

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

Sergei Tretiak (lecturer),

Andriy Zhugayevych (lecturer)

Dmitry Aksenov (lecturer)

Sergey Levchenko (lecturer)

Alexander Shapeev (lecturer)

Guest Lecturers (e.g. use of Abinit, FHI-aims, USPEX)

Christian Tantardini (teaching assistant)

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

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

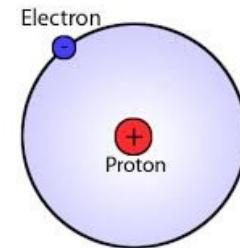
Other observables (generally described as KxK matrices), such as dipole operator

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

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

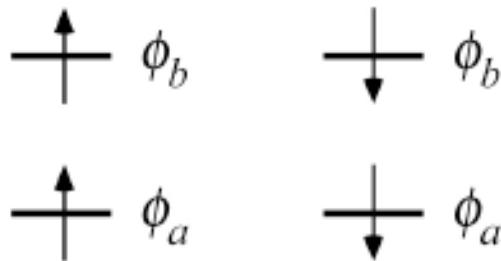
Example: singlet ($S=0$) and triplet ($S=1$) states of 2 electrons.

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

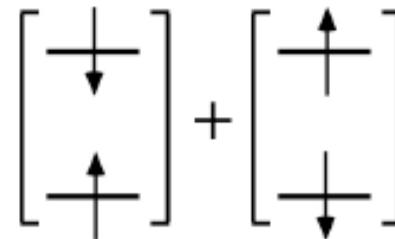
$$^1\Psi = \overbrace{\frac{1}{\sqrt{2}}(\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2))}^{\text{Symmetric}} \times \overbrace{\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)}^{\text{Antisymmetric}} \quad M_S = 0$$

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

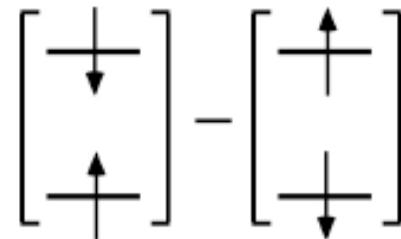
Or schematically:



$$^3\Psi(M_S = 1) \quad ^3\Psi(M_S = -1)$$

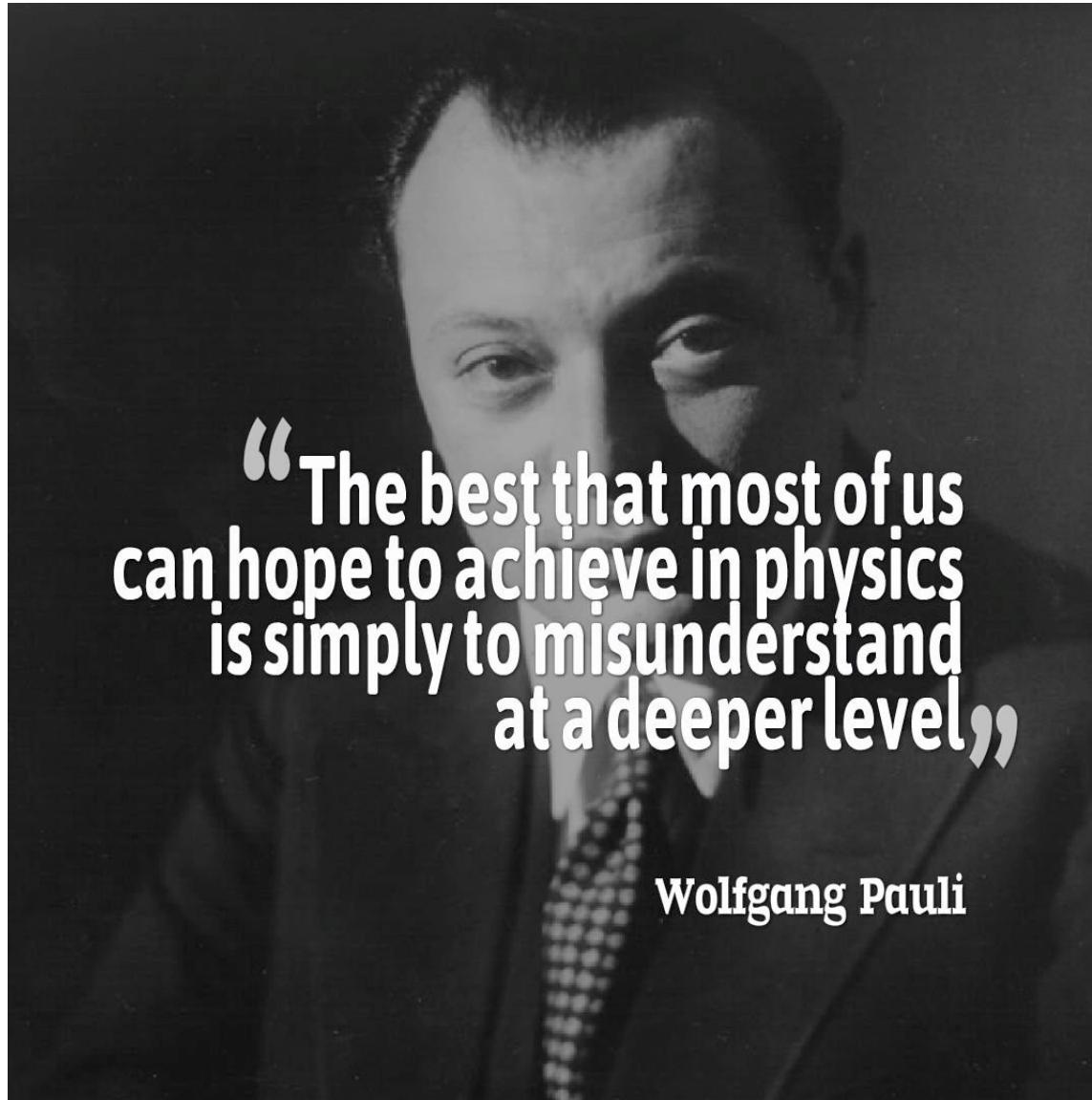


$$^1\Psi(M_S = 0)$$



$$^3\Psi(M_S = 0)$$

Wolfgang Pauli: “It is not even wrong”



Solving the many-body problem: Slater determinant

How to approach many-body wave-function $\Psi(x_1, x_2, \dots, x_N)$?

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: $\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_2, \mathbf{x}_1)$

Spin-orbitals

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

General form of Slater determinant for N-electrons

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} \quad \begin{array}{l} \text{Alternative notations} \\ \equiv |\chi_1, \chi_2, \dots, \chi_N\rangle \\ \equiv |1, 2, \dots, N\rangle, \end{array}$$

Basic properties:

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

Solving the many-body problem: Slater determinant

How to approach many-body wave-function $\Psi(x_1, x_2, \dots, x_N)$?

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: $\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_2, \mathbf{x}_1)$

Spin-orbitals

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

General form of Slater determinant for N-electrons

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} \quad \begin{matrix} & \text{Alternative notations} \\ & \equiv |\chi_1, \chi_2, \dots, \chi_N\rangle \\ & \equiv |1, 2, \dots, N\rangle, \end{matrix}$$

Basic properties:

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

Hartree-Fock method (coordinate representation)

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

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

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

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

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

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

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

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

Coulomb and exchange terms

In the Slater determinant, every electron belong 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:

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

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

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

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

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

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)

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

$V_i^{\text{HF}}\{j\}$

- 3) Energy of the Slater determinant:

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

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

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

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

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.

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

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

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

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$$

$$\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$$

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

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

Tetradic $KxKxKxK$ matrix*

Overlap intergrals (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

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

The Fock operator

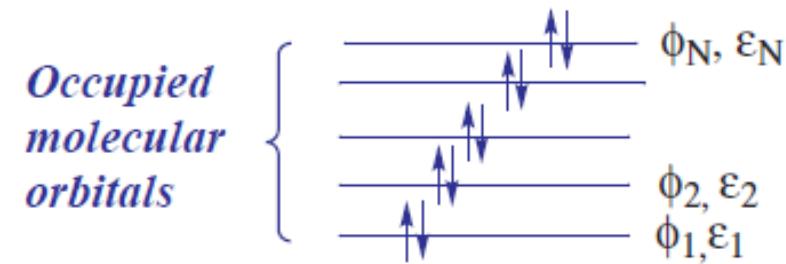
$$F(\bar{\rho})_{nm} = t_{nm} + V(\bar{\rho})_{nm}$$

The Coulomb operator (V or G ~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)

$$FC = SC\varepsilon$$



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

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**:

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

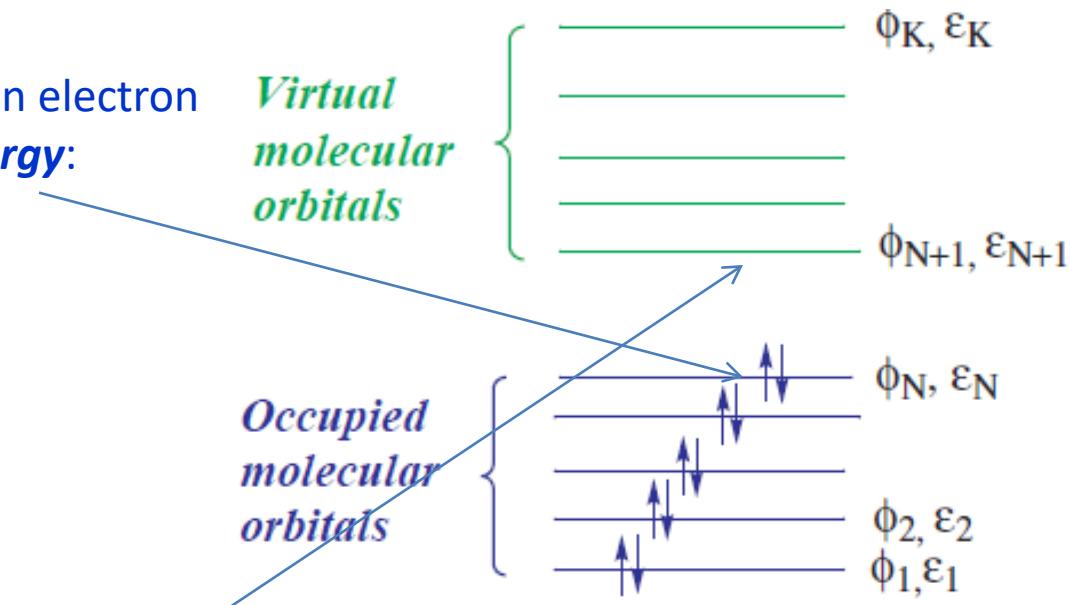
$${}^N E_0 = \langle {}^N \Psi_0 | \mathcal{H} | {}^N \Psi_0 \rangle$$

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

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

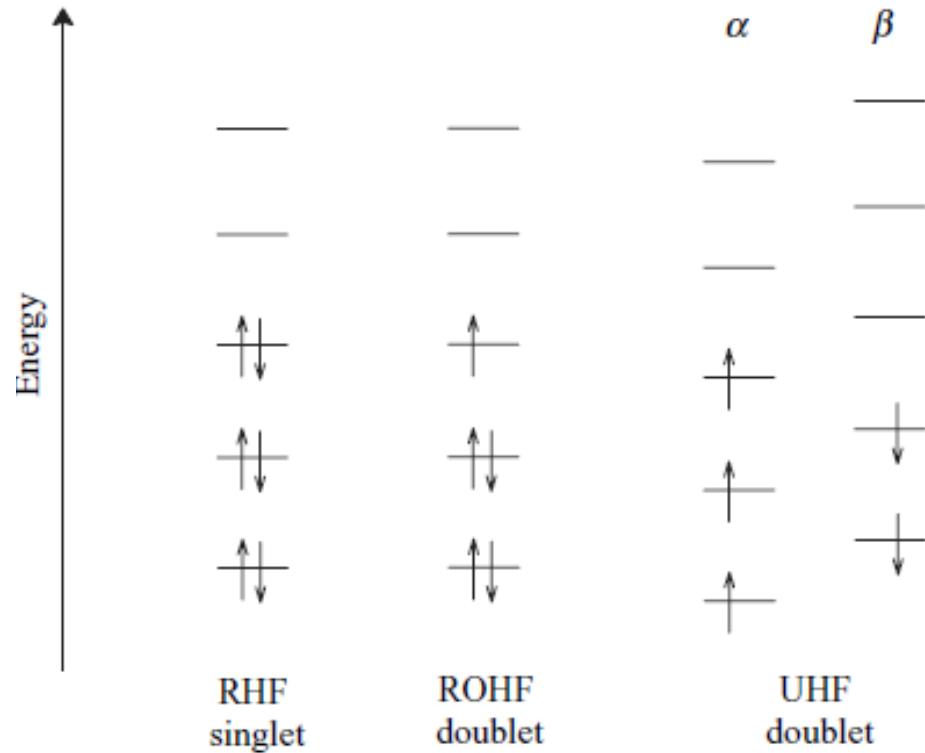
$$EA = {}^N E_0 - {}^{N+1} E_r = -\varepsilon_r$$

$${}^{N+1} E_r = \langle {}^{N+1} \Psi_r | \mathcal{H} | {}^{N+1} \Psi_r \rangle$$



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)**



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

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

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

Δ SCF technique can be considered as optimizations subject to spin constrains -> Voorhis's constrained DFT (CDFT) for evaluating energies of charge-transfer states.

