitations (CAS, RAS)



**Figure 4.11 (from Jensen)**

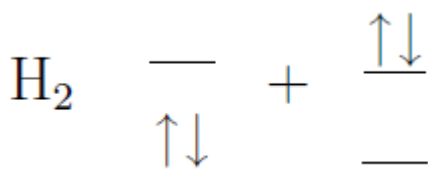
Illustrating the CAS and RAS orbital partitions

*Example: semiempirical ZINDO approach has been parameterized to reproduce electronic excitation energies in a window (+10 -10) at the CIS level*

# Beware of size-consistency and extensivity problems

*Notably, everything higher than CIS is not size-consistent!*

Example: CISD is exact for a two-electron system like H<sub>2</sub>



However, it is not exact for two non-interacting H<sub>2</sub>



Here quadruple excitations are needed to be factorized into products of doubles!

## Overall notes

- CISD, CISDT, etc. (but not CIS!) are used to correct ground state energy and ground state properties (e.g., chemical energies, barriers, etc);
- CIS, CISD, CISDT, etc. are used to obtain information on electronically excited states and spectroscopies. Here, in particular, size-consistency problems (above CIS) are escalating (e.g. for polarizabilities).
- Use of Coupled Cluster methods is preferable due to internal size-consistency.

# Case study 1: 2Ag and 1Bu states in polyenes

VOLUME 71, NUMBER 10

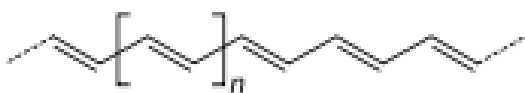
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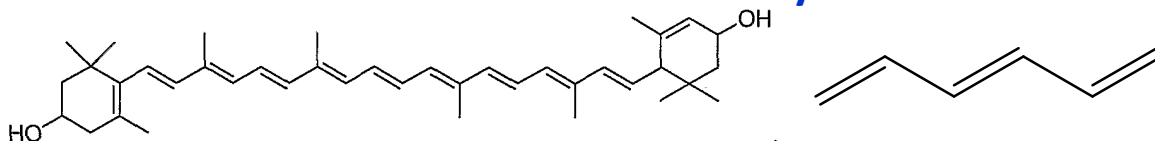
## Band to Correlated Crossover in Alternating Hubbard and Pariser-Parr-Pople Chains: Nature of the Lowest Singlet Excitation of Conjugated Polymers

Z. G. Soos,<sup>1</sup> S. Ramasesha,<sup>1,2</sup> and D. S. Galvão<sup>3</sup>

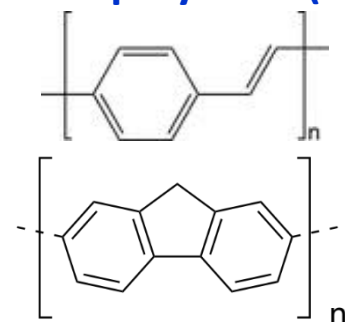
Non-luminescent polymers (e.g. polyacetylene)



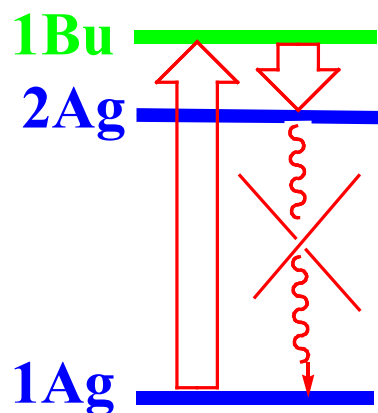
Also other molecules from this family:



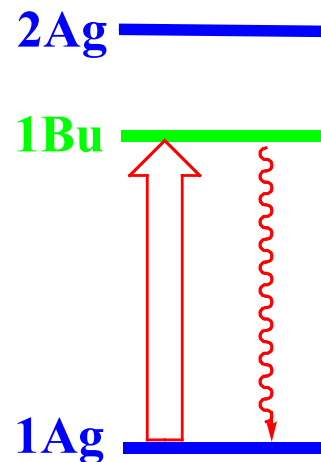
Luminescent polymers (e.g. PPV)



**Why? What is the difference in their electronic structure? Idea: different state order!**



But can this idea (and experimental data) be confirmed by theoretical calculations?



# Case study 1: 2Ag and 1Bu states in polyenes

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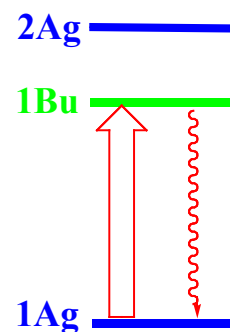
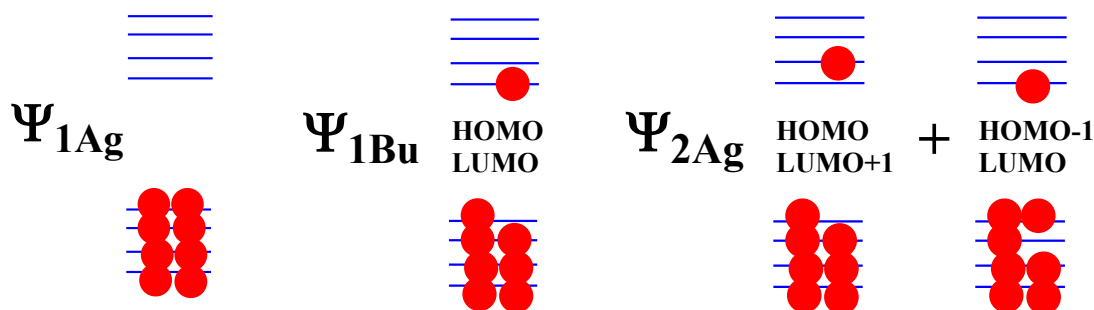
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Non-luminescent polymers (e.g. polyacetylene)

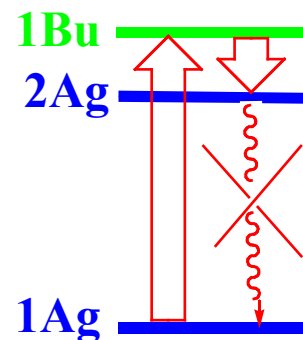
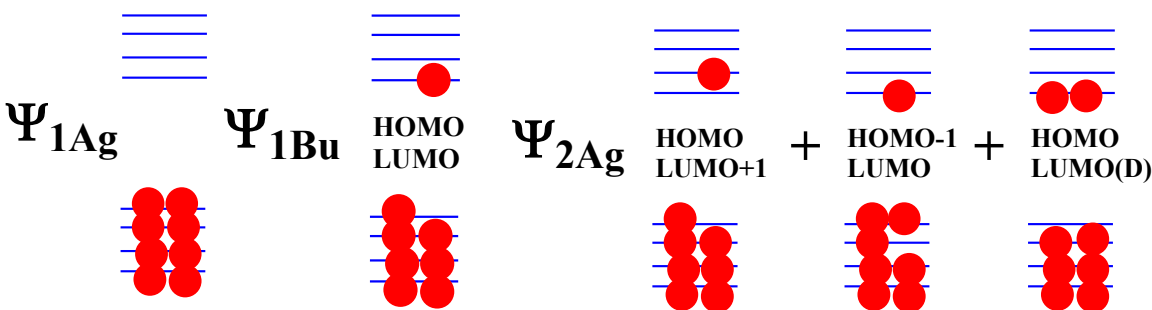
Luminescent polymers (e.g. PPV)

*Let apply CIS (or RPA) – i.e. single excitation-like framework*



The same state ordering is produced for both systems. Not enough electronic correlations!!!

*Let apply CISD (up to FCI) – i.e. include double excitations*



Now correct state ordering is restored for both systems!!!



# Many-Body (or Moller-Plesset, MP) Perturbation Theory (mostly dynamic correlations)

The essence of perturbation theory: the problem is split into a part that can be solved easily and a perturbation.

The effect of perturbation needs to be accounted order-by-order, by expressing the solution as a Taylor series in the perturbation strength

By inserting Taylor series into the Schrodinger equation and after collecting the terms of the same power in  $\lambda$ , we have:

**Our goal for the n-th order is to find corrections to the energy ( $W_1, W_2, \dots, W_n$ ) and wavefunction ( $\Psi_1, \Psi_2, \dots, \Psi_n$ ).**

$$\mathbf{H} = \mathbf{H}_0 + \lambda \mathbf{H}'$$

$$\mathbf{H}_0 \Phi_i = E_i \Phi_i \quad i = 0, 1, 2, \dots, \infty$$

$$\mathbf{H} \Psi = W \Psi$$

$$W = \lambda^0 W_0 + \lambda^1 W_1 + \lambda^2 W_2 + \lambda^3 W_3 + \dots$$

$$\Psi = \lambda^0 \Psi_0 + \lambda^1 \Psi_1 + \lambda^2 \Psi_2 + \lambda^3 \Psi_3 + \dots$$

$$\lambda^0: \mathbf{H}_0 \Psi_0 = W_0 \Psi_0$$

$$\lambda^1: \mathbf{H}_0 \Psi_1 + \mathbf{H}' \Psi_0 = W_0 \Psi_1 + W_1 \Psi_0$$

$$\lambda^2: \mathbf{H}_0 \Psi_2 + \mathbf{H}' \Psi_1 = W_0 \Psi_2 + W_1 \Psi_1 + W_2 \Psi_0$$

$$\lambda^n: \mathbf{H}_0 \Psi_n + \mathbf{H}' \Psi_{n-1} = \sum_{i=0}^n W_i \Psi_{n-i}$$

# Many-Body (or Moller-Plesset, MP) Perturbation Theory (mostly dynamic correlations)

The first order:

$$\Psi_1 = \sum_i c_i \Phi_i \quad W_1 = \langle \Phi_0 | \mathbf{H}' | \Phi_0 \rangle \quad c_j = \frac{\langle \Phi_j | \mathbf{H}' | \Phi_0 \rangle}{E_0 - E_j}$$

The second order:

$$\Psi_2 = \sum_i d_i \Phi_i \quad W_2 = \sum_i c_i \langle \Phi_0 | \mathbf{H}' | \Phi_i \rangle = \sum_{i \neq 0} \frac{\langle \Phi_0 | \mathbf{H}' | \Phi_i \rangle \langle \Phi_i | \mathbf{H}' | \Phi_0 \rangle}{E_0 - E_i}$$

$$d_j = \sum_{i \neq 0} \frac{\langle \Phi_j | \mathbf{H}' | \Phi_i \rangle \langle \Phi_i | \mathbf{H}' | \Phi_0 \rangle}{(E_0 - E_j)(E_0 - E_i)} - \frac{\langle \Phi_j | \mathbf{H}' | \Phi_0 \rangle \langle \Phi_0 | \mathbf{H}' | \Phi_0 \rangle}{(E_0 - E_j)^2}$$

