

CHM 673

Lecture 20: Electronic excited states, part 2

Suggested reading:

Chapter 4.14 from Jensen

EOM-CC: Q-Chem webinar:

https://www.youtube.com/watch?v=Adf_F6latrU&feature=youtu.be

Modeling excited states

Excited electronic states represent higher-energy solutions of the electronic Schrodinger equation

$$\hat{H}_{el}(r, R)\Psi_i(r; R) = E_i(R)\Psi_i(r; R)$$

Two ways to get them:

- Solve the electronic Schrodinger equation for multiple roots (CI and MCSCF methods, EOM-CC, ADC)
- Use response theory (TD-DFT, LR-CC)

Response Theory

The molecule is subjected to an electric field oscillating with frequency ω

Then the frequency-dependent polarizability of the molecule is

$$\langle \alpha \rangle_\omega = \sum_{i \neq 0}^{\text{states}} \frac{|\langle \Psi_0 | \hat{\mu} | \Psi_i \rangle|^2}{\omega - (E_i - E_0)}$$

We can find excitation energies $\Delta E = (E_i - E_0)$ from the poles of $\langle \alpha \rangle$, i.e. when $\omega = \Delta E$

Variational principle for excited states

If $\Psi_0, \Psi_1, \dots \Psi_N$ are exact lowest eigenstates of Hamiltonian H,

Build a trial wavefunction $\tilde{\Psi}$: $\langle \tilde{\Psi} | \tilde{\Psi} \rangle = 1$ and $\langle \tilde{\Psi} | \Psi_k \rangle = 0, k = 0, 1, \dots N$

i.e., $\tilde{\Psi}$ is orthogonal to the lowest N eigenstates

Then $\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle \geq E_{N+1}$

Ψ_0	\dots	Ψ_N	$\tilde{\Psi}$
Ψ_0		0	
:		:	
Ψ_N		0	
$\tilde{\Psi}$	0	...	0

$\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle$

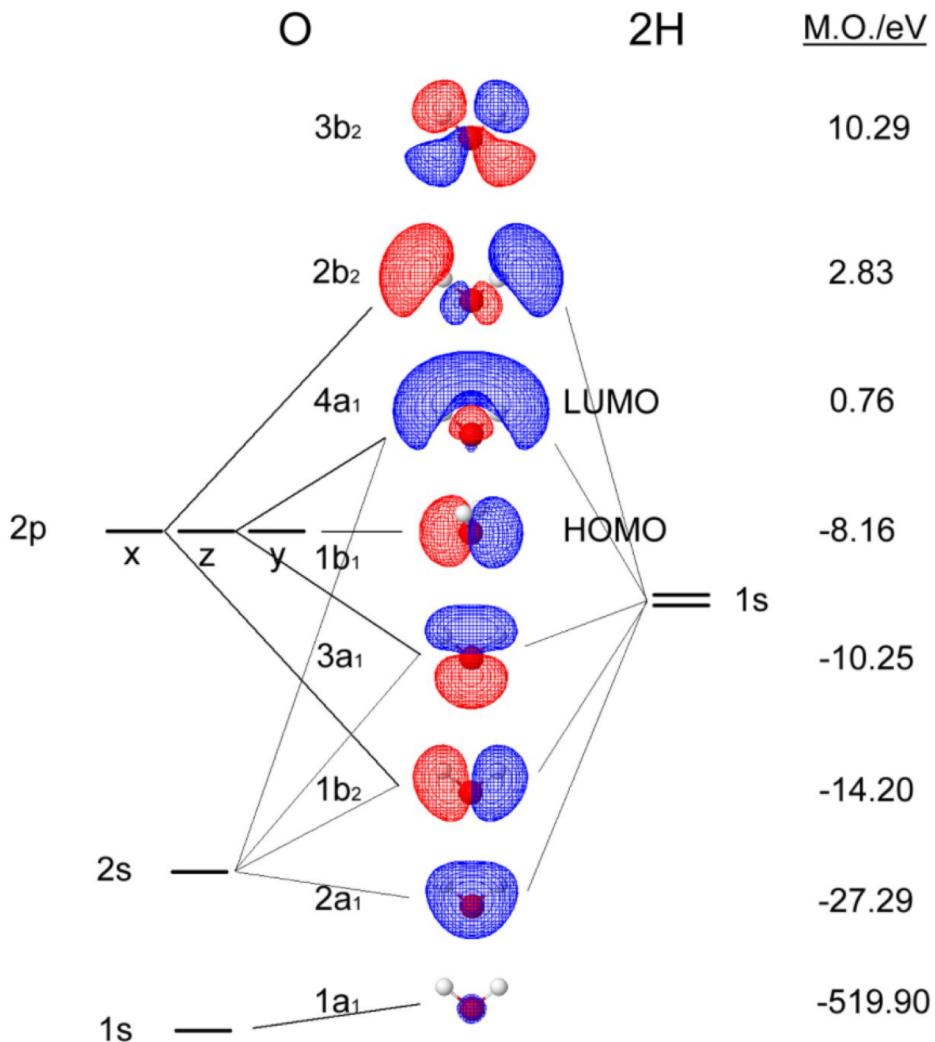
Effectively, these conditions mean that Ψ_k and $\tilde{\Psi}$ are not coupled through Hamiltonian