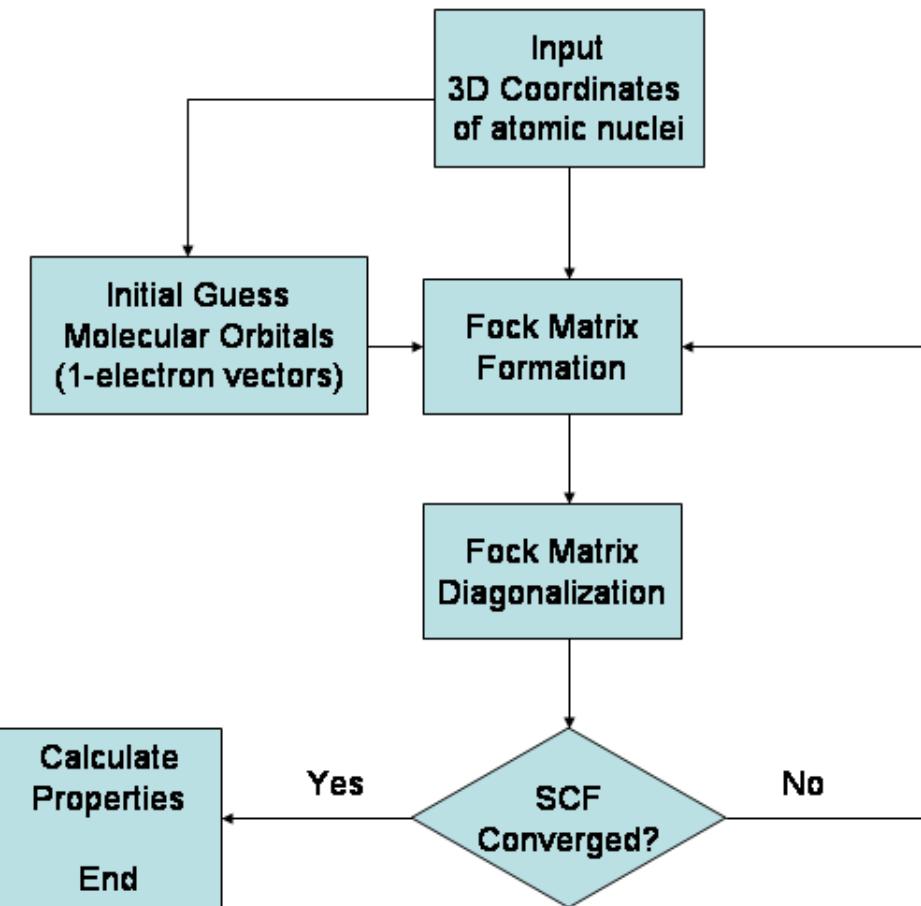
The SCF algorithm

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 ρ_{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)



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

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!

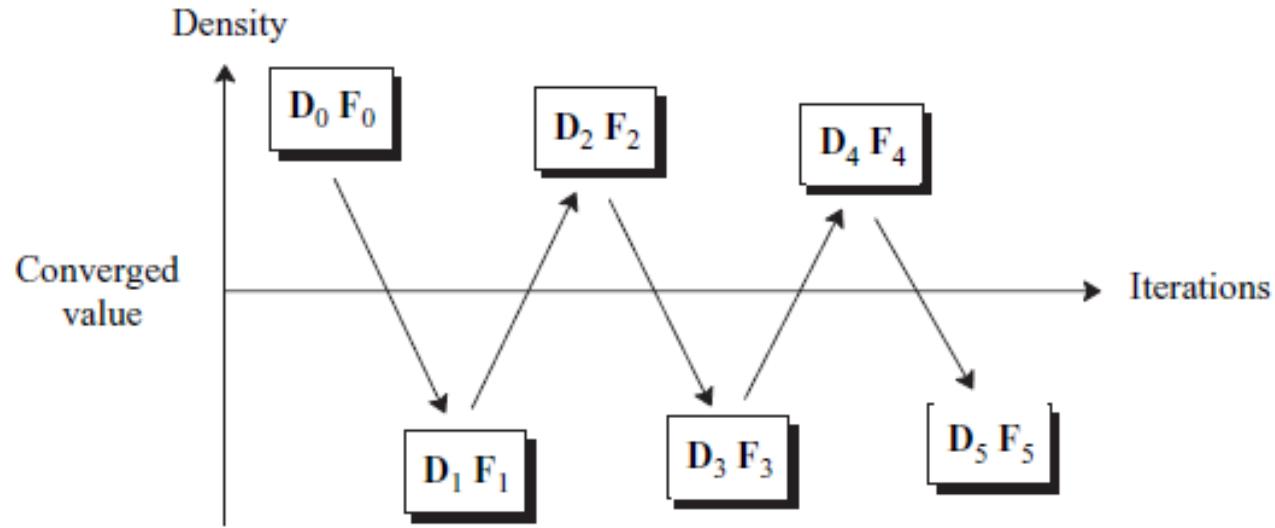


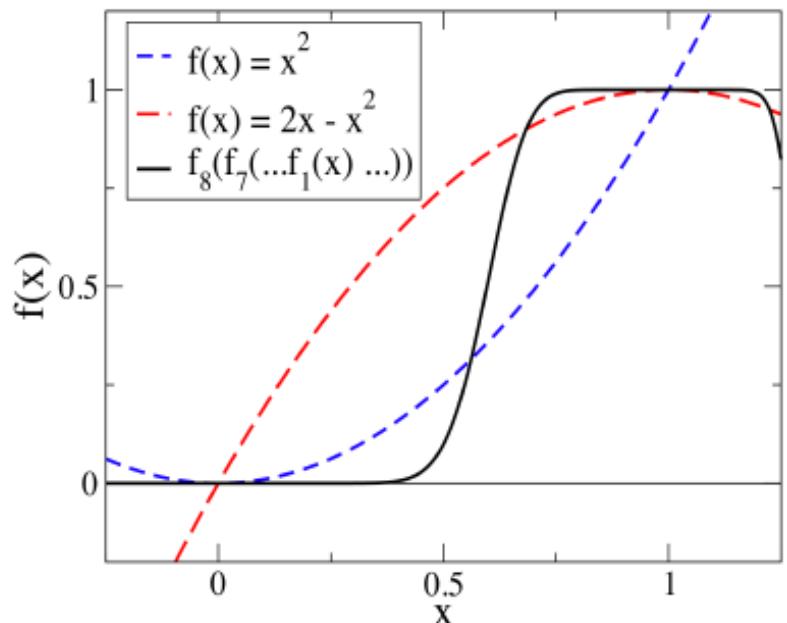
Figure 3.5 (from Jansen) An oscillating SCF procedure

- *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

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



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

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

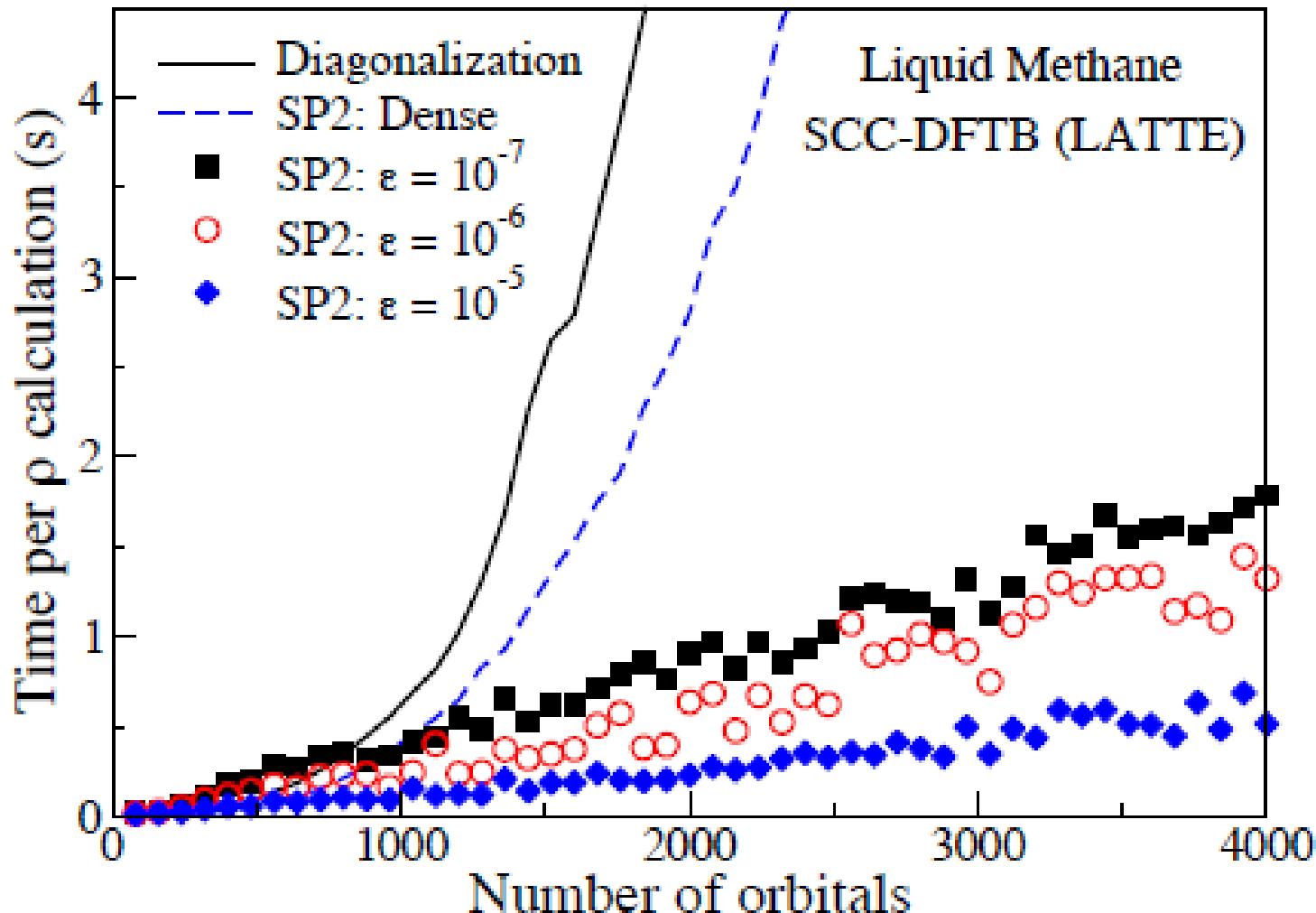
$$\mathbf{X}_{n+1} = 2\mathbf{X}_n - \mathbf{X}_n^2 \quad \text{else}$$

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

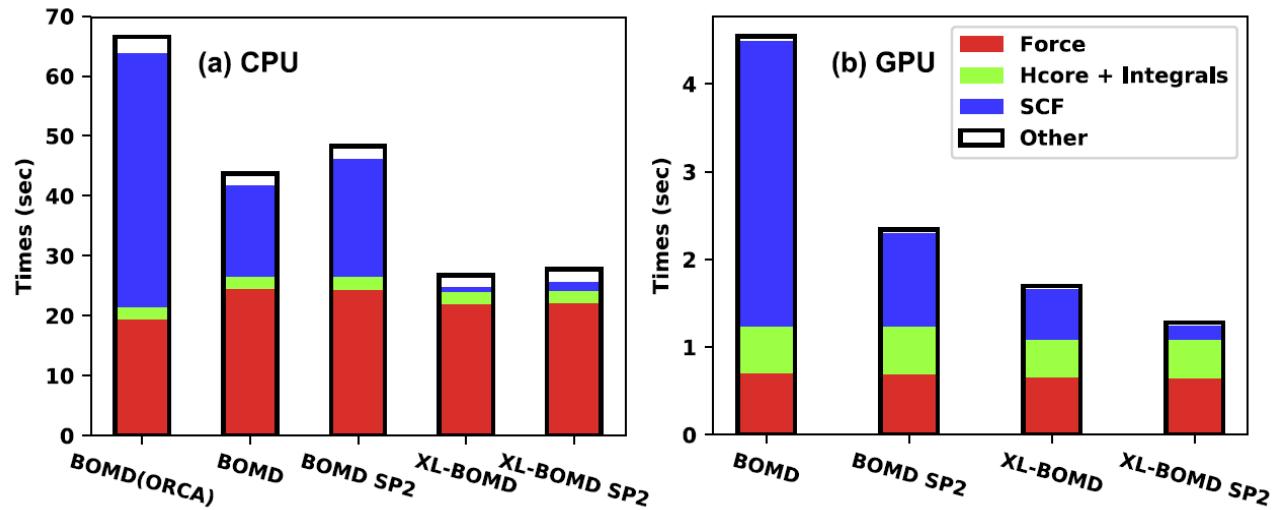
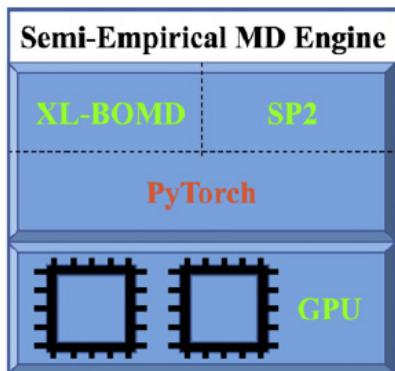
30 multiplications gives an expansion order > 1 Billion!
No Gibbs oscillations!