In our case the perturbation is deviation of the actual electron-electron potential from the Hartree-Fock (mean-field) potential

$$\mathbf{H}_0 = \sum_{i=1}^{N_{\text{elec}}} \left( \mathbf{h}_i + \sum_{j=1}^{N_{\text{elec}}} (\mathbf{J}_j - \mathbf{K}_j) \right) = \sum_{i=1}^{N_{\text{elec}}} \mathbf{h}_i + 2 \langle \mathbf{V}_{\text{ee}} \rangle$$

$$\mathbf{H}' = \mathbf{H} - \mathbf{H}_0 = \mathbf{V}_{\text{ee}} - 2 \langle \mathbf{V}_{\text{ee}} \rangle$$

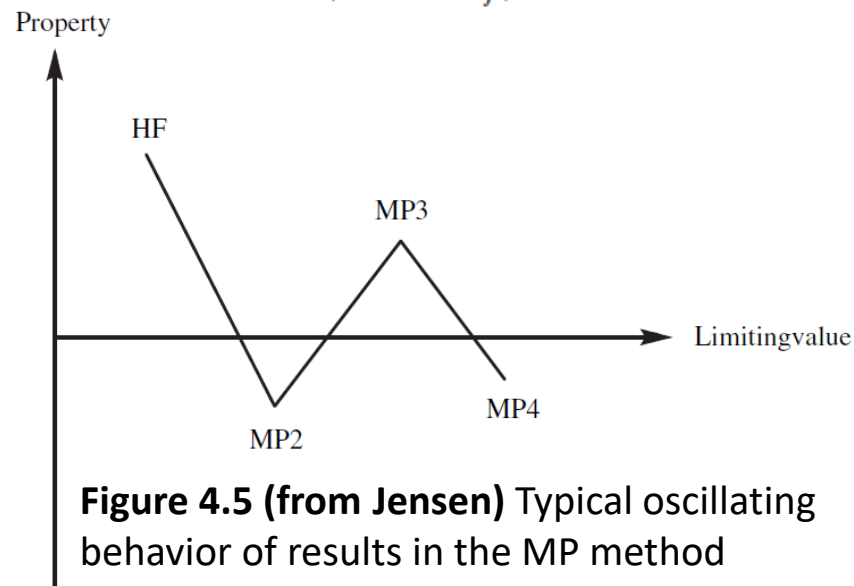


Figure 4.5 (from Jensen) Typical oscillating behavior of results in the MP method

# Many-Body (or Moller-Plesset, MP) Perturbation Theory

**The zero order:**  $W_0 = \langle \Phi_0 | \mathbf{H}_0 | \Phi_0 \rangle = \left\langle \Phi_0 \left| \sum_{i=1}^{N_{\text{elec}}} \mathbf{F}_i \right| \Phi_0 \right\rangle = \sum_{i=1}^{N_{\text{elec}}} \epsilon_i$        $MP0 = E(MP0) = \sum_{i=1}^{N_{\text{elec}}} \epsilon_i$

**The first order:**  $W_1 = \langle \Phi_0 | \mathbf{H}' | \Phi_0 \rangle = \langle \mathbf{V}_{ee} \rangle - 2\langle \mathbf{V}_{ee} \rangle = -\langle \mathbf{V}_{ee} \rangle$        $MP1 = E(MP0) + E(MP1) = E(HF)$

Given the choice of  $\mathbf{H}_0$  (Hartree-Fock potential), electron correlation energy starts at order two!

**The second order:** The numerator is zero for all other determinants except double excitations

$$W_2 = \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{vir}} \frac{\langle \Phi_0 | \mathbf{H}' | \Phi_{ij}^{ab} \rangle \langle \Phi_{ij}^{ab} | \mathbf{H}' | \Phi_0 \rangle}{E_0 - E_{ij}^{ab}}$$

$$E(MP2) = \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{vir}} \frac{(\langle \phi_i \phi_j | \phi_a \phi_b \rangle - \langle \phi_i \phi_j | \phi_b \phi_a \rangle)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

Second-order energy correction is negative; electron correlation stabilizes the energy. Usually perturbation theory is taken through second order (MP2), which scales as  $O(N^5)$ .

- *Not variational (i.e., can give energy lower than the 'exact' energy)*
- *Size extensive! No problems when going from monomer to dimer to trimer, etc.*
- *MP2 accounts for about 80-90% of correlation energy, one of the 'cheapest' approaches*
- *Still 'perturbation theory' - fails miserably when going beyond perturbation regime*

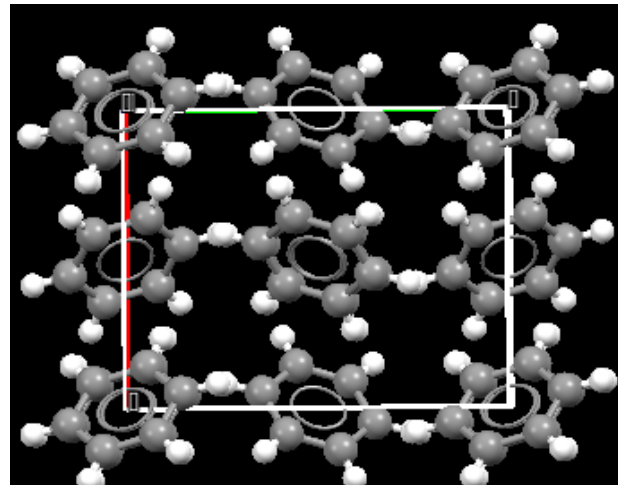
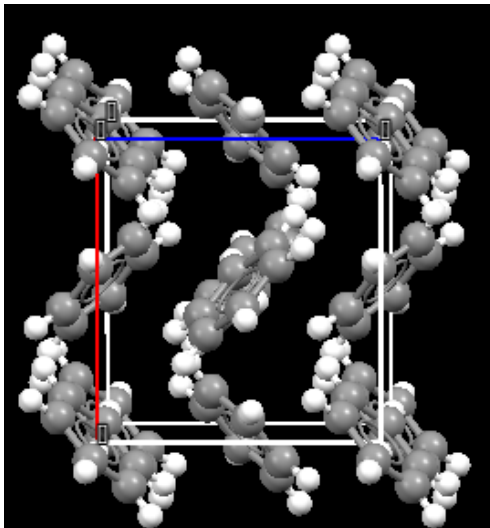
# Case study 2: Dispersive interactions

## Van der Waals' forces

- force between two permanent dipoles (Keesom force)
- force between a permanent dipole and a corresponding induced dipole (Debye force)
- force between two instantaneously induced dipoles (London dispersion force).



***The force that holds together many molecular crystals!***



**Benzene crystal (from Mercury)**

**Wikipedia:**  
Gecko  
climbing  
glass



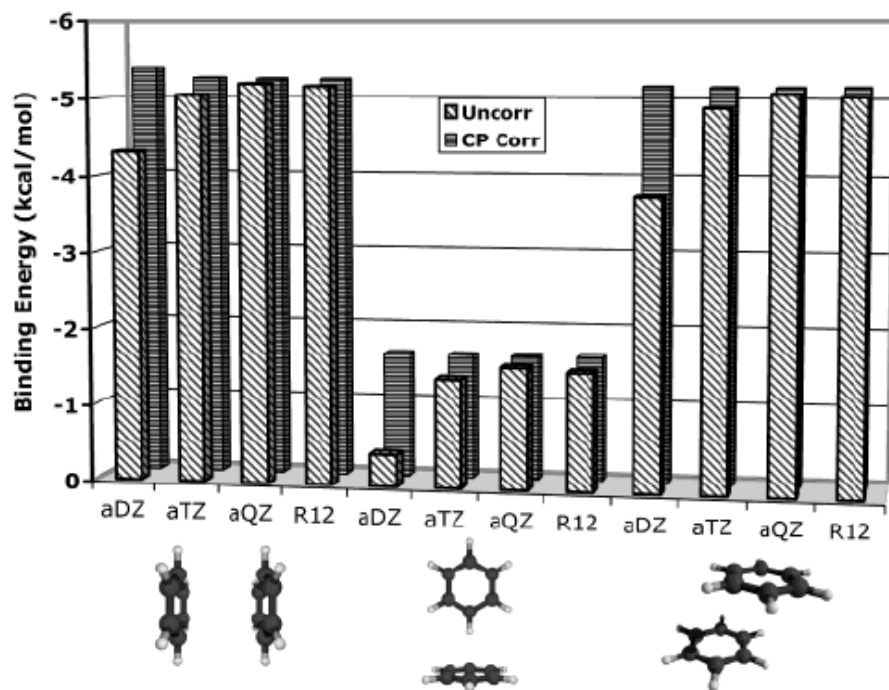
# Case study 2: Dispersive interactions

## Estimates of the Ab Initio Limit for $\pi-\pi$ Interactions: The Benzene Dimer

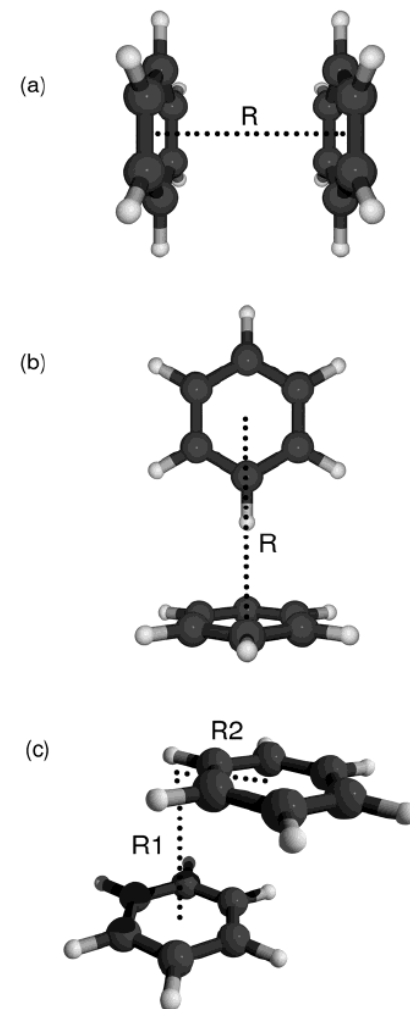
Mutasem Omar Sinnokrot, Edward F. Valeev, and C. David Sherrill\*

J. AM. CHEM. SOC. 2002, 124, 10887–10893 ■ 10887

*Oops, Hartree-Fock does not reproduce bound states!*



**Figure 6.** Hartree-Fock binding energies for each dimer structure as a function of basis set. All computations were performed at the same best estimate geometry for each configuration. All energies are negative (repulsive).



