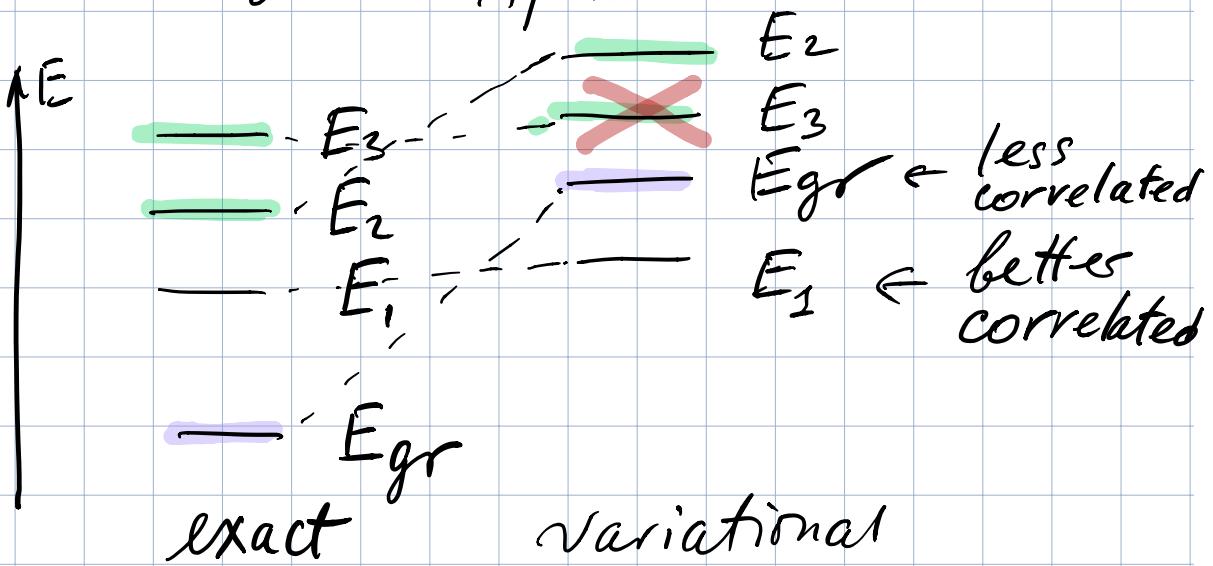


Lab 4 : Excited states is on github
due April 21



CIS configuration interaction singles

$$H^{\text{CIS}} = \begin{pmatrix} E_{\text{HF}} & 0 \\ 0 & E_i^a \end{pmatrix} \quad \text{Brillouin's theorem}$$

$$\psi^{\text{CIS}} = \sum_{ia} c_i^a \phi_i^a \quad \text{size occ. x vir}$$

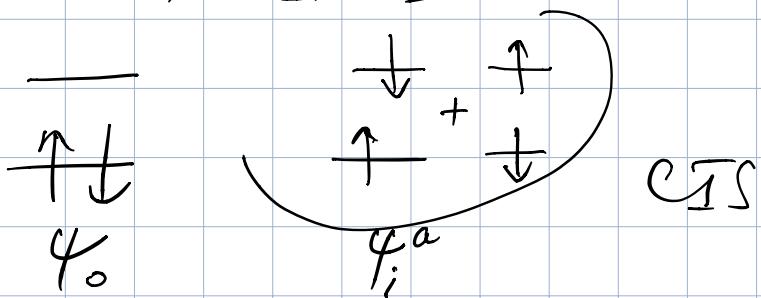
$$H^{\text{CIS}} C^{\text{CIS}} = E C^{\text{CIS}}$$

Scaling : N^5

Size-extensive
variational

Limitations of CIS:

- cannot describe any doubly excited states
- no dynamical correlation \rightarrow errors of $\sim 1\text{eV}$ (\sim corr. en. of a pair of electrons)
- no non-dynamical correlation (CIS breaks when HF breaks)
describes some non-dyn. corr. for exc. states



Relative order of exc. states is typically correct

CIS(D) includes double excitation perturbatively
analogous to MP2 for the gr. state

$$E_{MP2} = \langle \Phi_0 | \hat{V} | T_2 \Phi_0 \rangle$$

$$E_{\text{CIS}(D)} = \langle \psi_{\text{CIS}} | \hat{V} | U_2 \Phi_0 \rangle +$$

\approx

$$\langle \psi_{\text{CIS}} | \hat{V} | U_1 T_2 \Phi_0 \rangle$$

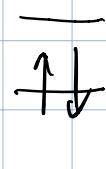
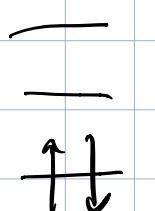
found
pertur-
batively

Scaling N^5

added dynamical correlation \rightarrow
error decreases to 0.2-0.5 eV

$\text{CIS}(D)$ fails when CIS fails
also when CIS states are degenerate

Higher-order CI: CISD, CISDT, ...