SP2 example

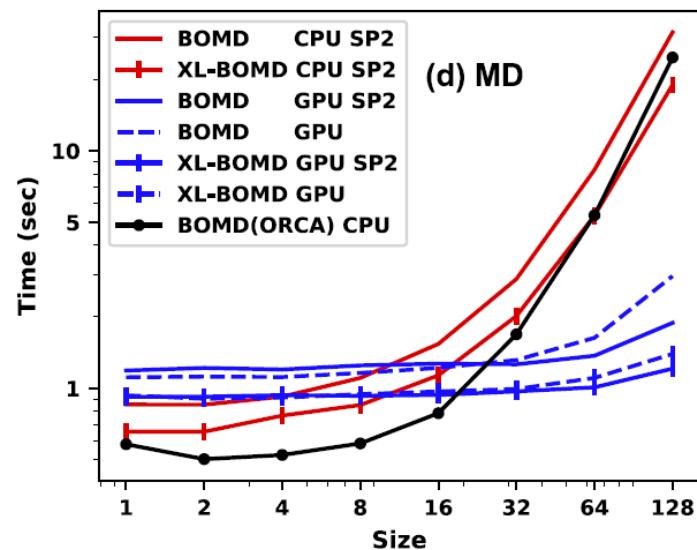
Cawkwell and Niklasson (2011)



PyTorch semiempirical quantum mechanics(PySQM)



molecules $\text{H}-(\text{C}_2\text{H}_4)_n-\text{H}$ with size $n = 1, 2, \dots, 128$



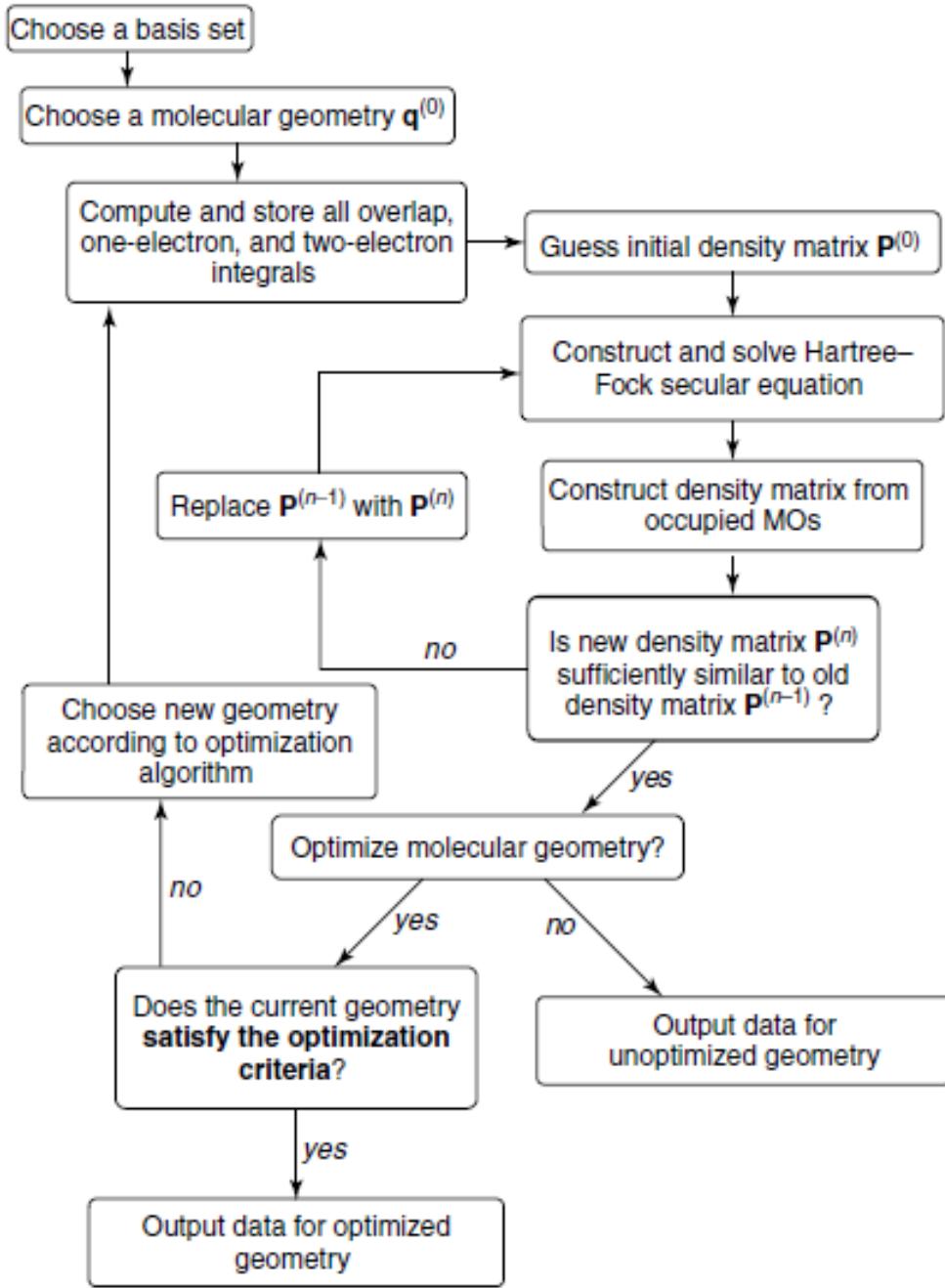
- PyTorch = native interface to machine learning;
- Natively CPU and GPU compatible, parallel;
- Common semiempirical models AM1, PM3... now PM6 (d-functions, metals)
- SP2 linear + XL Born-Oppenheimer ground state dynamics

<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

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

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

1) Numerical gradients (inaccurate and numerically demanding): increase computational cost xN

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

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

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

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

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

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

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

The Fock operator

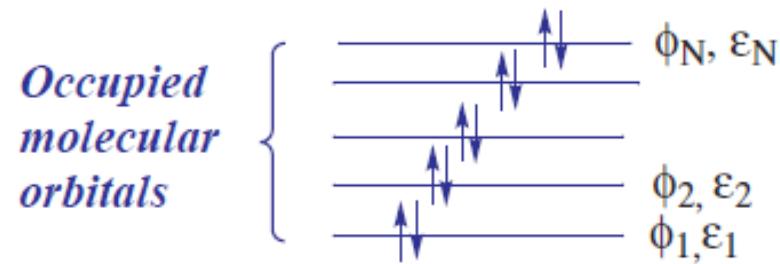
$$F(\bar{\rho})_{nm} = t_{nm} + V(\bar{\rho})_{nm}$$

The Coulomb operator (V or G ~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)

$$FC = SC\varepsilon$$



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

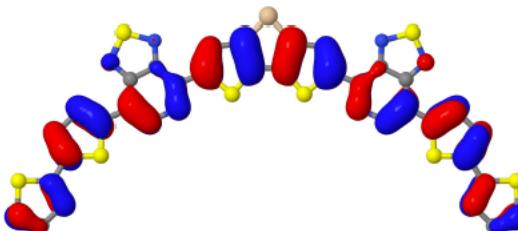
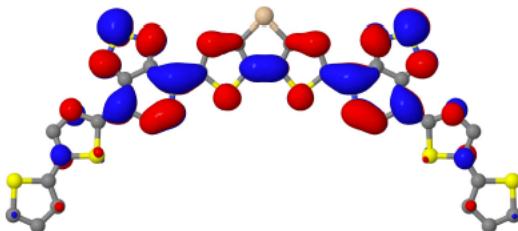
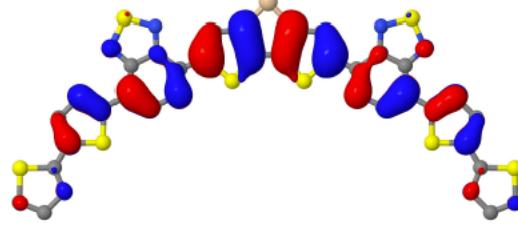
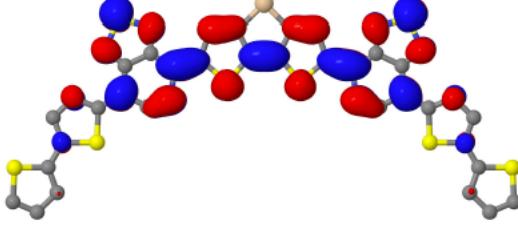
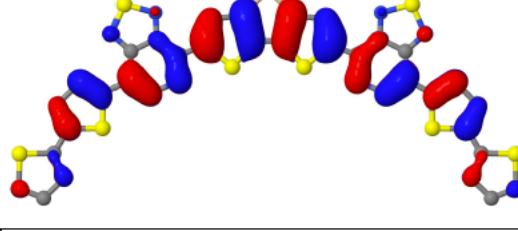
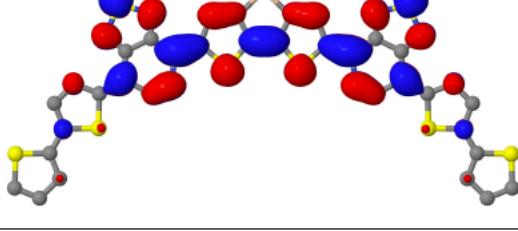
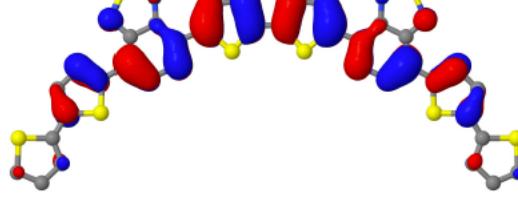
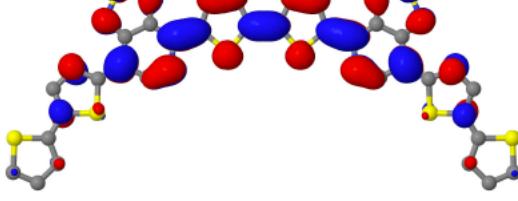
The total energy $E + \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}$

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 $\rho_{\Psi}^{1e}(\xi; \eta) = N \int \Psi(\xi, \zeta_2, \dots, \zeta_N) \overline{\Psi}(\eta, \zeta_2, \dots, \zeta_N) d\zeta$
- natural transition orbitals (NTO) – the same for transition density matrix $\rho_{\Psi\Phi}^{1e}(\xi; \eta) = N \int \Psi(\xi, \zeta_2, \dots, \zeta_N) \overline{\Phi}(\eta, \zeta_2, \dots, \zeta_N) d\zeta$

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!

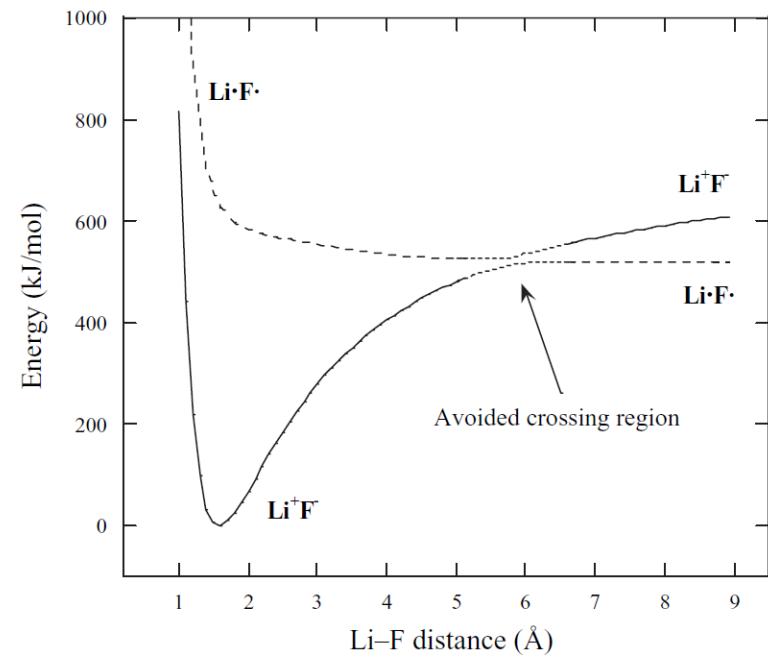
Static and dynamic electronic correlations

- 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 H₂O with a DZ Basis

Geometry	E _{corr} (hartree) ^a
R _e	-0.148028
1.5 R _e	-0.210992
2.0 R _e	-0.310067

^aData 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.

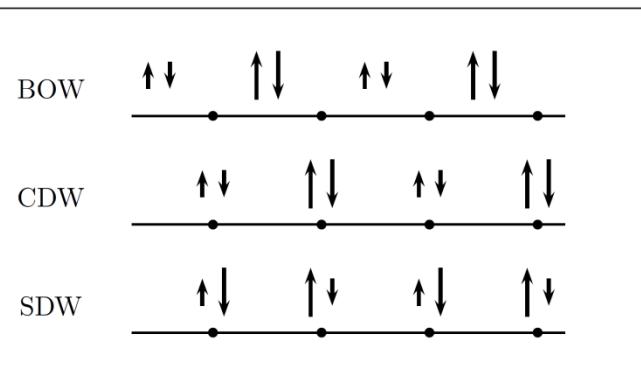
Examples – molecular deformation

- Jahn-Teller effect
 - Octahedral transition metal sites in oxides are often deformed
 - Huckel's rule – no fully symmetric cyclic π -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^{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)

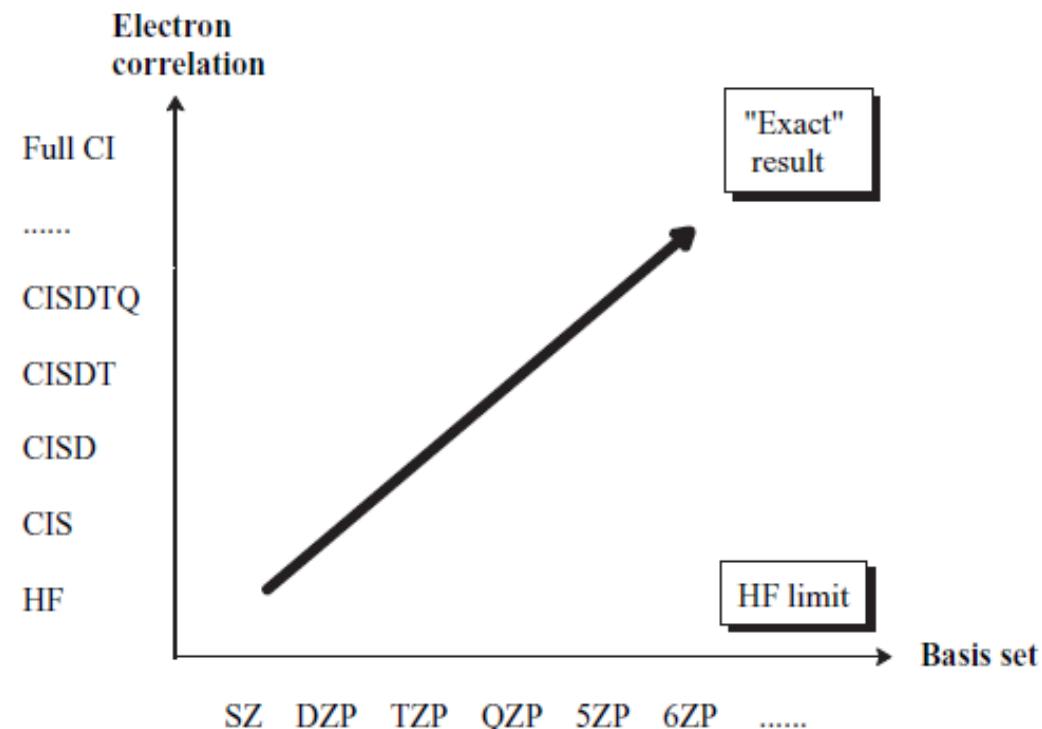


Figure 4.3 (from Jensen)
Convergence to the exact solution

Configuration interaction (CI)