**Figure 1.** Sandwich, T-shaped, and parallel-displaced configurations of the benzene dimer.

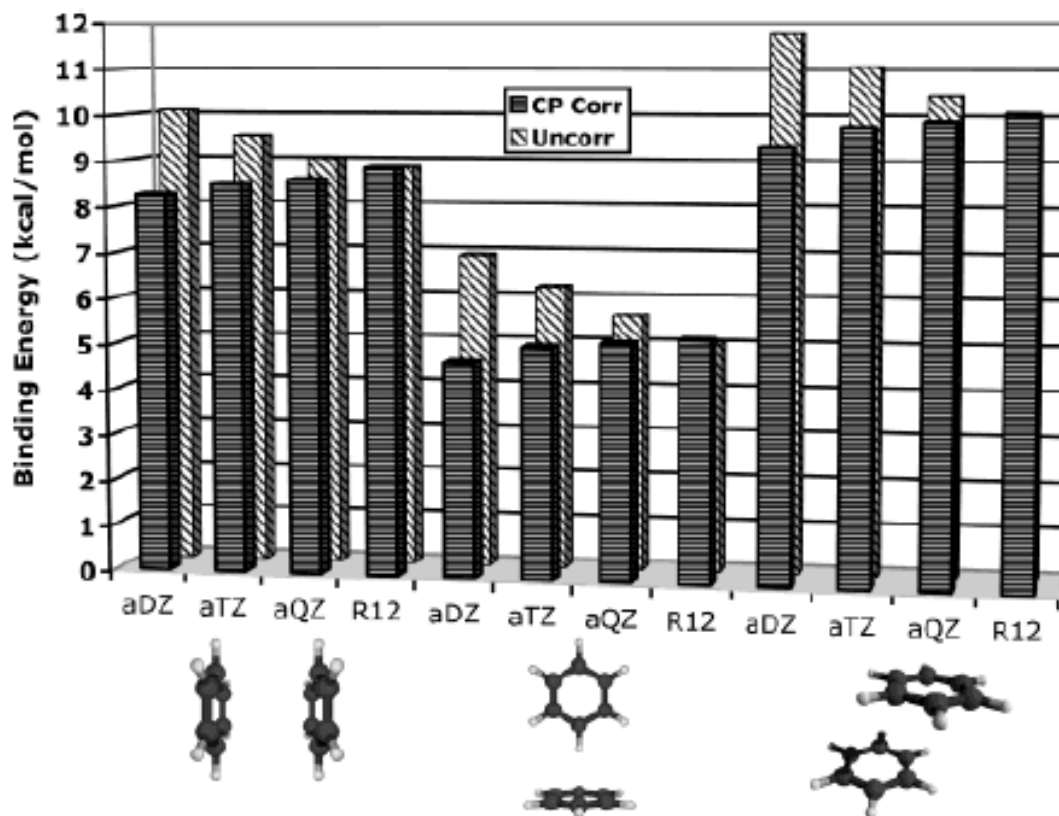
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**Figure 7.** MP2 electron correlation energy contributions to binding energies for each dimer structure as a function of basis set. The total MP2 binding energies are obtained by adding these values to the Hartree-Fock contributions in the previous figure.

# Discussion

1. Why examination of molecular orbitals is useful?
2. Question to all: write on the chat any examples of molecules, materials or processes where mean-field HF description may fail.
3. What are the advantages of a variational procedure?

# Coupled Cluster (CC) methods

**Coupled Cluster approach: include ALL corrections of a given type to infinite order**

Excitation operator  $\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2 + \mathbf{T}_3 + \dots + \mathbf{T}_{N_{elec}}$   $\mathbf{T}_1\Phi_0 = \sum_i^{occ} \sum_a^{vir} t_i^a \Phi_i^a$   $\mathbf{T}_2\Phi_0 = \sum_{i<j}^{occ} \sum_{a<b}^{vir} t_{ij}^{ab} \Phi_{ij}^{ab}$

The CI wavefunction  $\Psi_{CI} = (\mathbf{1} + \mathbf{T})\Phi_0 = (\mathbf{1} + \mathbf{T}_1 + \mathbf{T}_2 + \mathbf{T}_3 + \mathbf{T}_4 + \dots)\Phi_0$

The coupled cluster wavefunction  $\Psi_{CC} = e^{\mathbf{T}}\Phi_0$   $e^{\mathbf{T}} = \mathbf{1} + \mathbf{T} + \frac{1}{2}\mathbf{T}^2 + \frac{1}{6}\mathbf{T}^3 + \dots = \sum_{k=0}^{\infty} \frac{1}{k!}\mathbf{T}^k$

The Schrodinger equation  $\mathbf{H}e^{\mathbf{T}}\Phi_0 = Ee^{\mathbf{T}}\Phi_0$

The Coupled Cluster energy  $E_{CC}^{var} = \frac{\langle \Psi_{CC} | \mathbf{H} | \Psi_{CC} \rangle}{\langle \Psi_{CC} | \Psi_{CC} \rangle} = \frac{\langle e^{\mathbf{T}}\Phi_0 | \mathbf{H} | e^{\mathbf{T}}\Phi_0 \rangle}{\langle e^{\mathbf{T}}\Phi_0 | e^{\mathbf{T}}\Phi_0 \rangle}$

Similarity transform (eigenproblem of transformed non-Hermitian Hamiltonian):  $e^{-\mathbf{T}}\mathbf{H}e^{\mathbf{T}}\Phi_0 = E_{CC}\Phi_0$   $E_{CC} = \langle \Phi_0 | e^{-\mathbf{T}}\mathbf{H}e^{\mathbf{T}} | \Phi_0 \rangle$

**The CC computational problem is determination of the cluster amplitudes  $t$  for all of the operators included in the particular approximation.**

$$e^{\mathbf{T}} = \mathbf{1} + \mathbf{T}_1 + (\mathbf{T}_2 + \frac{1}{2}\mathbf{T}_1^2)$$

$$E_{CC} = E_0 + \sum_i^{occ} \sum_a^{vir} t_i^a \langle \Phi_0 | \mathbf{H} | \Phi_i^a \rangle + \sum_{i<j}^{occ} \sum_{a<b}^{vir} (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) \langle \Phi_0 | \mathbf{H} | \Phi_{ij}^{ab} \rangle$$



# Coupled Cluster: typical approaches

**CCSD: Cost  $O(N^6)$**   $\hat{T} = \hat{T}_1 + \hat{T}_2$   $|\Psi_{CC}\rangle = e^{\hat{T}}|\Phi_0\rangle$

**CCSD(T): Cost  $O(N^7)$**  Adds perturbative correction for  $T_3$

**Alternative implementations of CCSD and CCSDT are CC2 and CC3**

Computational cost: HF  $\ll$  CC2 < CCSD < CC3 < CCSDT

Similar to CI, computational cost of CC approaches grows dramatically with higher level.

Also EOM-CC (Equations of Motion) for accurate excited states, Spin-Flip methods, Direct methods, Inter-electronic distance methods, Quantum Monte-Carlo Methods, etc.

**Table 4.7** Limiting scaling in terms of basis set size  $M$  for various methods

Scaling	CI methods	MP methods	CC methods (iterative)
$M^5$	CIS	MP2	CC2
$M^6$	CISD	MP3	CCSD
$M^7$		MP4	CC3, CCSD(T)
$M^8$	CISDT	MP5	CCSDT
$M^9$		MP6	
$M^{10}$	CISDTQ	MP7	CCSDTQ

# Coupled Cluster method accuracy (a golden standard of comp. chemistry)

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Bond lengths	$\pm 0.004 \text{ \AA}$
Bond angles	$\pm 0.3^\circ$
Harmonic frequencies	$+2\%$
Dipole moments	$\pm 0.05 \text{ D}$
IR intensities	$\pm 20\%$
Excitation energies	$\pm 0.2 \text{ eV}$

---

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Expected Errors for Large-Basis CCSD(T)

***Coupled-Cluster Theory: An Ab Initio Success Story***

# Case study 2: Approximation CCSD(T)\* / CBS?

The linear-scaling domain-localized DPLNO-CCSD(T) method by Neese et al J. Chem. Phys. 2016, 144 (2)

$$E_{CCSD(T)}^{cc-pVTZ} \approx E_{Normal-DPLNO-CCSD(T)}^{cc-pVTZ} + (E_{Tight-DPLNO-CCSD(T)}^{cc-pVDZ} - E_{Normal-DPLNO-CCSD(T)}^{cc-pVDZ})$$

Complete basis set extrapolation (CBS)

$$E_{total}^{CBS} \approx E_{HF}^{CBS} + E_{MP2}^{CBS} + (E_{CCSD(T)}^{cc-pVTZ} - E_{MP2}^{cc-pVTZ})$$

S66 and W4-11

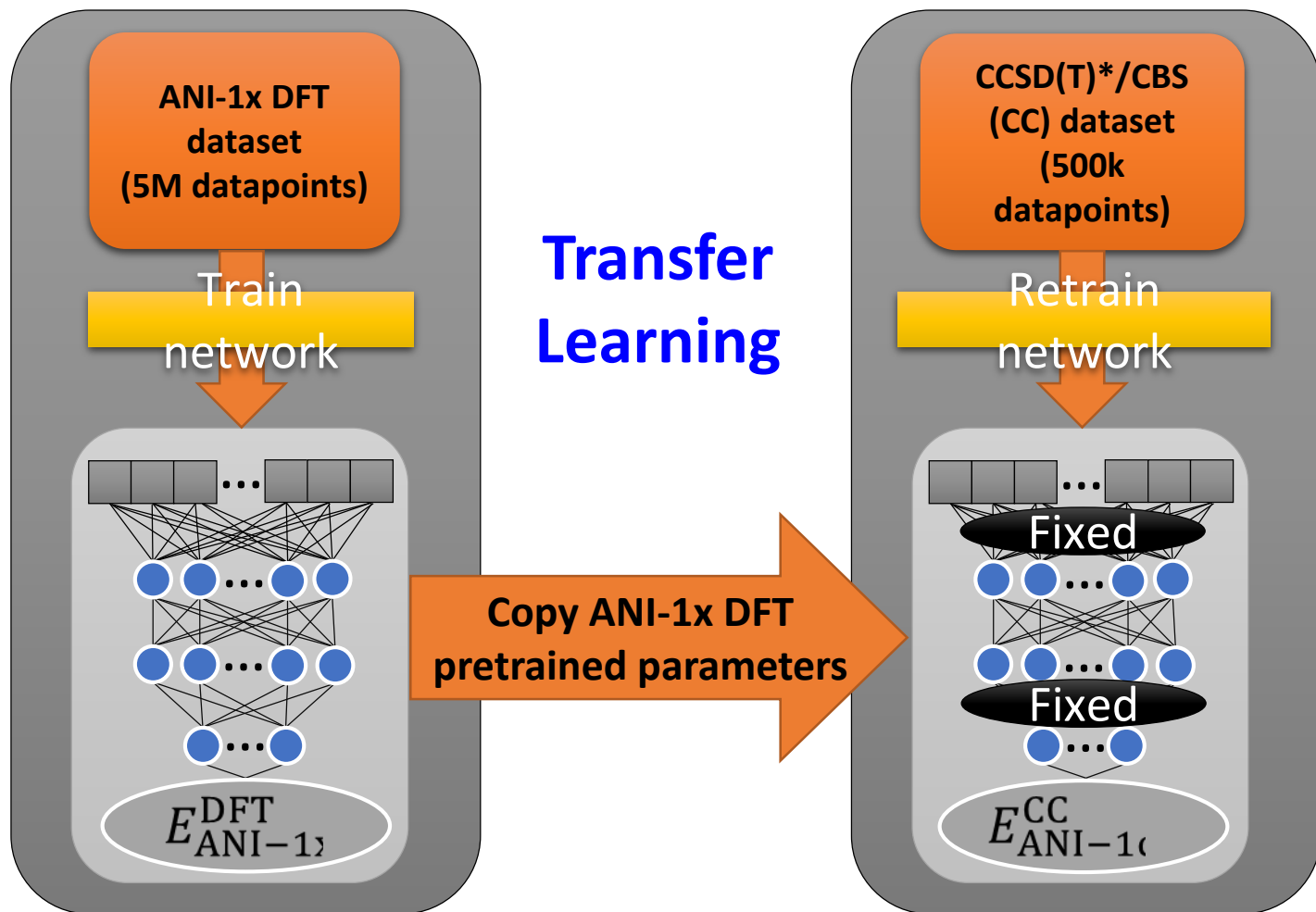
benchmarks are calculated using CCSD(T)-F12 method