Practically, can be useful for electronic states of different symmetries, either spatial or spin

Consider H₂O as example

Variational principle for excited states. Example: water

Molecular Orbitals for Water

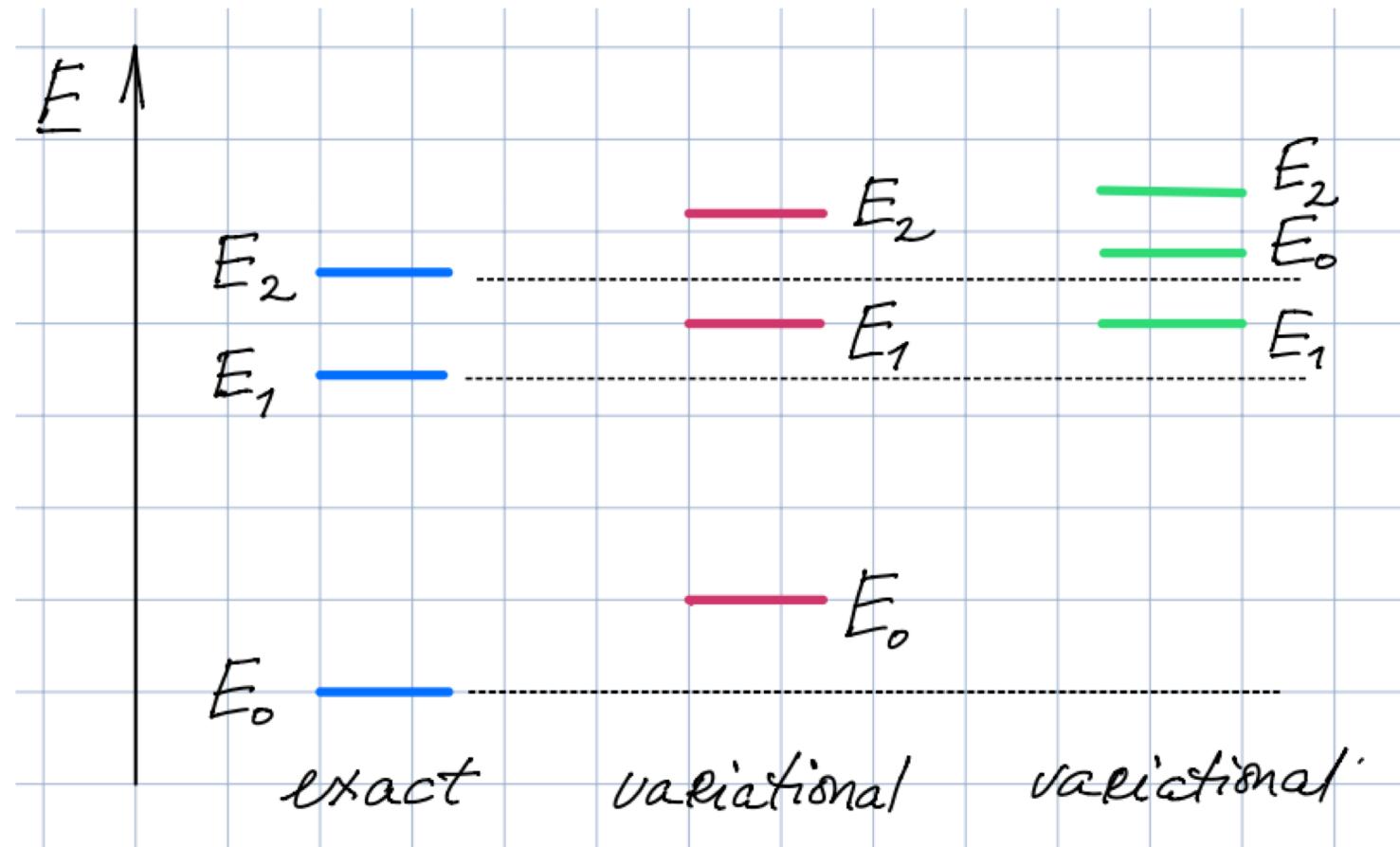


Which states can be described using “ground state” approach?

Ritz variational principle

In a linear subspace of wavefunctions, $\tilde{E}_i \geq E_i^{exact}$

Any eigenvalue \tilde{E}_i is an upper bound to the exact excitation energy E_i^{exact}



Configuration interaction singles (CIS)

CIS – the simplest CI model for the excited states

$$H^{CIS} = \begin{pmatrix} E_{HF} & 0 \\ 0 & E_i^a \end{pmatrix}$$

Brillouin's theorem
Size: $N_{\text{OCC}} \times N_{\text{VIR}}$

$$\Psi^{CIS} = \sum_{ia} c_i^a \Phi_i^a$$

$$\hat{H}^{CIS} C^{CIS} = EC^{CIS}$$

Scaling: N^5

CIS is size extensive and variational

Configuration interaction singles (CIS)

CIS: pros and cons:

- Cannot describe any doubly excited states
- No dynamical correlation → errors of ~1 eV. This is a differential correlation effect – a change in dynamical correlation upon excitation (1 eV is a typical correlation energy of a pair of electrons)
- No non-dynamical correlation for the ground state (CIS breaks when HF breaks)
- However, CIS includes some non-dynamical correlation for excited states, e.g., CIS can describe singly-excited states that are linear combinations of two determinants
- Ordering of states is often correct

Configuration interaction singles with perturbative doubles: CIS(D)

CIS(D) incorporates dynamical correlation by including double excitations perturbatively