Both static and dynamic correlations

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

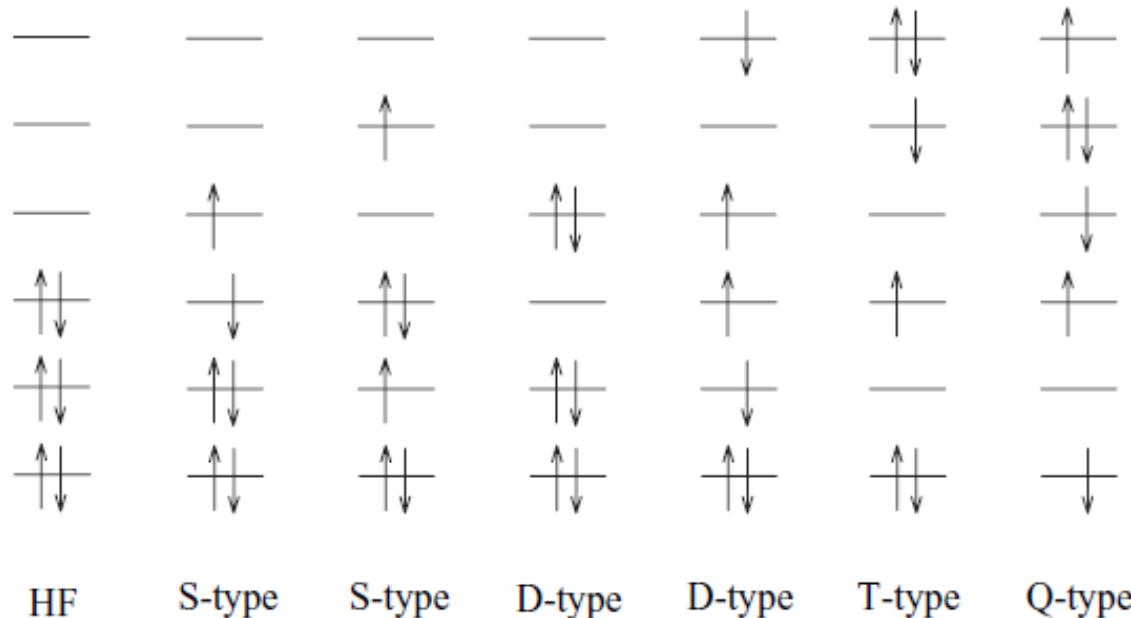
AO \rightarrow MO \rightarrow SD \rightarrow ME

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

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

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



The CI wavefunction:

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

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

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 Slates.

$$\begin{pmatrix} (\Phi_{\text{HF}} & \Phi_s & \Phi_d & \Phi_t & \Phi_q & \Phi_s & \cdots) \\ \Phi_{\text{HF}} & E_{\text{HF}} & 0 & x & 0 & 0 & 0 \\ \Phi_s & 0 & E_s & x & x & 0 & 0 \\ \Phi_d & x & x & E_d & x & x & 0 \\ \Phi_t & 0 & x & x & E_t & x & x \\ \Phi_q & 0 & 0 & x & x & E_q & x \\ \Phi_s & 0 & 0 & 0 & x & x & E_s \\ \vdots & 0 & 0 & 0 & 0 & x & x \\ & & & & & & \ddots \end{pmatrix}$$

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
- 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)

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

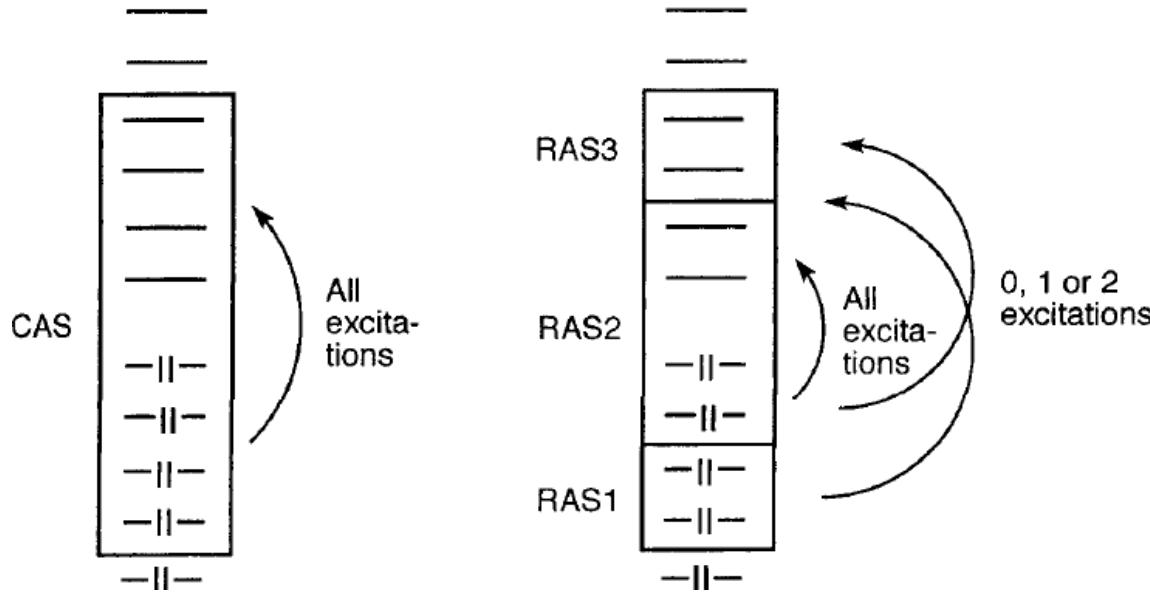


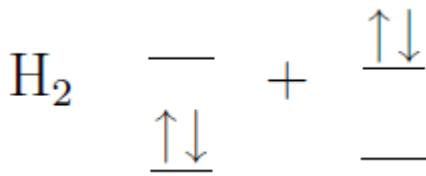
Figure 4.11 (from Jensen)
Illustrating the CAS and RAS orbital partitions

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 H₂



However, it is not exact for two non-interacting H₂



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

PHYSICAL REVIEW LETTERS

6 SEPTEMBER 1993

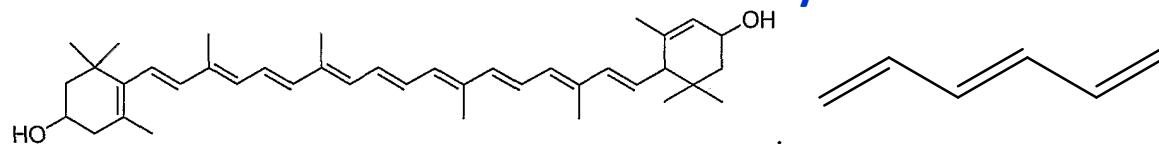
Band to Correlated Crossover in Alternating Hubbard and Pariser-Parr-Pople Chains: Nature of the Lowest Singlet Excitation of Conjugated Polymers

Z. G. Soos,¹ S. Ramasesha,^{1,2} and D. S. Galvão³

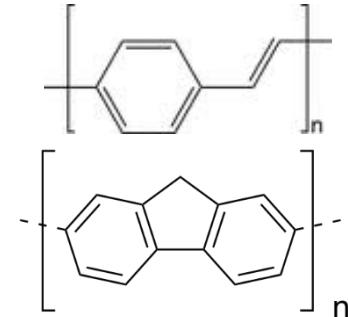
Non-luminescent polymers (e.g. polyacetylene)



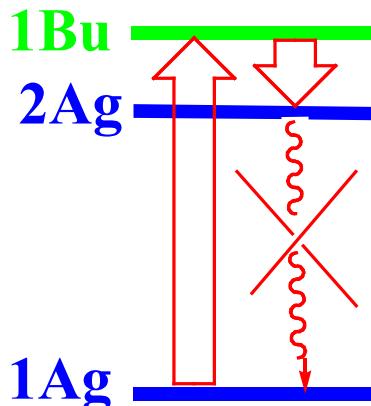
Also other molecules from this family:



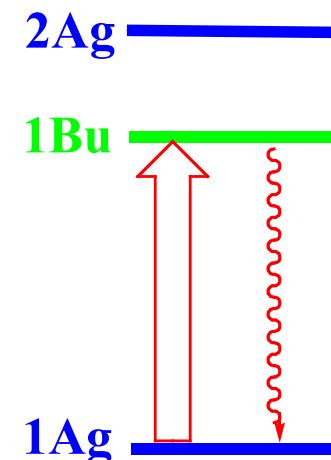
Luminescent polymers (e.g. PPV)



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

VOLUME 71, NUMBER 10

PHYSICAL REVIEW LETTERS

6 SEPTEMBER 1993

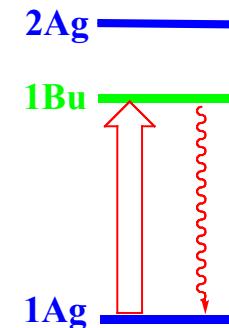
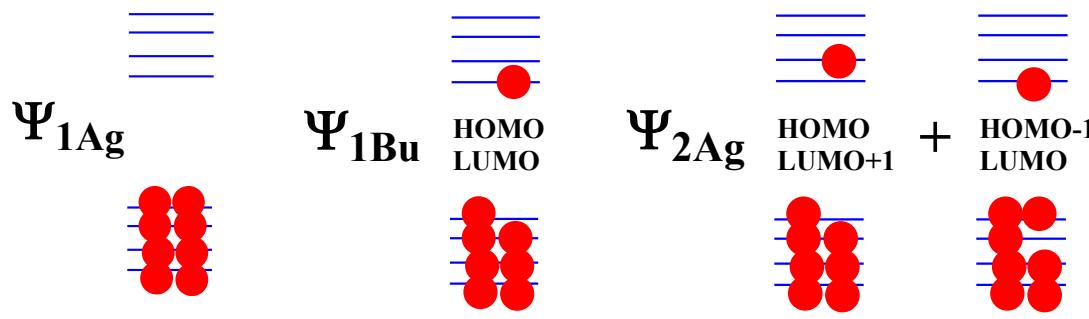
Band to Correlated Crossover in Alternating Hubbard and Pariser-Parr-Pople Chains: Nature of the Lowest Singlet Excitation of Conjugated Polymers

Z. G. Soos,¹ S. Ramasesha,^{1,2} and D. S. Galvão³

Non-luminescent polymers (e.g. polyacetylene)

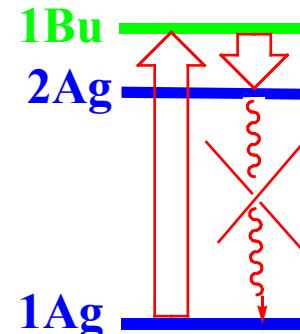
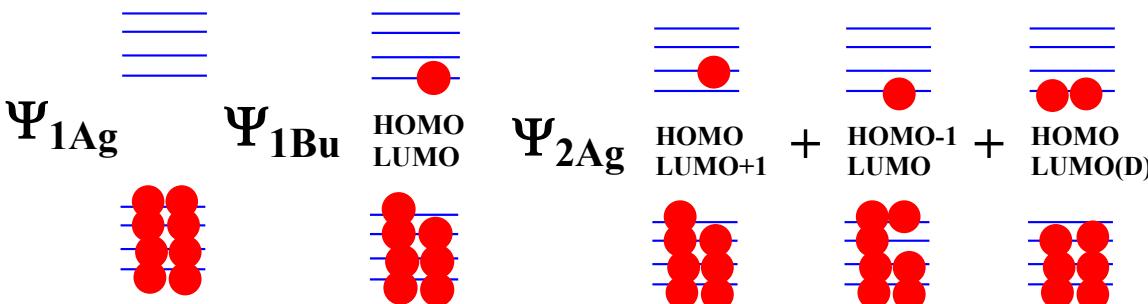
Luminescent polymers (e.g. PPV)

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 λ , 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

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

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

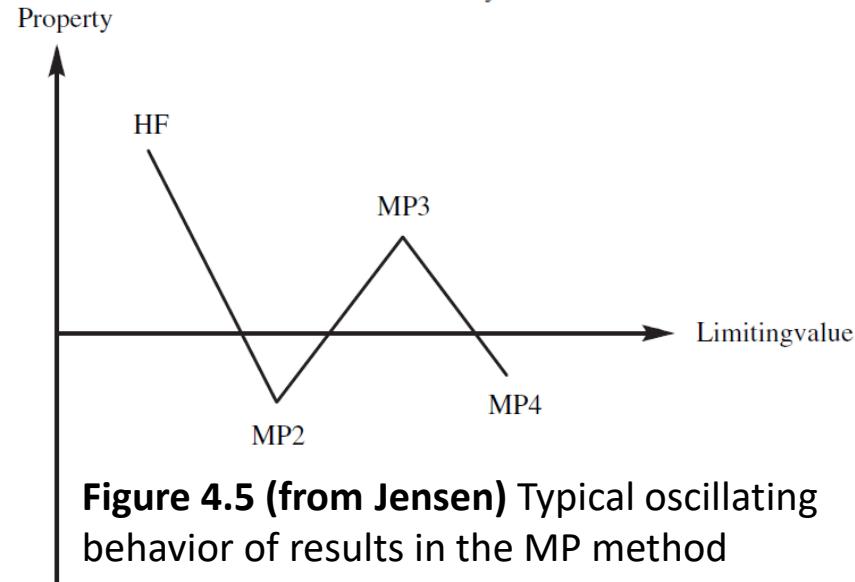


Figure 4.5 (from Jensen) Typical oscillating behavior of results in the MP method