Method	CPU-core hours <sup>a</sup>		MAE / RMSD, kcal/mol	
	Alanine	Aspirin	S66	W4-11
CCSD(T)/CBS(aDZ)	1.53	42.79	0.08 / 0.10	1.58 / 1.85
CCSD(T)/CBS(haTZ)	9.13	427.00	0.03 / 0.04	1.31 / 1.53
NormalPNO-CCSD(T)/CBS(aDZ)	0.78	4.63	0.31 / 0.39	2.35 / 2.59
NormalPNO-CCSD(T)/CBS(haTZ)	1.85	16.83	0.27 / 0.36	1.91 / 1.66
TightPNO-CCSD(T)/CBS(TZ)	1.56	16.70	0.16 / 0.10	1.40 / 1.50
<b>CCSD(T)* / CBS (our reference)</b>	<b>1.44</b>	<b>7.44</b>	<b>0.09 / 0.10</b>	<b>1.46 / 1.55</b>

J.S. Smith, B.T. Nebgen, R. Zubatyuk, N. Lubbers, C. Devereux, K. Barros, S. Tretiak, O. Isayev, A.E. Roitberg, "Outsmarting Quantum Chemistry Through Transfer Learning" *Nature Comm.* 10, 2903 (2019)

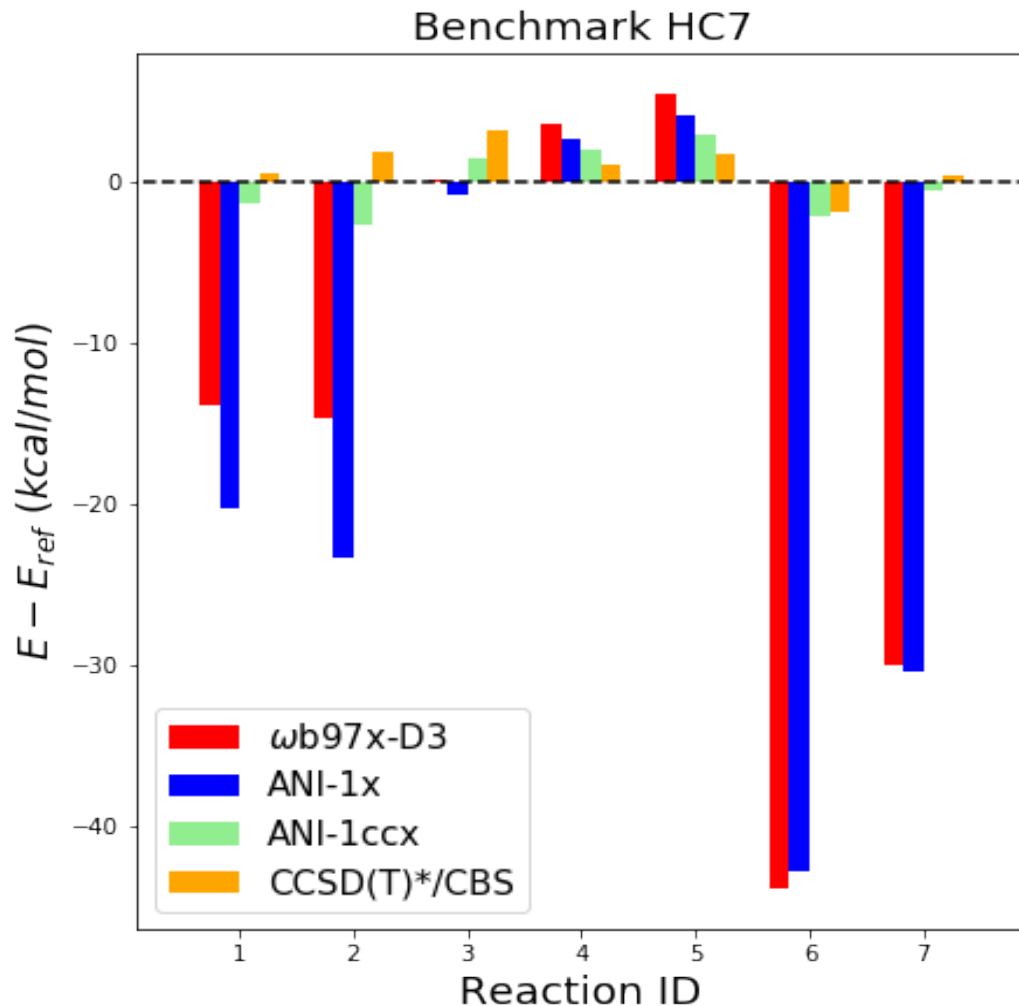
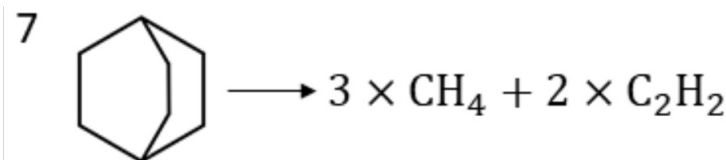
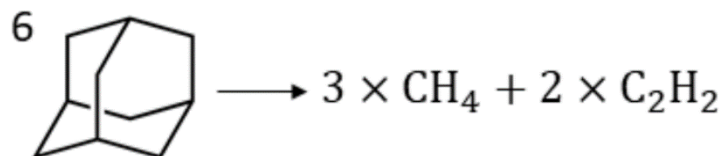
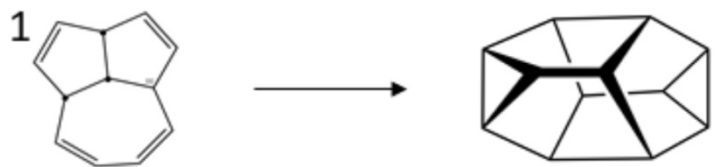
# Case study: Machine learning and Data Science to complement conventional QC

- Subsample 10% of ANI-1x training data (0.5M of 5M)
- Recompute CCSD(T)/CBS level
- 340k parameters fixed, re-train 60k
- $10^7$  faster than DFT



*J.S. Smith, B.T. Nebgen, R. Zubatyuk, N. Lubbers, C. Devereux, K. Barros, S. Tretiak, O. Isayev, A.E. Roitberg, "Outsmarting Quantum Chemistry Through Transfer Learning" Nature Comm. 10, 2903 (2019)*

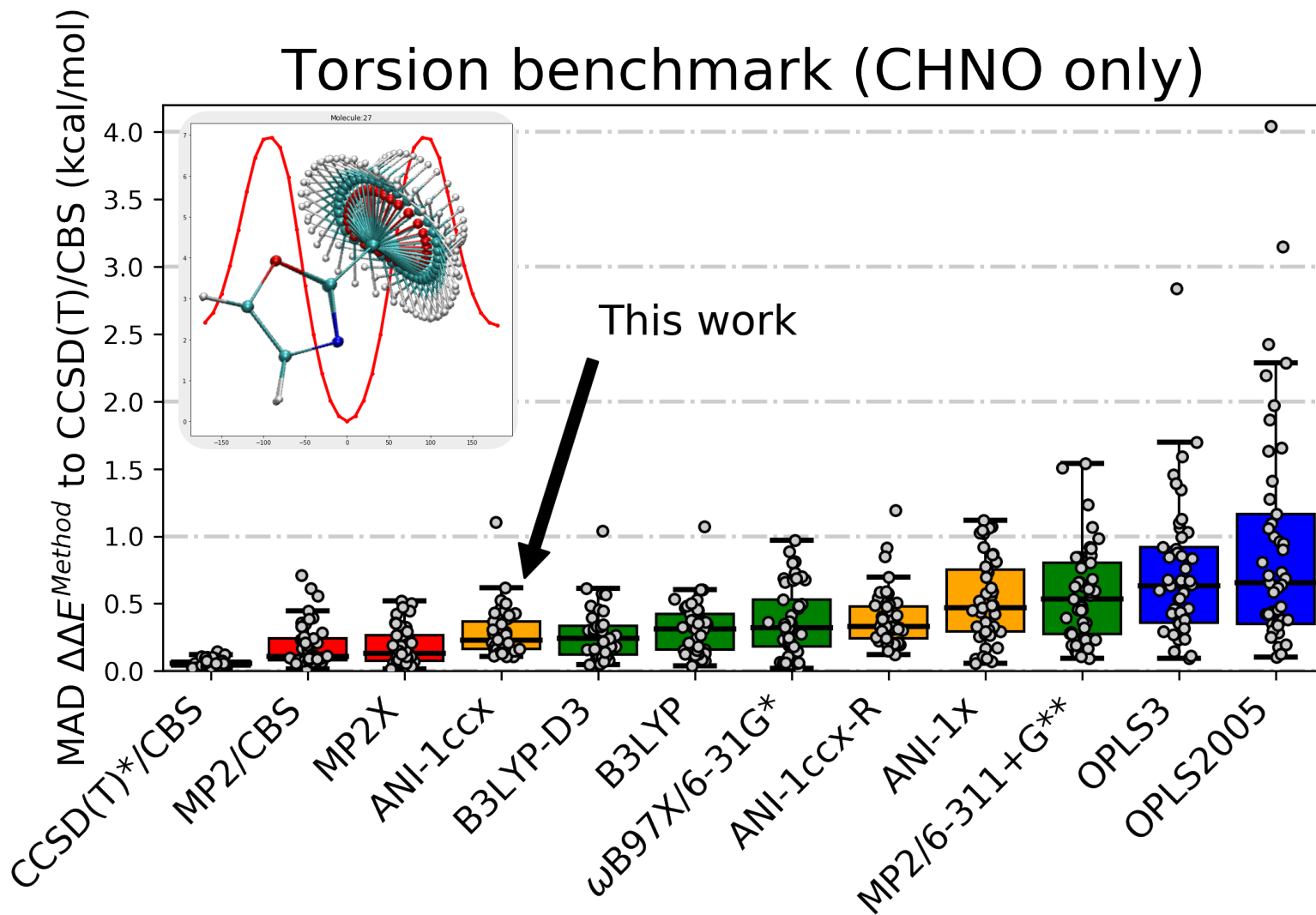
# Hydrocarbon isomerization benchmark



Reference data: R. Peverati, Y. Zhao, D. G. Truhlar, *J. Phys. Chem. Lett.* **2**, 1991 (2011)