CIS(D) is analogues to MP2 for the ground state

$$E_{MP2} = \langle \Phi_0 | \hat{V} | \hat{T}_2 \Phi_0 \rangle$$

$$E_{CIS(D)} = \langle \Psi_{CIS} | \hat{V} | \hat{U}_2 \Phi_0 \rangle + \langle \Psi_{CIS} | \hat{V} | \hat{U}_1 \hat{T}_2 \Phi_0 \rangle$$

Scaling: N^5

Added dynamical correlation → errors in excitation energies decrease to 0.2-0.5 eV

CIS(D) fails when CIS fails

CIS(D) is problematic if CIS states are degenerate

CIS(D) cannot describe doubly excited states

CISD, CISDT, ...

Higher-order CI methods (CISD, CISDT,...)

The accuracy of description of excited states is not improved.

Reason: different excited states converge to the exact energies at different pace → transition energies can be strongly in error

CISD:

- Singly-excited states are described with errors ~0.1-0.3 eV
- Errors for doubly-excited states ~1 eV
- Not size-extensive

Equation of motion coupled cluster (EOM-CC)

EOM-CCSD – equation of motion coupled cluster method with single and double excitations:
truncation at singles and doubles

$$\Psi_{CC} = e^{\hat{T}} \Phi_0 \quad T - \text{excitation operator}$$

$$\Psi_{EOM} = \hat{R} e^{\hat{T}} \Phi_0 \quad R - \text{excitation operator}, R = R_1 + R_2 + R_3 \dots$$

$$\hat{H} \hat{R} e^{\hat{T}} \Phi_0 = E \hat{R} e^{\hat{T}} \Phi_0 \quad R \text{ and } T \text{ commute} \rightarrow$$

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} \hat{R} \Phi_0 = E \hat{R} \Phi_0 \quad \hat{\hat{H}} = e^{-\hat{T}} \hat{H} e^{\hat{T}} \quad \text{similarity transformed Hamiltonian}$$

$$\hat{\hat{H}} \hat{R} \Phi_0 = E \hat{R} \Phi_0 \quad \text{EOM-CC equations}$$