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

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

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

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

$$W_2 = \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{vir}} \frac{\langle \Phi_0 | \mathbf{H}' | \Phi_{ij}^{ab} \rangle \langle \Phi_{ij}^{ab} | \mathbf{H}' | \Phi_0 \rangle}{E_0 - E_{ij}^{ab}} \quad E(MP2) = \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{vir}} \frac{(\langle \phi_i \phi_j | \phi_a \phi_b \rangle - \langle \phi_i \phi_j | \phi_b \phi_a \rangle)}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

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

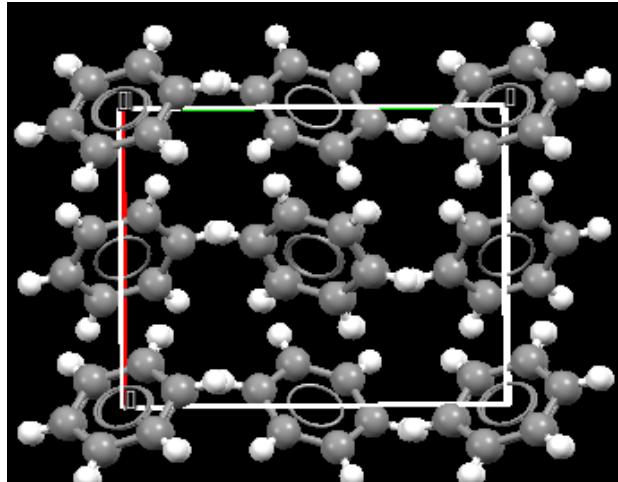
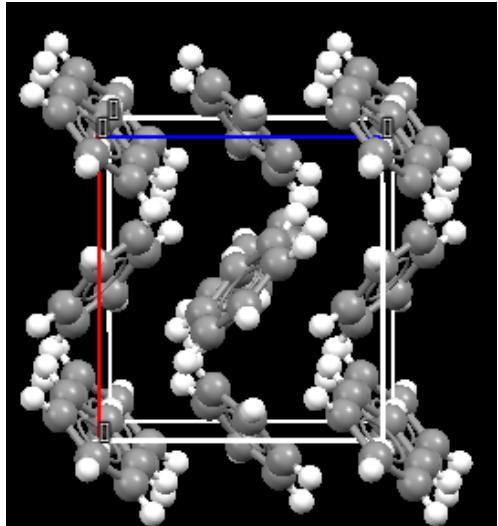
Case study 2: Dispersive interactions

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!

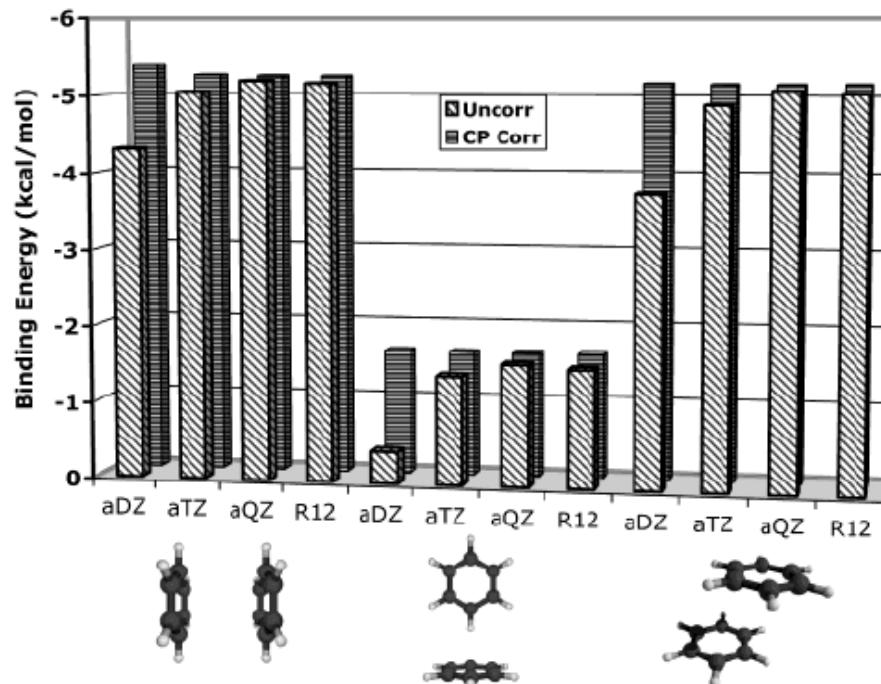


Figure 6. Hartree-Fock binding energies for each dimer structure as a function of basis set. All computations were performed at the same best estimate geometry for each configuration. All energies are negative (repulsive).

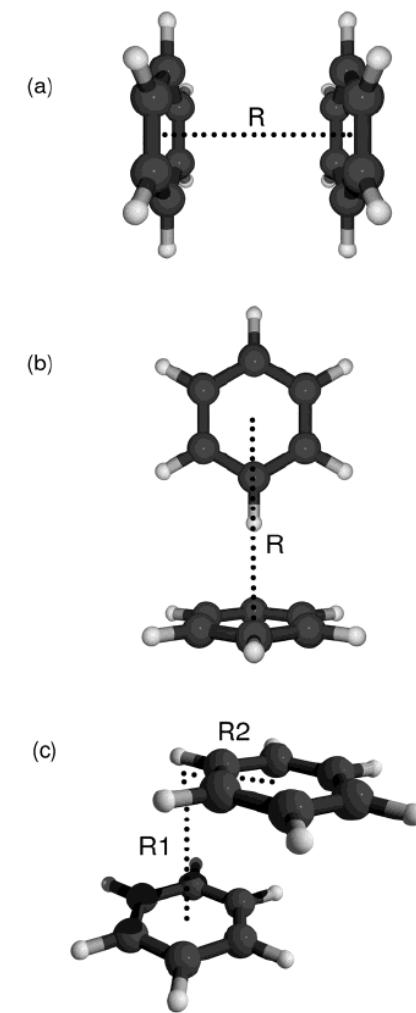


Figure 1. Sandwich, T-shaped, and parallel-displaced configurations of the benzene dimer.

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!

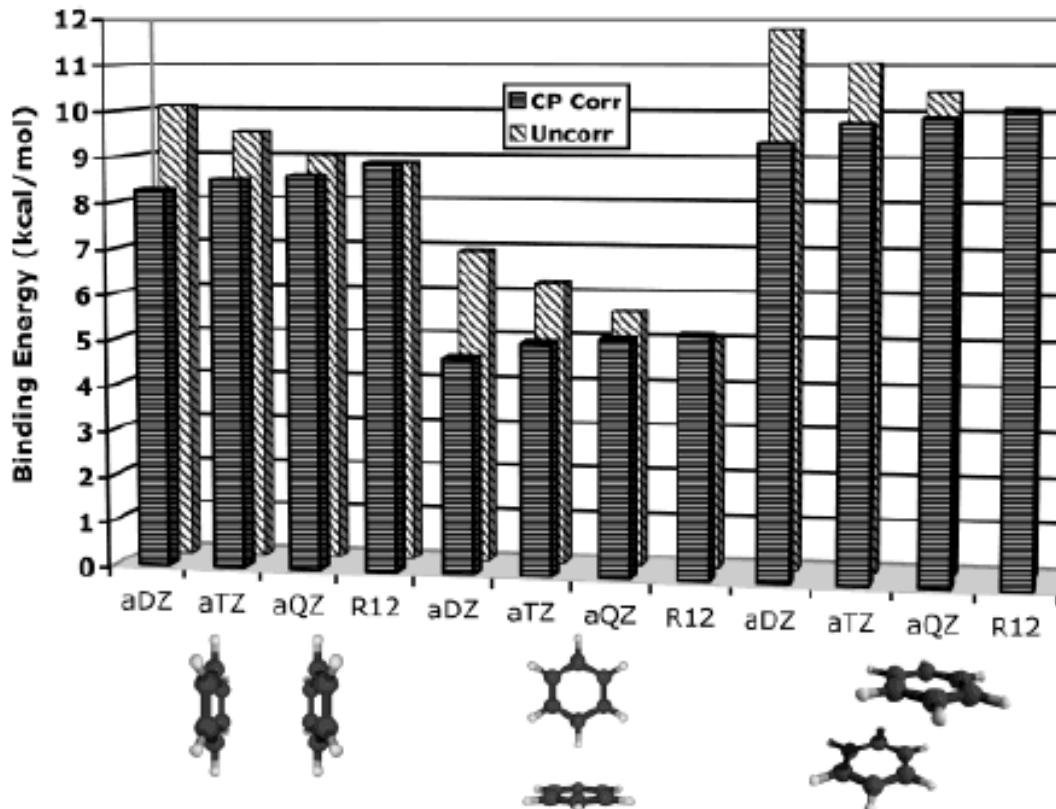


Figure 7. MP2 electron correlation energy contributions to binding energies for each dimer structure as a function of basis set. The total MP2 binding energies are obtained by adding these values to the Hartree-Fock contributions in the previous figure.

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

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

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

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

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

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

The CC computational problem is determination of the cluster amplitudes t for all of the operators included in the particular approximation. $e^{\mathbf{T}} = \mathbf{1} + \mathbf{T}_1 + (\mathbf{T}_2 + \frac{1}{2} \mathbf{T}_1^2)$

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

Coupled Cluster: typical approaches

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

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 << 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)

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	$\pm 0.2 \text{ eV}$

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)

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

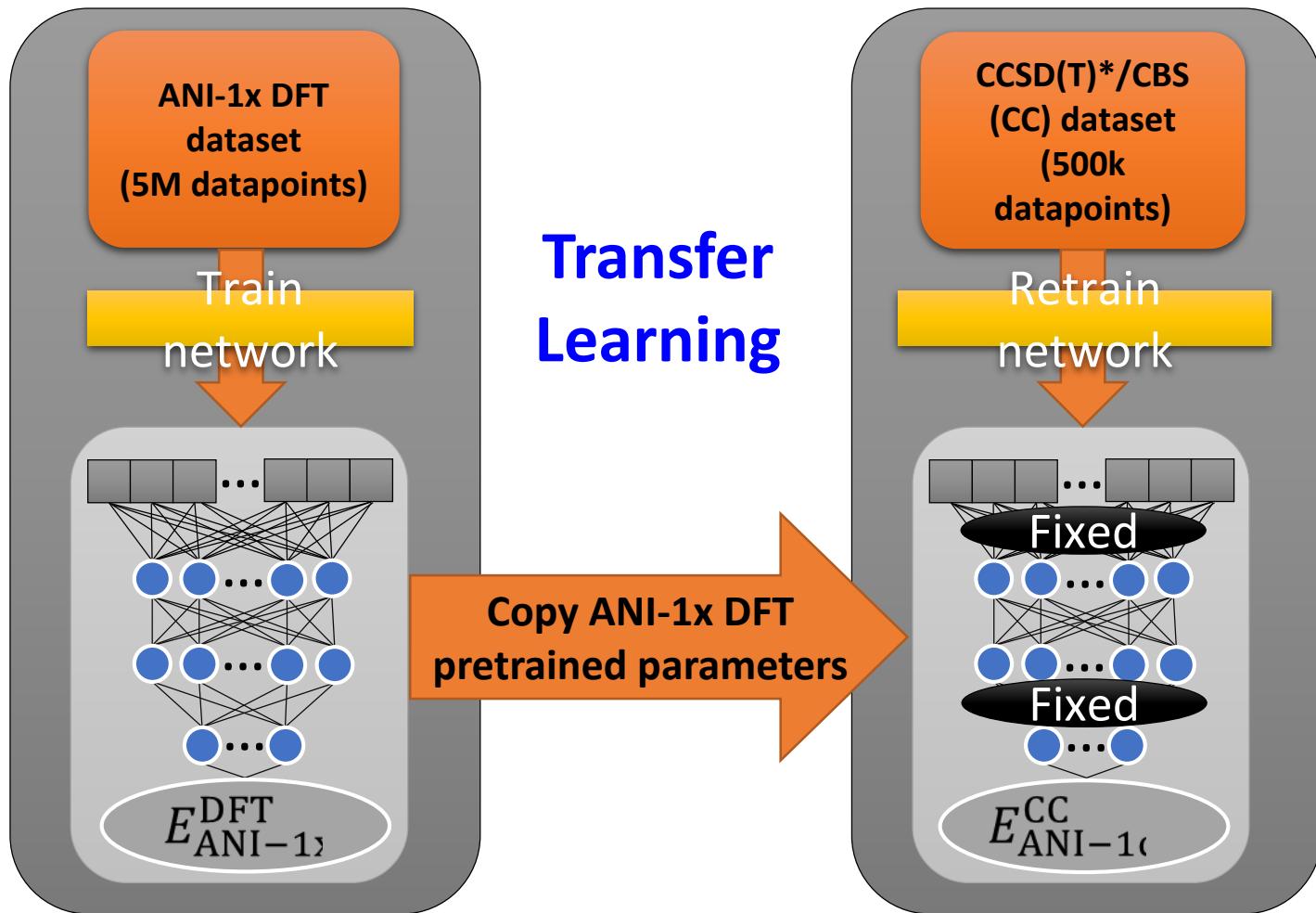
S66 and W4-11

benchmarks are calculated using CCSD(T)-F12 method

Method	CPU-core hours ^a		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
CCSD(T)*/CBS (our reference)	1.44	7.44	0.09 / 0.10	1.46 / 1.55