# Torsional Benchmark

Torsion benchmark (CHNO only)



Reference data: B.D. Sellers, N.C. James, A.J. Gobbi, *Chem. Inf. Model.* 57,1265 (2017)

J. S. Smith, B.T. Nebgen, R. Zubatyuk, N. Lubbers, C. Devereux, K. Barros, S. Tretiak, O. Isayev, A.E. Roitberg, *Nature Comm.* 10, 2903 (2019)

# Brief summary of post-HF methods

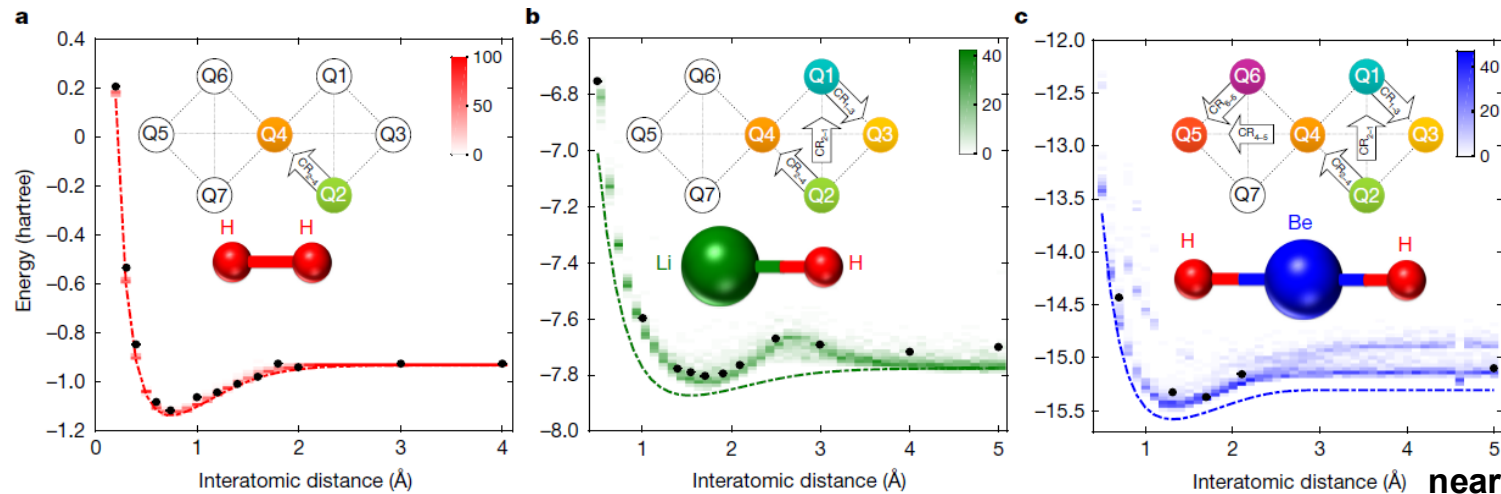
	CI	MP	CC
Size extensivity	no	yes	yes
Excited states	yes	no	yes
Ground state corrections beyond HF	yes	yes	yes
Ground state analytic gradients (low orders)	yes	yes	yes
Gaussian 09	QCISD,CAS	MP4	CCSD(T)
Firefly 8	yes	MP4	no
Q-Chem, Turbomole, GAMESS	yes	yes	yes

- **Accuracy:**  $HF \ll MP2 < CISD < MP4(SDQ) \sim QCISD \sim CCSD < MP4 < CCSD(T)$
- **Reference state:** HF ground state
- They work 'the best' when the reference HF state is accurate
- Shortcuts like restricting 'active space' are possible but use with caution
- Basis set complexity should increase concomitantly with method complexity

**Use them when you can afford their cost!**  
**Systematic convergence to the exact answer**

# AND now quantum computing

Promises to solve the electronic structure problem EXACTLY (i.e. Full CI level)



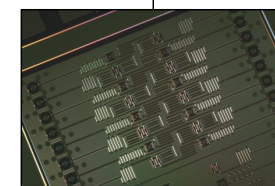
FROM IBM: Nature 549, 242 (2017)

near-term “gate-based” quantum computers

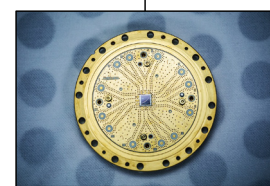
## CURRENT PRACTICAL APPROACHES

- Choose your basis set, print  $1e$  and  $2e$  integrals
- Map quantum-chemical results into quantum-computer language by apply Jordan-Wigner or Bravyi-Kitayev transformation;
- Implemented in Open Fermion code (Jarrod McClean)
- Use Variational Quantum Eigensolver (VQE) algorithm to get quantum-mechanical energy from QPU

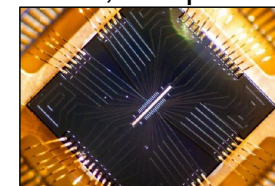
**MAIN PROBLEM: Number of qubits grows as  $\sim N^4$  with basis set**



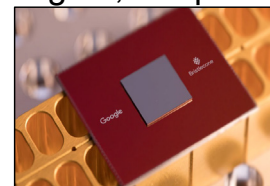
IBM, 20 qubits



Rigetti, 20 qubits



IonQ, 79 qubits



Google, 72 qubits

NISQ (Noisy Intermediate Scale Quantum) devices

S. McArdle, S. Endo, A. Aspuru-Guzik, S. Benjamin, and X. Yuan, “Quantum computational chemistry” Review arXiv:1808.10402v2 (2019)



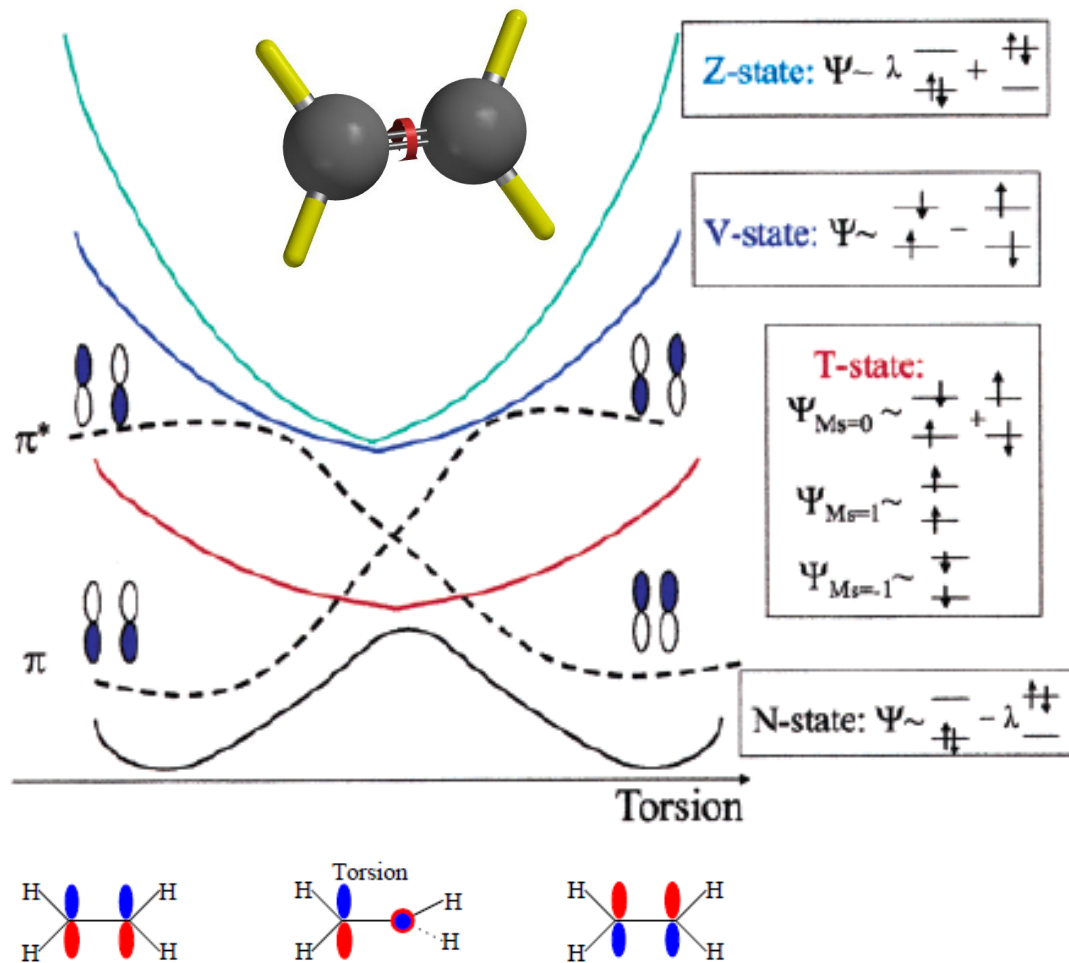
# Case study 3: Bond-breaking (ethylene)

## Spin-Flip Equation-of-Motion Coupled-Cluster Electronic Structure Method for a Description of Excited States, Bond Breaking, Diradicals, and Triradicals

ANNA I. KRYLOV\*

VOL. 39, NO. 2, 2006 / ACCOUNTS OF CHEMICAL RESEARCH

**FIGURE 2.** Around equilibrium, the ground-state (*N*-state) wave function of ethylene is dominated by the  $\pi^2$  configuration. However, as a degeneracy between  $\pi$  and  $\pi^*$  develops along the torsional coordinate, the importance of the  $(\pi^*)^2$  configuration increases. At the barrier, where  $\pi$  and  $\pi^*$  are exactly degenerate, the qualitatively correct wave function for the *N*-state must include both configurations with equal weights. That is why the quality of the SR wave functions degrades as the molecule is twisted: even when the second configuration is explicitly present in a wave function (e.g., as in the CCSD or CISD models), it is not treated on the same footing as the reference configuration,  $\pi^2$ . The singlet and triplet  $\pi\pi^*$  states (the *V* and *T* states, respectively) are formally single-electron excitations from the *N*-state and are well-described by the SR excited states' models (despite the fact that both the singlet and the  $M_s = 0$  component of the triplet are two-configurational and therefore are not accessible by the ground-state SR methods). The *Z*-state, however, is formally a doubly excited state with respect to the *N*-state, and therefore, SR models will not treat it accurately. Note that the high-spin  $M_s = \pm 1$  components of the triplet *T*-state remain single-determinantal at all of the torsional angles. Moreover,