Spectrum of \bar{H} is the same as spectrum of H

Equation of motion coupled cluster (EOM-CC)

Both T and R should be truncated for practical simulations



EOM(2,2) = EOM-CCSD

- Computational cost and scaling (N^6) is similar to CISD, but
- Size-extensive
- Higher-order correlation is folded in \bar{H}

EOM(3,3) = EOM-CCSDT

- Scaling N^8

EOM(2,3) possible but not widely used

EOM-CCSD computational procedure:

1. Solve HF
2. Solve CCSD equations for the ground state
3. Solve EOM (~CI) equations for \bar{H}

Different variants of EOM-CC method

In EOM-CC formalism, we have a freedom to

- Pick a reference determinant (not necessarily the ground state)!
- specify excitation operator R (electron excitation, electron attachment, electron ionization)

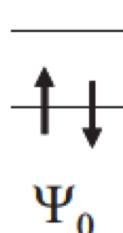
Why? To be able to describe various multi-configurational excited states

Let's start with a standard scenario: **EOM-CC for the excitation energies (EOM-EE)**

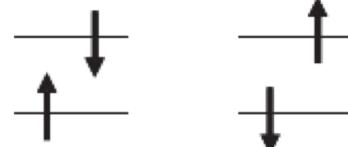
- Reference determinant is a closed-shell ground state
- R is an excitation operator that preserves the number and spin of electrons

EOM-EE:

$$\Psi(M_s=0) = R(M_s=0)\Psi_0(M_s=0)$$



Ψ_0



Ψ_i^a



Ψ_{ij}^{ab}

EOM-EE:

- Describes singly-excited states nicely
- Doubly-excited states with much larger errors

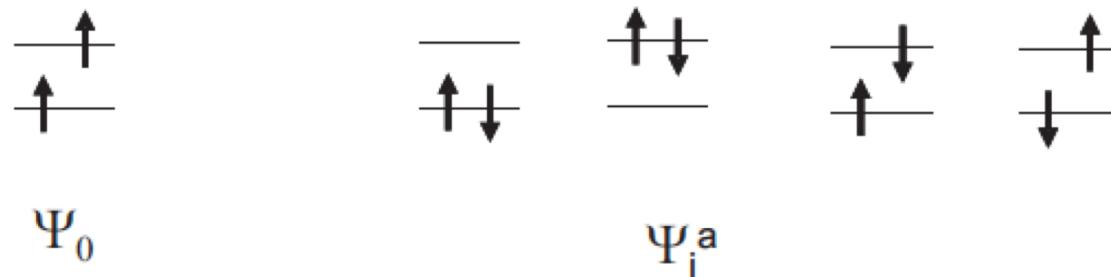
Different variants of EOM-CC method

How to accurately describe doubly-excited states, e.g. in diradicals and near bond-breaking?