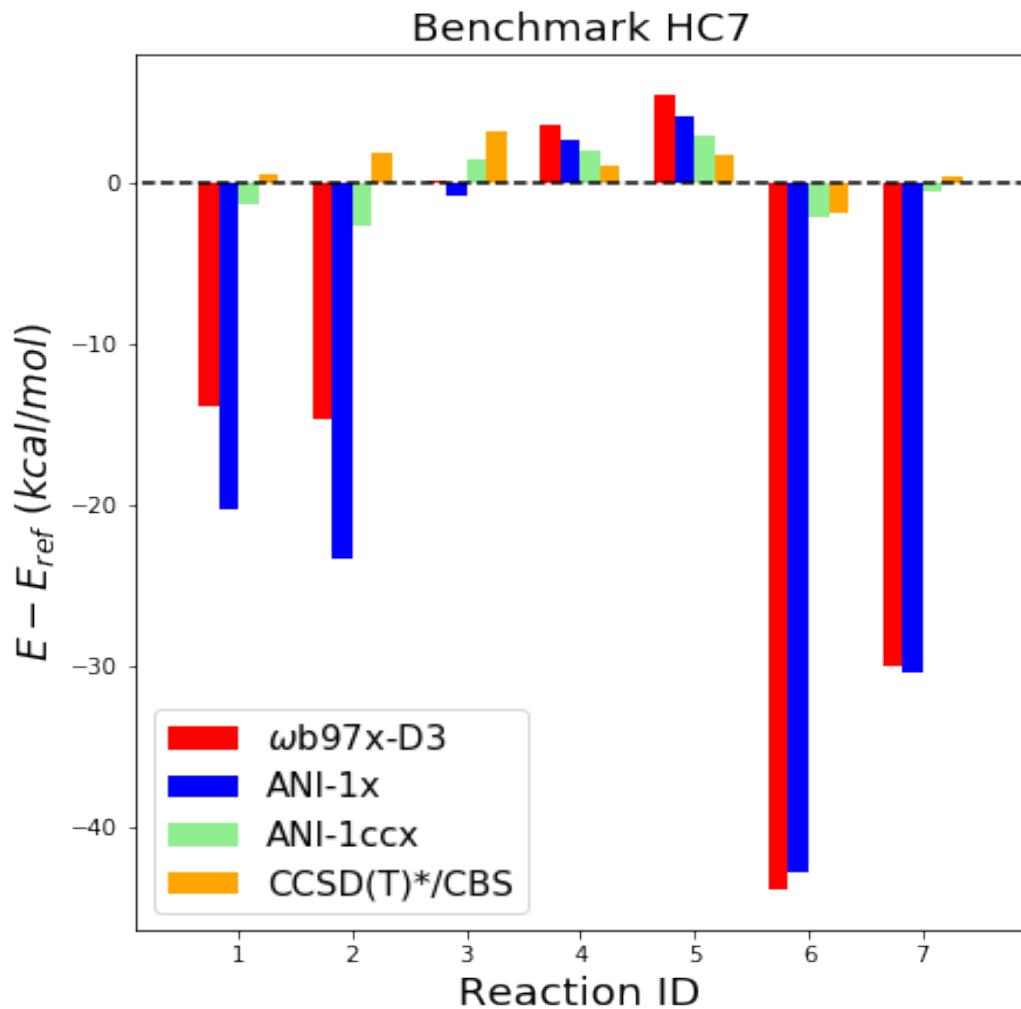
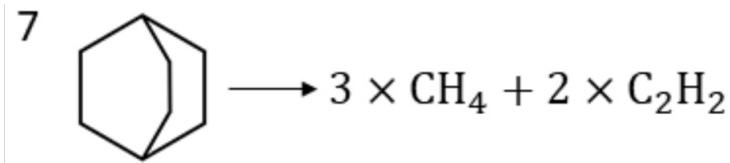
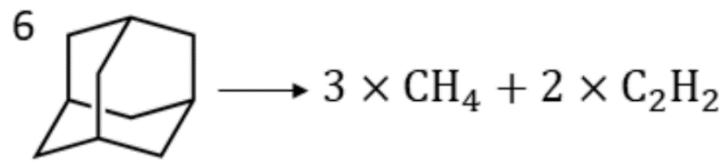
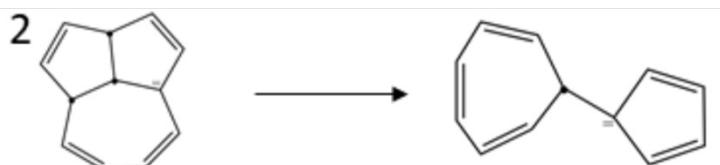
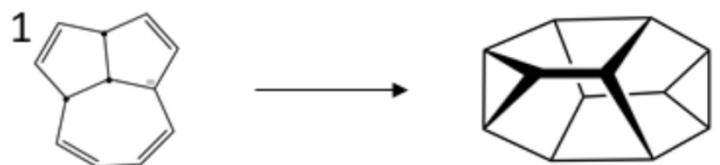
Case study: Machine learning and Data Science to complement conventional QC

- 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)

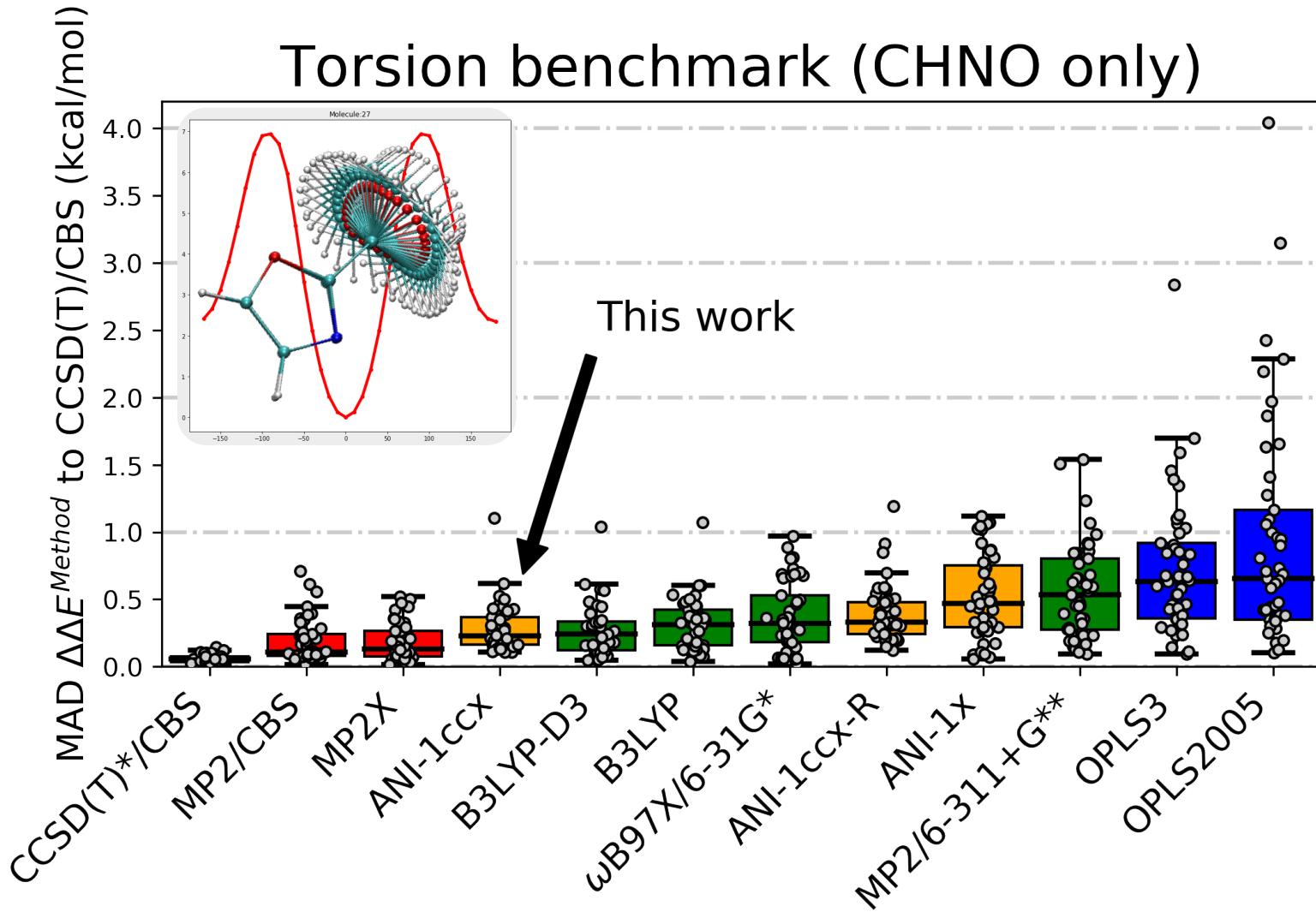
Hydrocarbon isomerization benchmark



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)

Brief summary of post-HF methods

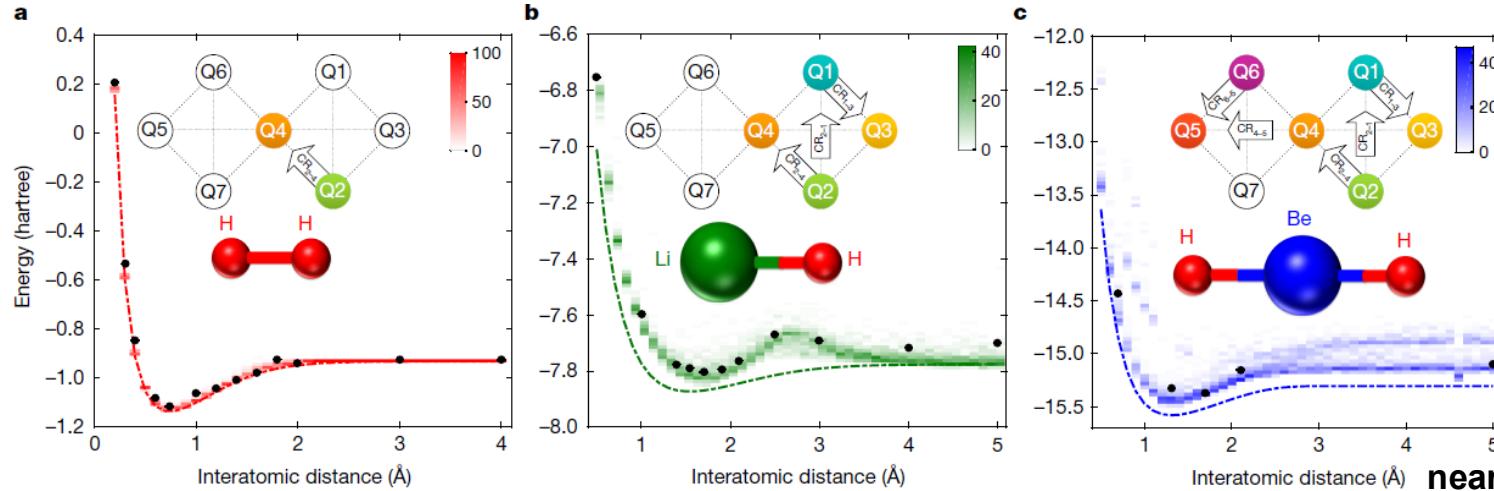
	CI	MP	CC
Size extensivity	no	yes	yes
Excited states	yes	no	yes
Ground state corrections beyond HF	yes	yes	yes
Ground state analytic gradients (low orders)	yes	yes	yes
Gaussian 09	QCISD,CAS	MP4	CCSD(T)
Firefly 8	yes	MP4	no
Q-Chem, Turbomole, GAMESS	yes	yes	yes