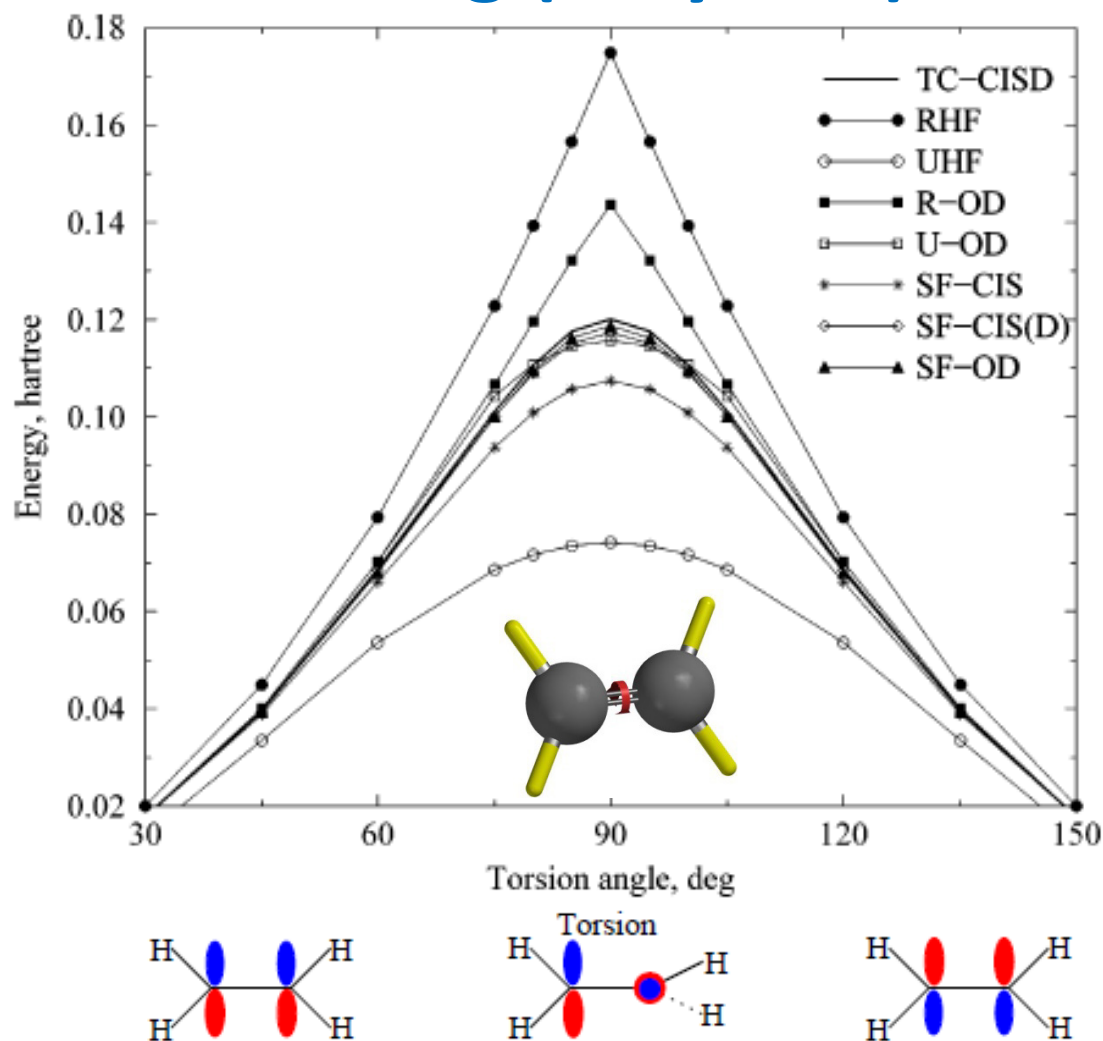


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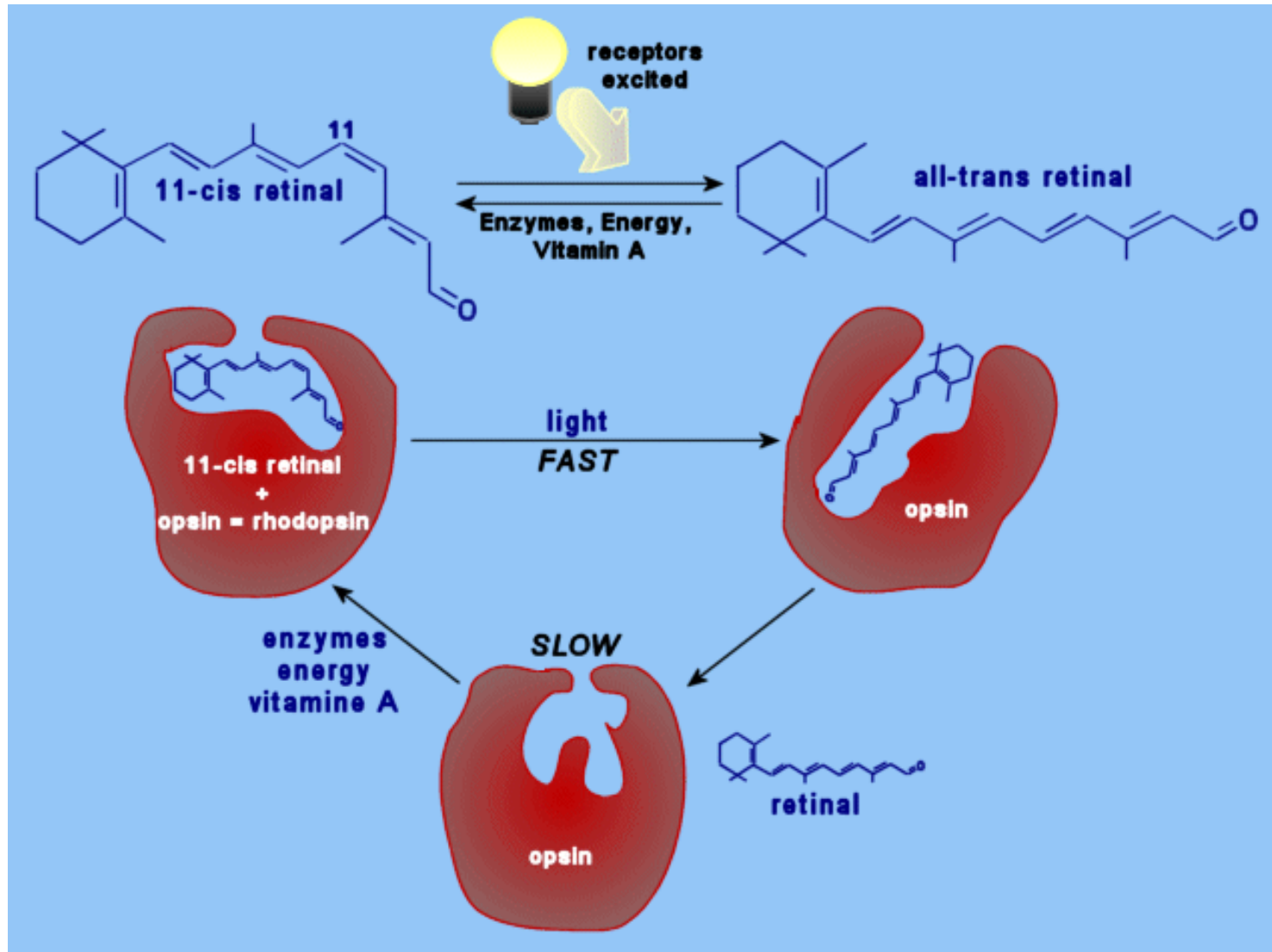
VOL. 39, NO. 2, 2006 / ACCOUNTS OF CHEMICAL RESEARCH



**FIGURE 6.** Ethylene torsion, DZP basis. All curves are shifted such that the energy at  $0^\circ$  is zero. The spin-flip curves do not exhibit an unphysical cusp and are closer to the reference TC-CISD curve than the corresponding spin-restricted and spin-unrestricted models.

# Case study 4: Photoexcited dynamics

Ultrafast conformational changes of the retinal after absorbing a quantum of light constitutes the primary process of human/animal vision



# Case study 4: Photoexcited dynamics

## Insights for Light-Driven Molecular Devices from *Ab Initio* Multiple Spawning Excited-State Dynamics of Organic and Biological Chromophores

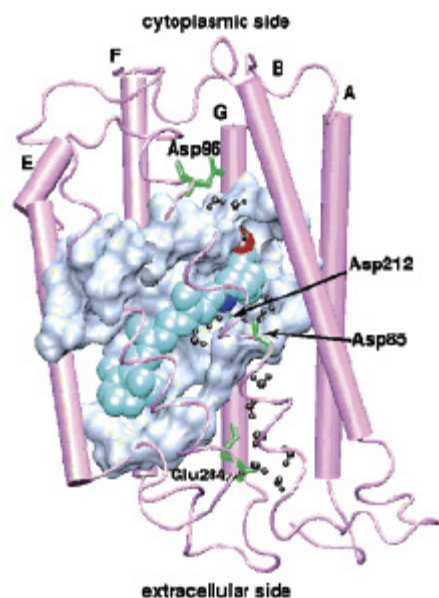
TODD J. MARTINEZ\*

Department of Chemistry, Beckman Institute, and The Frederick Seitz Materials Research Laboratory, University of Illinois, 600 S. Mathews Avenue, Urbana, Illinois 61801

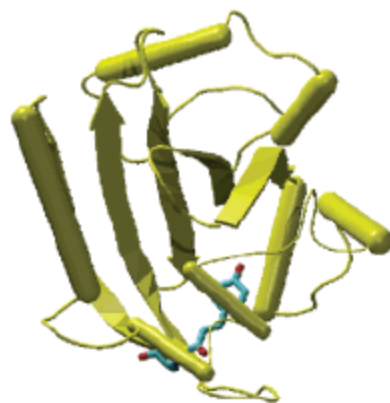
Received May 2, 2005

*Acc. Chem. Res.* 2006, 39, 119–126

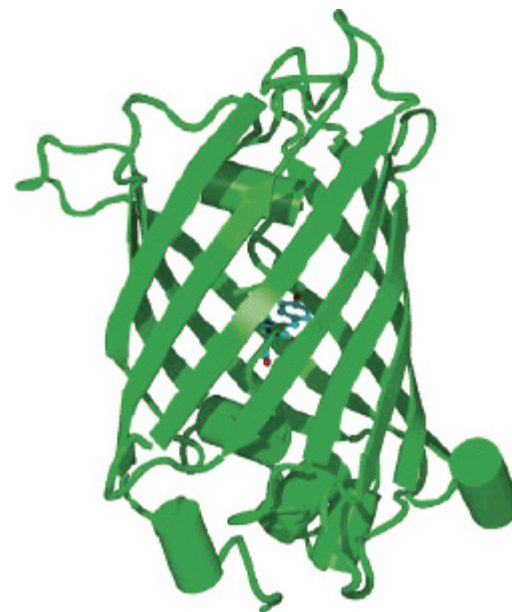
- ***Photo-isomerization is non-radiative molecular relaxation back to the ground state concurrent with substantial conformational changes;***
- ***A common deactivation channel of photoactive proteins (bR, PYP, GFP, etc.)***
- ***Difficult to model due to non-adiabatic dynamics involving multiple potential energy surfaces***