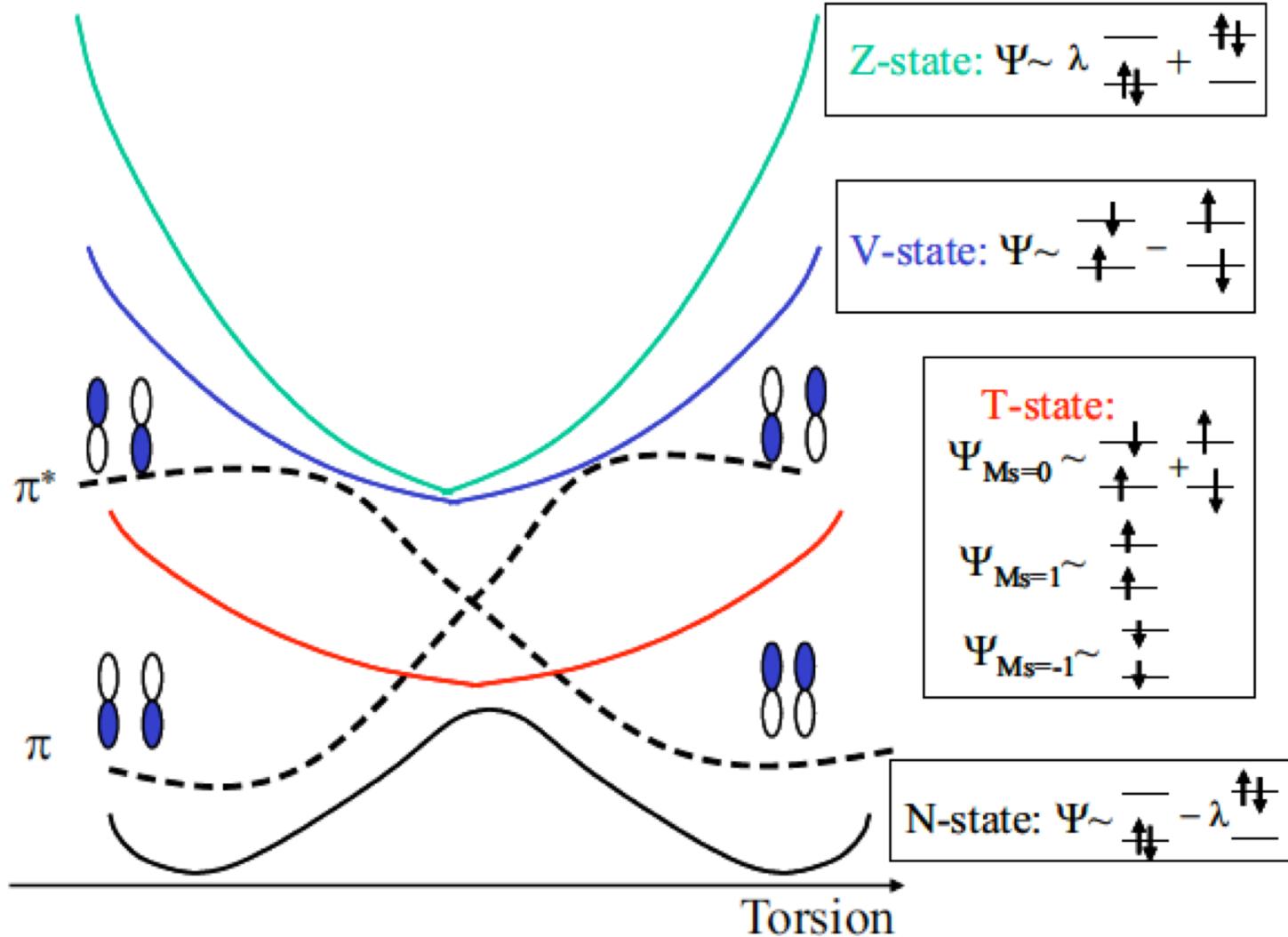
Solution: Spin-Flip EOM-CC (EOM-SF)

- Reference determinant is a high-spin triplet state
- R is an excitation operator that preserves the number but flips spin of one electron

EOM-SF: $\Psi(M_s=0) = R(M_s=-1)\Psi_0(M_s=1)$



Example: isomerization in ethylene



Different variants of EOM-CC method

How to accurately describe excited states in radicals? Problem: radicals are often strongly spin-contaminated

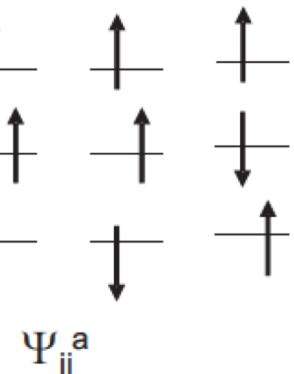
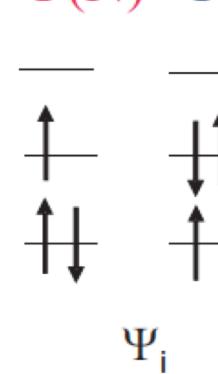
Solution 1: EOM-CC for Ionization Potentials (EOM-IP)

- Reference determinant is a closed-shell state with $N+1$ electrons
- R is an excitation operator that annihilates one electron

EOM-IP:



$$\Psi(N) = R(-1)\Psi_0(N+1)$$



Solution 2: EOM-CC for Electron Affinities (EOM-EA)

- Reference determinant is a closed-shell state with $N-1$ electrons
- R is an excitation operator that creates one electron

EOM-EA:



$$\Psi(N) = R(+1)\Psi_0(N-1)$$