- 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

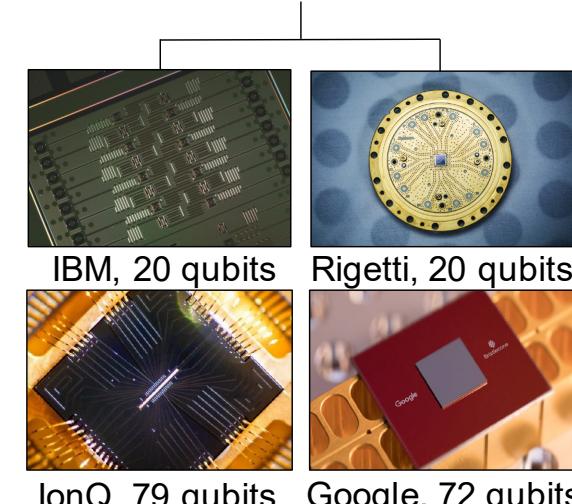
AND now quantum computing

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

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

NISQ (Noisy Intermediate Scale Quantum) devices

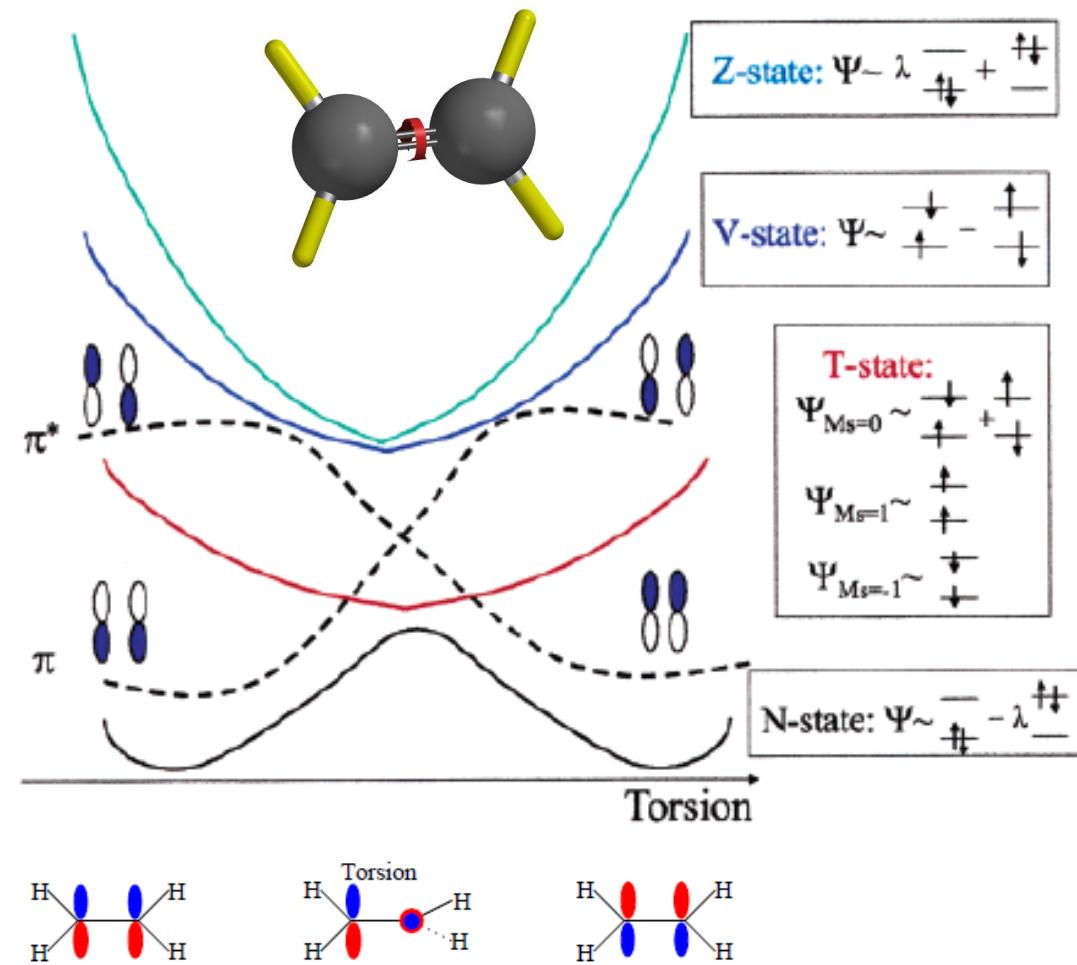
Case study 3: Bond-breaking (ethylene)

**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 π^2 configuration. However, as a degeneracy between π and π^* develops along the torsional coordinate, the importance of the $(\pi^*)^2$ configuration increases. At the barrier, where π and π^* 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, π^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,



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

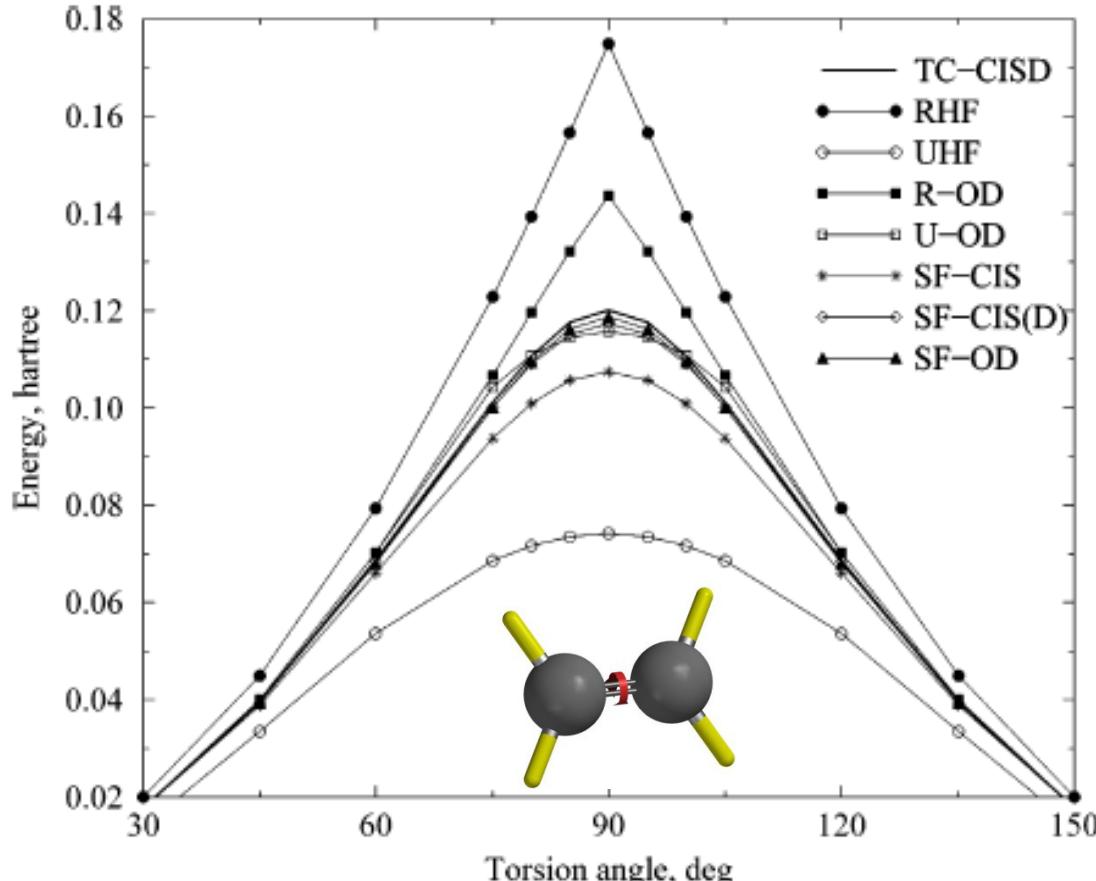
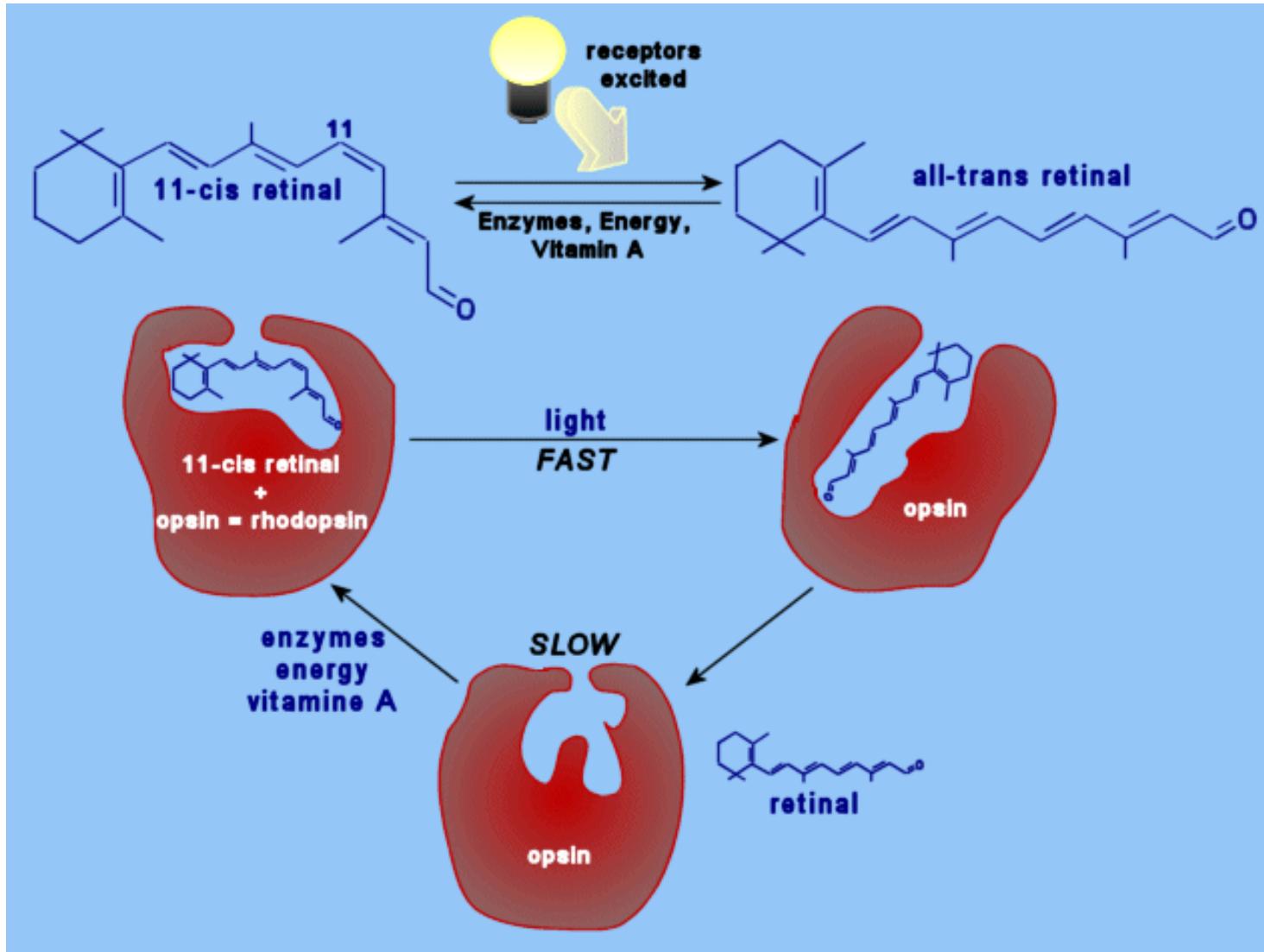


FIGURE 6. Ethylene torsion, DZP basis. All curves are shifted such that the energy at 0° is zero. The spin-flip curves do not exhibit an unphysical cusp and are closer to the reference TC-CISD curve than the corresponding spin-restricted and spin-unrestricted models.

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

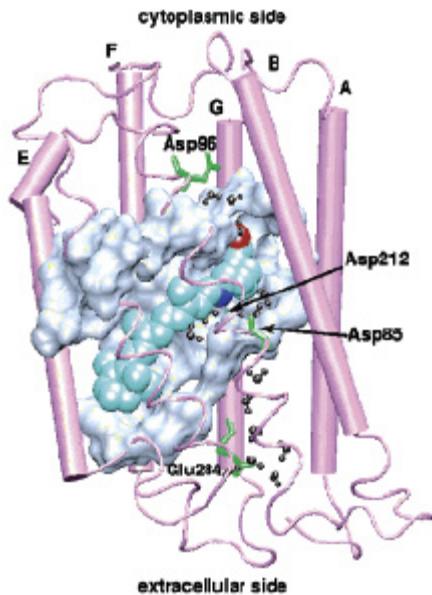
Insights for Light-Driven Molecular Devices from *Ab Initio* Multiple Spawning Excited-State Dynamics of Organic and Biological Chromophores

TODD J. MARTINEZ*

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

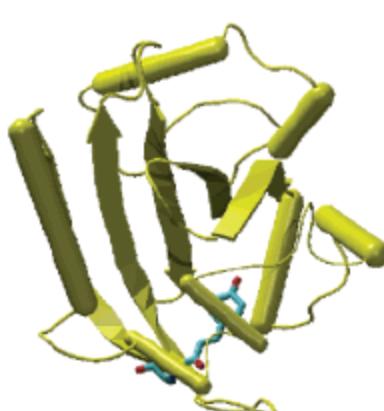
Received May 2, 2005

Acc. Chem. Res. 2006, 39, 119–126

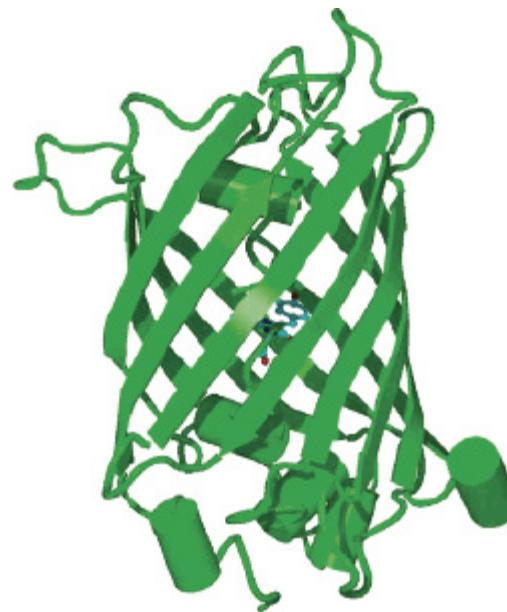


Bacteriorhodopsin (bR)

- **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**



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*

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

Received May 2, 2005

Acc. Chem. Res. 2006, 39, 119–126

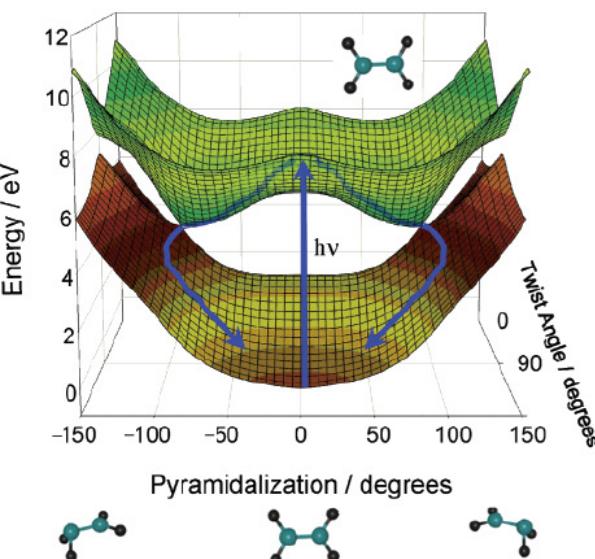
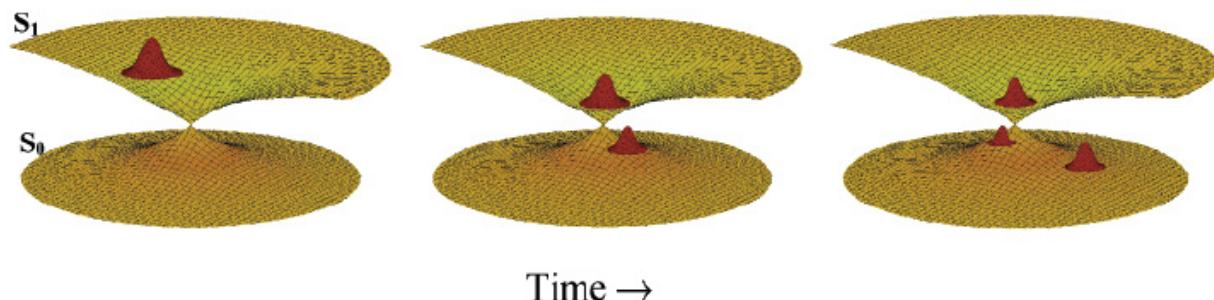


FIGURE 4. Ground- and excited-state potential energy surfaces. Presence of charges (i.e. dielectric environment) affect the photoisomerization mechanism

FIGURE 2. Schematic description of the multiple spawning method.