Bacteriorhodopsin (bR)



Photoactive Yellow Protein (PYP)



Green Fluorescent Protein (GFP)

# Case study 4: Photoexcited dynamics

## Insights for Light-Driven Molecular Devices from *Ab Initio* Multiple Spawning Excited-State Dynamics of Organic and Biological Chromophores

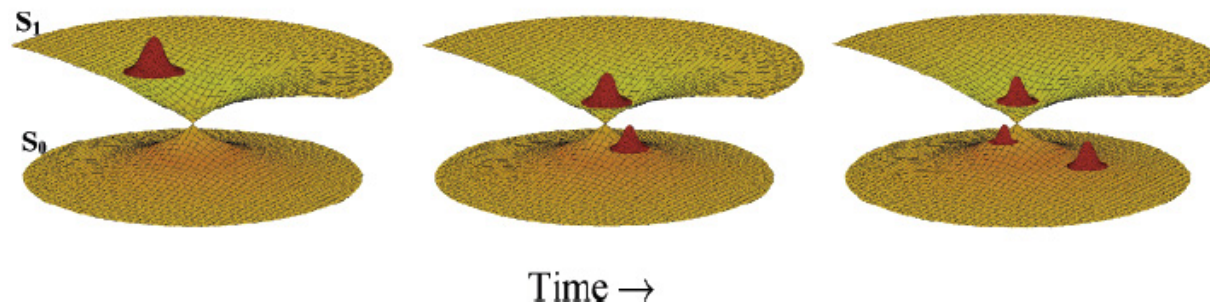
TODD J. MARTINEZ\*

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FIGURE 2. Schematic description of the multiple spawning method.



## “Simple” case – ethylene photoisomerization

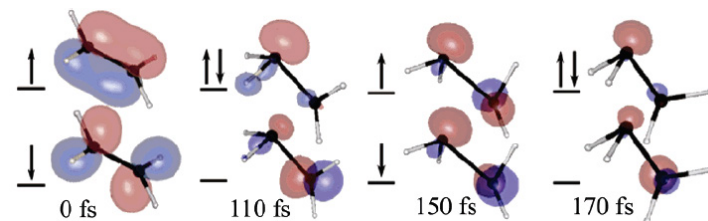
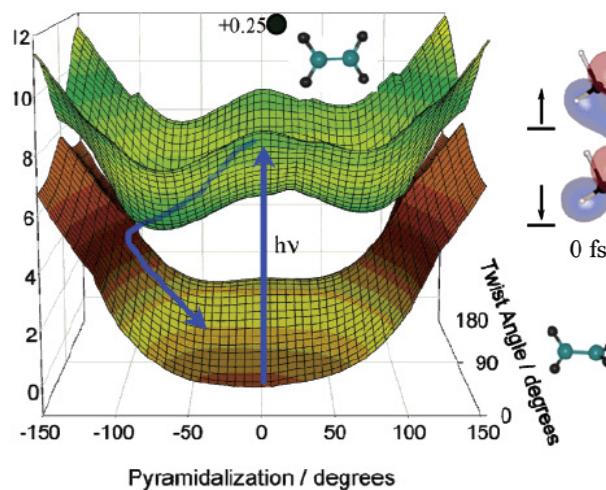
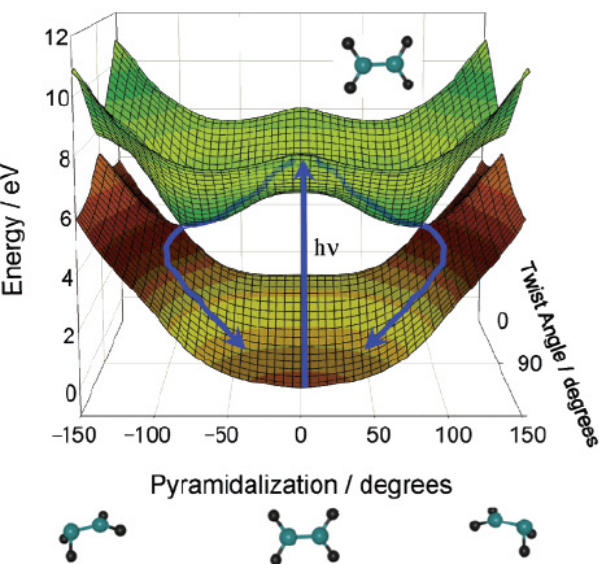


FIGURE 3. Changes in π – orbitals illustrate the intramolecular electron-transfer character of the excited-state dynamics.

FIGURE 4. Ground- and excited-state potential energy surfaces. Presence of charges (i.e. dielectric environment) affect the photoisomerization mechanism

**Methods used: CASSCF**

# Case study 4: Photoexcited dynamics

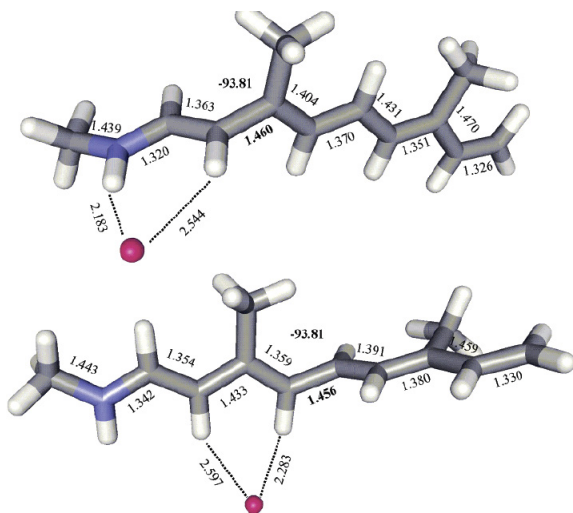
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*Acc. Chem. Res.* 2006, 39, 119–126

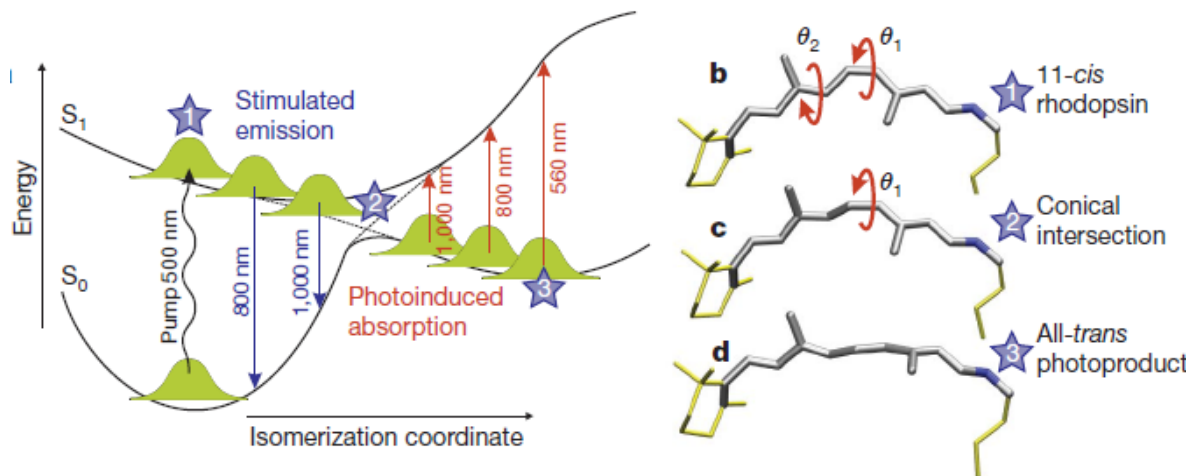


**FIGURE 5.** Dielectric environment and intramolecular electron-transfer play an important role in the retinal the excited-state dynamics and photoisomerization.

## Conical intersection dynamics of the primary photoisomerization event in vision

Dario Polli<sup>1</sup>, Piero Altoè<sup>2</sup>, Oliver Weingart<sup>3,4</sup>, Katelyn M. Spillane<sup>5</sup>, Cristian Manzoni<sup>1</sup>, Daniele Brida<sup>1</sup>, Gaia Tomasello<sup>2</sup>, Giorgio Orlandi<sup>2</sup>, Philipp Kukura<sup>6</sup>, Richard A. Mathies<sup>5</sup>, Marco Garavelli<sup>2</sup> & Giulio Cerullo<sup>1</sup>

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**FIGURE 2.** Isomerization potential energy surfaces of rhodopsin

**Direct experimental evidence on the role of conical intersection between ground and excited state in the ultrafast (~200fs) in rhodopsin photoisomerization**

# Case study 5

## Calculation of heat of formation: molecule in gas phase

### Basic thermodynamics

- Thermal energy  $E(S, V) = E_0 + E_{\text{rot+vib}}(T) + E_{\text{translat}}(T, V)$
- Enthalpy  $H(S, p) = F + pV$
- Free energy  $F(T, V) = E - TS = -T \ln Z$
- For ideal gas  $pV = NT$ ,  $E_{\text{translat}} = (3/2)T$ , and

$$\frac{S}{N} = \frac{5}{2} + \ln \left[ \left( \frac{m_{\text{molecule}}}{2\pi\hbar^2} \right)^{3/2} \frac{T^{5/2}}{p} \right] + \ln(\text{spin multiplicity})$$

### Reference state

- Standard conditions:  $T = 298.15$  K,  $p = 1$  atm
- Atomization energy – fully separated atoms
- Heat (enthalpy) of formation – atoms in their ground states<sup>1</sup>

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<sup>1</sup>H – H<sub>2</sub> gas, O – O<sub>2</sub> gas, Br – Br<sub>2</sub> liquid, C – graphite, S – rhombic sulfur <sup>63</sup>

# Predictions on molecules with 10-13 heavy atoms

**ANI-1ccx predicts accurate forces compared to MP2/TZ**

	ANI-1ccx	ANI-1x	$\omega$ B97X-D3	MP2/DZ
MP2/TZ	3.4	4.7	3.7	4.6

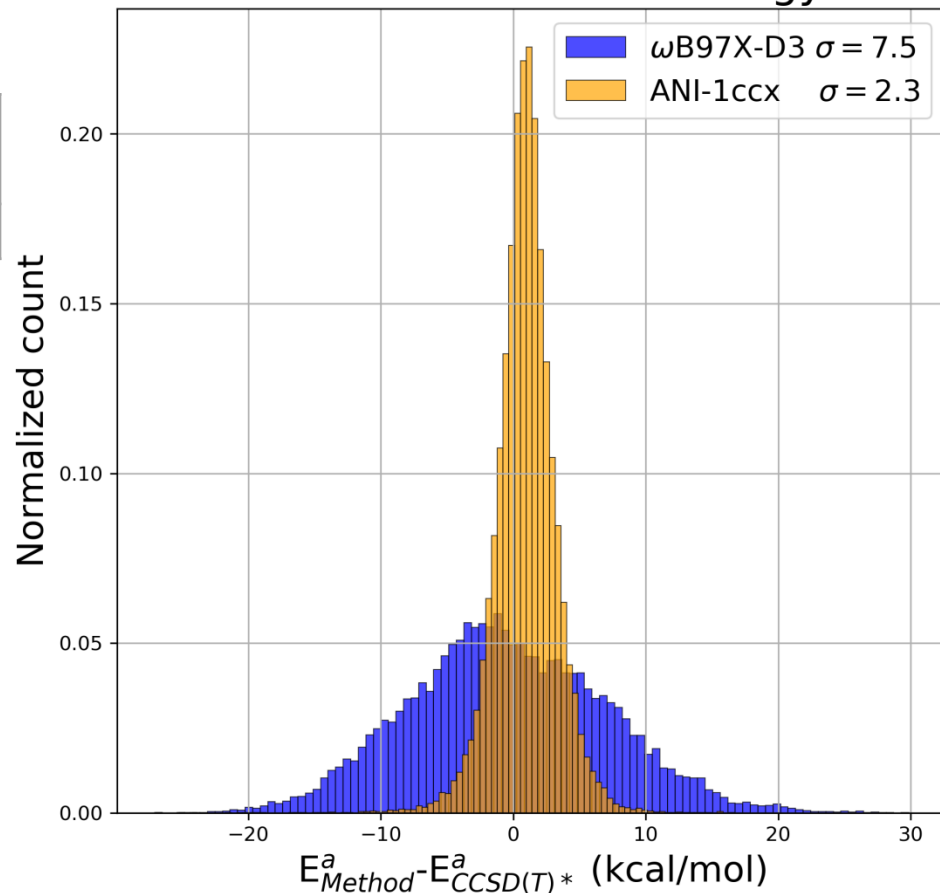
Units: kcal/mol/A (error MAD)

**ANI-1ccx predicts accurate relative energies compared to CCSD(T)**

	ANI-1ccx	ANI-1ccx-R	ANI-1x	$\omega$ B97X-D3
MAD	1.5	1.8	2.0	1.4

Units: kcal/mol

GDB-10to13 atomization energy error



*J. S. Smith, B.T. Nebgen, R. Zubatyuk, N. Lubbers, C. Devereux, K. Barros, S. Tretiak, O. Isayev, A.E. Roitberg, Nature Comm. 10, 2903 (2019)*



# Case study 5

## Calculation of heat of formation: practical aspects

Challenge: get 1 kcal/mol accuracy, while absolute error in total energy calculation is usually  $\gg 1$  kcal/mol

### Approach 1: Atomization

- $X = \sum_i n_i A_i$
- $\Delta H(X) = \sum_i n_i [\Delta H(A_i) - E_0(A_i)] - \frac{5}{2} NT + H(X)$
- Take  $\Delta H(A_i)$  from reference tables
- Calculate  $H(X)$  accurately, e.g. by composite G1-G4 methods
- Use precalculated  $E_0(A_i)$

### Approach 2: Isodesmic reaction

- $X = \sum_i \nu_i Y_i$ ,  $\nu_i$  may be negative and rational
- $\Delta H(X) = \sum_i \nu_i [\Delta H(Y_i) - H(Y_i)] + H(X)$
- Take  $\Delta H(Y_i)$  from reference tables
- Calculate  $H(X)$  and  $H(Y_i)$  with DFT-level accuracy

# Discussion

- 1. Do you believe that conventional computing reached its limits?**
- 2. Can quantum computing provide an advance? Why?**
- 3. Can machine learning provide an advance? Why?**

# Individual studies:

- **Reading.**

**Required:** Jensen (4.1-4.10)

**Additional:** Cramer (7.1-7.5)

Szabo (Ch.4, 5, 6)

# Static correlations: 2c2e model

$\uparrow\downarrow$	—	20
—	$\uparrow\downarrow$	02
$\uparrow$	$\uparrow$	$\alpha\alpha$
$\downarrow$	$\downarrow$	$\beta\beta$
$\uparrow$	$\downarrow$	$\alpha\beta$
$\downarrow$	$\uparrow$	$\beta\alpha$

	S	$S_z$	$\chi$	
	1	1	$\alpha\alpha$	the only states representable by HF
	1	-1	$\beta\beta$	
spin contamination	1	0	$\alpha\beta - \beta\alpha$	no single Slater determinant
	0	0	$\alpha\beta + \beta\alpha$	
static correlations	0	0	20	
	0	0	02	

$$\beta\alpha = \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix} \equiv \begin{vmatrix} 2 \\ 1 \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_2(x_1)\chi_{\uparrow}(\sigma_1) & \varphi_1(x_1)\chi_{\downarrow}(\sigma_1) \\ \varphi_2(x_2)\chi_{\uparrow}(\sigma_2) & \varphi_1(x_2)\chi_{\downarrow}(\sigma_2) \end{vmatrix}$$

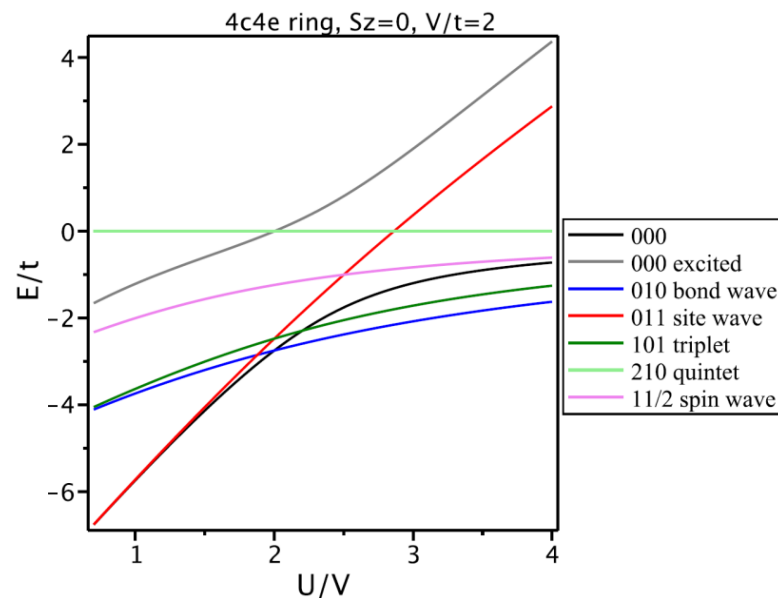
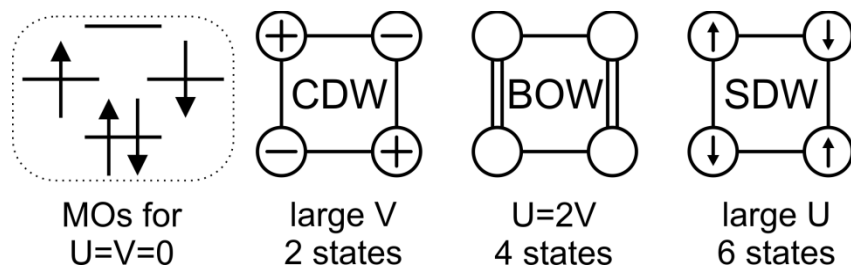
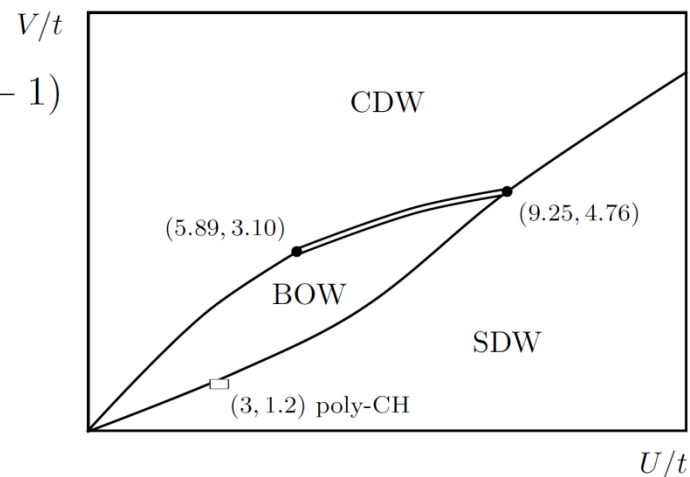
# Static correlations: 4c4e model

(the simplest one featuring 1D Extended Hubbard model)

$$\hat{H} = \sum_i \varepsilon_i \hat{n}_i + \sum_{i<j} t_{ij} \hat{T}_{ij} + \sum_i U_i \hat{n}_i^\uparrow \hat{n}_i^\downarrow + \sum_{i<j} V_{ij} (\hat{n}_i - 1)(\hat{n}_j - 1)$$

$$\hat{T}_{ij} = \sum_{\sigma} (c_{i\sigma}^+ c_{j\sigma} + c_{i\sigma} c_{j\sigma}^+)$$

- Three kinds of electron density waves
- Quantum phase transition at  $U=2V$
- Ground state degeneracy
- Levels crowding at large  $U$
- Meaningless noninteracting MOs
- Two Slater determinants for variational function



# Example: Full CI analytically for 4-site model

*Symmetries:* particle number, spin, spin projection, translation, inversion, particle-hole

256 total configuration space

36 subspace  $Q=0, S_z=0$

4 largest irreducible representation after all symmetries are taken into account

S	T	inversion	particle-hole
0	$-\frac{1}{2}$	<i>undefined</i>	$(E^2 - 2EU + EV + U^2 - UV - 4) (E^2 - 3EU + EV + 2U^2 - 2UV - 4)$
0	$\frac{1}{2}$	<i>undefined</i>	$(E^2 - 2EU + EV + U^2 - UV - 4) (E^2 - 3EU + EV + 2U^2 - 2UV - 4)$
1	$-\frac{1}{2}$	<i>undefined</i>	$(E^2 - EU + EV - 4) (E^2 - 2EU + EV + U^2 - UV - 4)$
1	$\frac{1}{2}$	<i>undefined</i>	$(E^2 - EU + EV - 4) (E^2 - 2EU + EV + U^2 - UV - 4)$
0	0	0	$(E - U) (E^4 - 5E^3U + 5E^3V + 8E^2U^2 - 16E^2UV + 4E^2V^2 - 4EU^3 + 12EU^2V - 8EUV^2 - 16E^2 + 40EU - 32EV - 16U^2 + 32UV)$
0	0	1	$E + V - U$
0	1	0	$E^3 - 3E^2U + E^2V + 2EU^2 - 2EUV - 16E + 24U$
0	1	1	$E^3 - 4E^2U + 5E^2V + 5EU^2 - 11EUV + 4EV^2 - 2U^3 + 6U^2V - 4UV^2 - 16E + 24U - 32V$
1	0	0	$E + V - U$
1	0	1	$E^3 - 2E^2U + E^2V + EU^2 - EUV - 16E + 8U$
1	1	0	$(E - U) (E + V - U)$
1	1	1	$E + V - U$
2	1	0	$E$

# Electronic correlations: NO occupations

Strong correlations: Extended Hubbard model

Population analysis: ground state, hole, exciton;  $U/V = 2/1$  vs  $16/4$