“Simple” case – ethylene photoisomerization

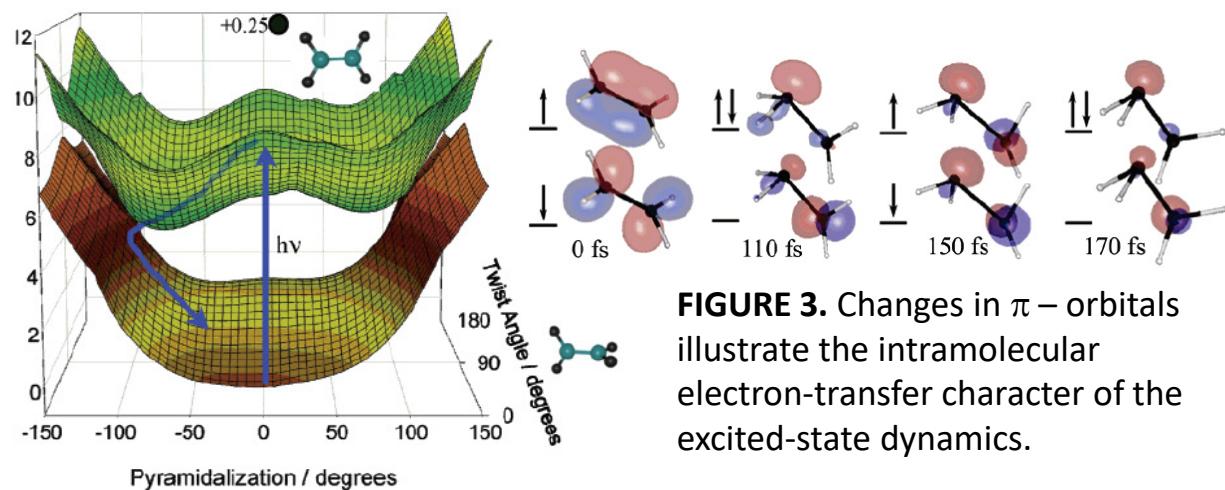


FIGURE 3. Changes in π -orbitals illustrate the intramolecular electron-transfer character of the excited-state dynamics.

Methods used: CASSCF

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. Matthews Avenue, Urbana, Illinois 61801

Received May 2, 2005

Acc. Chem. Res. 2006, 39, 119–126

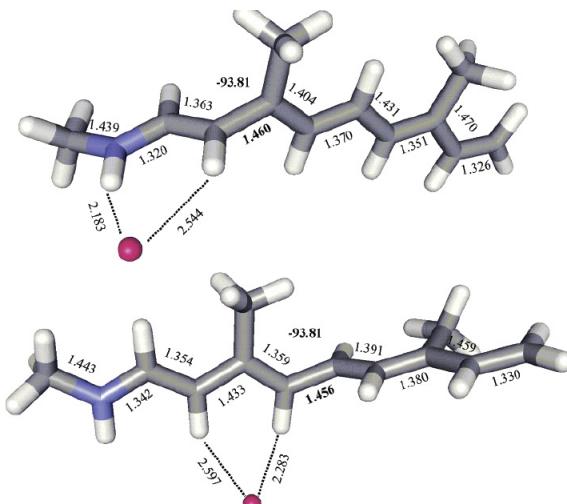


FIGURE 5. Dielectric environment and intramolecular electron-transfer play an important role in the retinal the excited-state dynamics and photoisomerization.

Conical intersection dynamics of the primary photoisomerization event in vision

Dario Polli¹, Piero Altoè², Oliver Weingart^{3,4}, Katelyn M. Spillane⁵, Cristian Manzoni¹, Daniele Brida¹, Gaia Tomasello², Giorgio Orlandi², Philipp Kukura⁶, Richard A. Mathies⁵, Marco Garavelli² & Giulio Cerullo¹

440 | NATURE | VOL 467 | 23 SEPTEMBER 2010

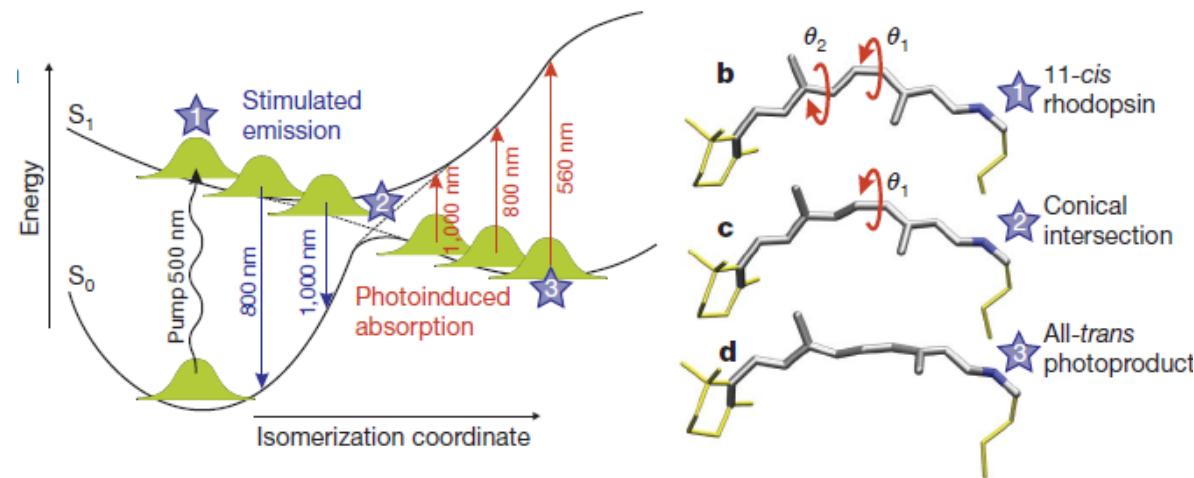


FIGURE 2. Isomerization potential energy surfaces of rhodopsin

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 states¹

¹H – H₂ gas, O – O₂ gas, Br – Br₂ liquid, C – graphite, S – rhombic sulfur 63

Predictions on molecules with 10-13 heavy atoms

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

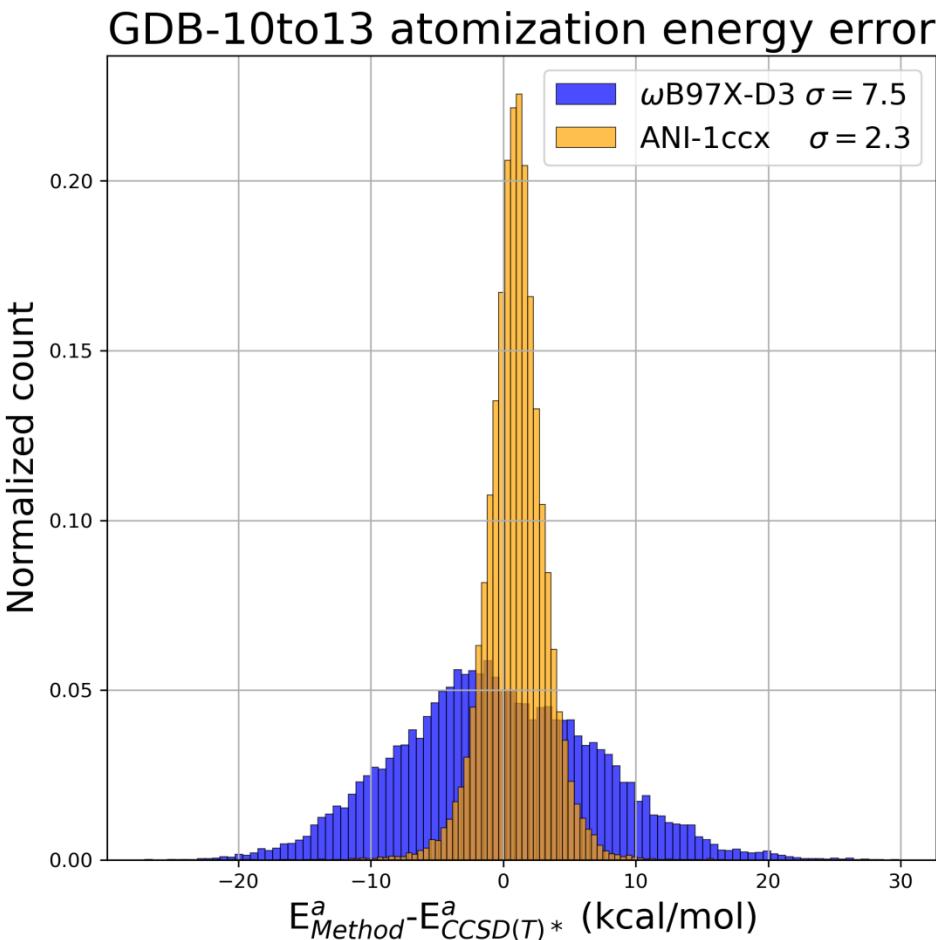
	ANI-1ccx	ANI-1x	ω B97X-D3	MP2/DZ
MP2/TZ	3.4	4.7	3.7	4.6

Units: kcal/mol/A (error MAD)

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

	ANI-1ccx	ANI-1ccx-R	ANI-1x	ω B97X-D3
MAD	1.5	1.8	2.0	1.4

Units: kcal/mol



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

- $X = \sum_i \nu_i Y_i$, ν_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

	—	20
	—	02
	αα	
	ββ	
	αβ	
	βα	

spin contamination

static correlations

S	S _z	χ
1	1	αα
1	-1	ββ
1	0	αβ-βα
0	0	αβ+βα
0	0	20
0	0	02

the only states representable by HF

no single Slater determinant

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

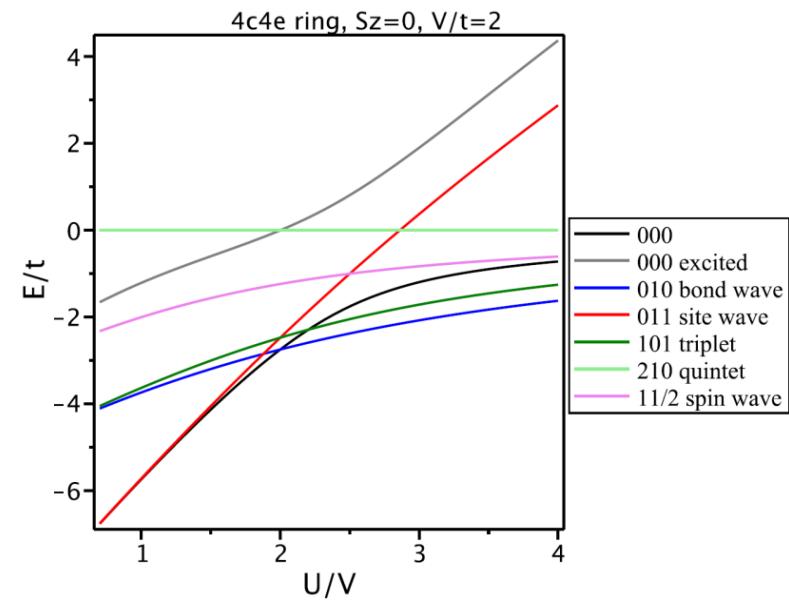
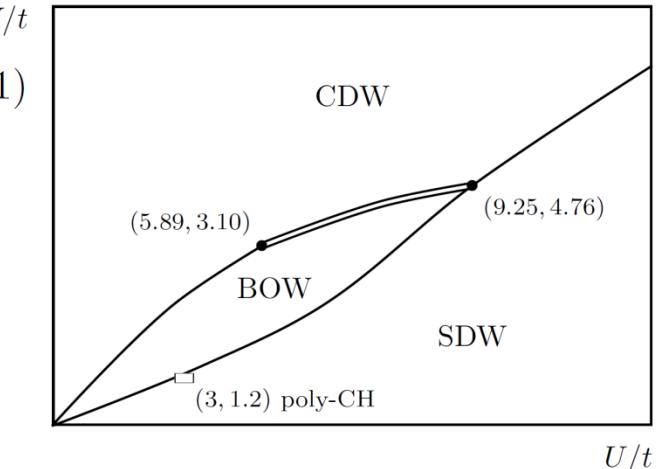
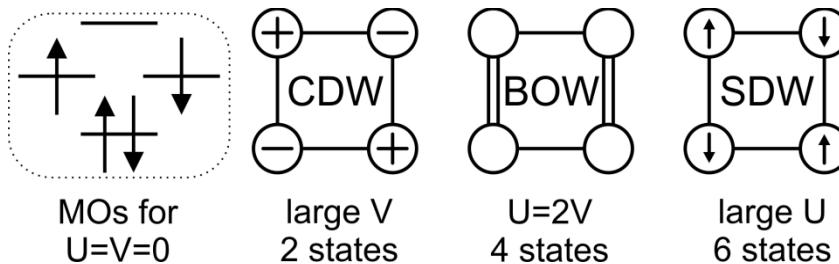
Static correlations: 4c4e model

(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 $16/4$