CISD

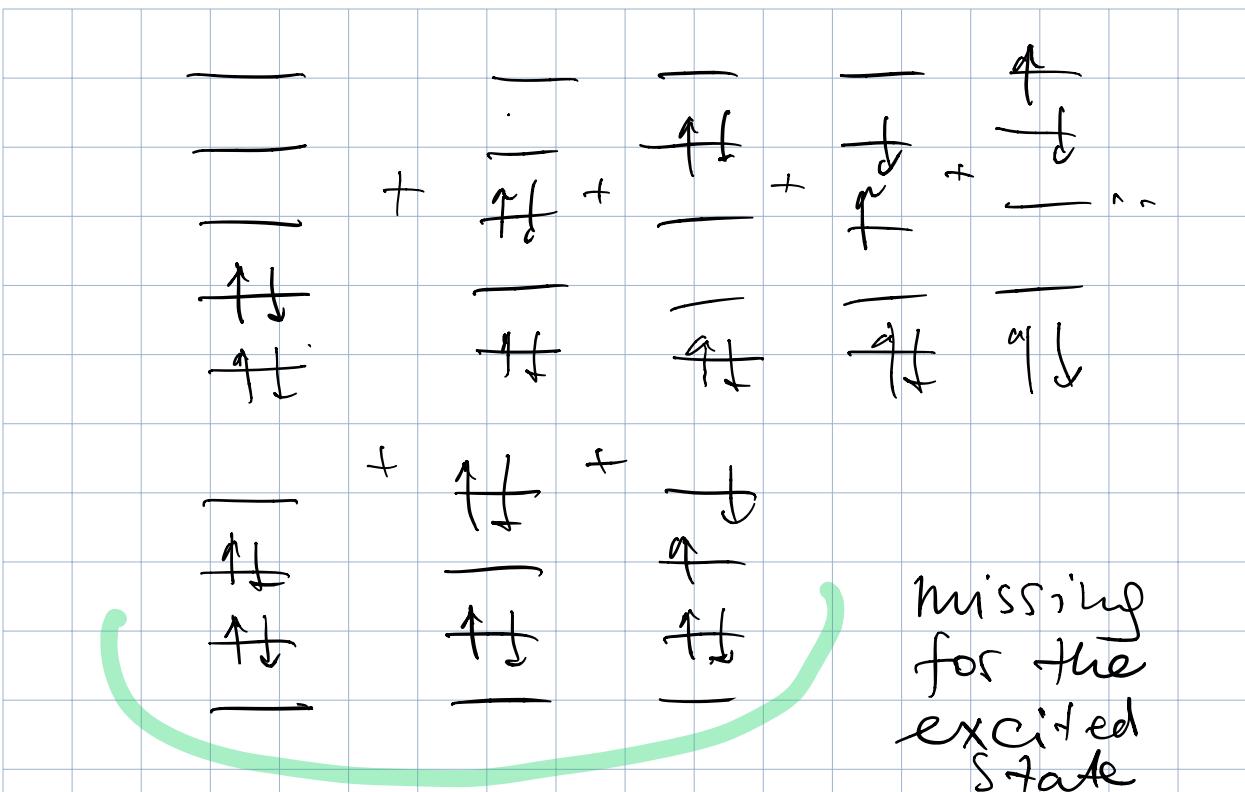
Ψ_0
correlated
with single &
double excitations

ψ_{ij}^{ab}

not correlated

$$\Psi = \overline{\Psi_0} + 1 \underline{\Psi_D}$$

at bond-
breaking



CISD: singly-excited states
are described with error
0.1 - 0.3 eV
doubly exc. states error ~ 1eV
also not size extensive!

EOM-CC

equation of motion coupled cluster

EOM-CCSD truncated at singles
& doubles

$$\psi_{cc} = e^{\hat{T}} \phi_0 \quad T\text{-exc. operator}$$

$$\underset{EOM}{\psi} = \hat{R} e^{\hat{T}} \phi_0 \quad R\text{-exc. operator}$$

$$\hat{R} = \hat{R}_1 + \hat{R}_2 + \hat{R}_3 + \dots$$

$$\hat{H} \hat{R} e^{\hat{T}} |\phi_0\rangle = E \hat{R} e^{\hat{T}} |\phi_0\rangle$$

\hat{R} and \hat{T} commute

$$\underline{(e^{-\hat{T}} \hat{H} e^{\hat{T}}) \hat{R} |\phi_0\rangle} = E \hat{R} |\phi_0\rangle$$

$$\hat{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$$

similarity
transformed \hat{H}

$$\hat{H} \hat{R} |\phi_0\rangle = E \hat{R} |\phi_0\rangle$$

EOM CC
eq-n

Spectrum of \hat{H} is the same as H

both \hat{T} and \hat{R} should be truncated

$$EOM(2,2) \equiv EOM-CCSD$$

comp. cost & scaling similar to
 $CISD$ but

size-extensive &
fold in correlation in \hat{H}

$$EOM(3,3) \equiv EOM-CCSQT$$

scaling N^8
 $EOM(2,3)$ possible but not widely used

$EOM-CCSD$:
 $N^6 \rightarrow$ 1) solve HF
 $N^6 \rightarrow$ 2) solve CCSD for gr. state
 $N^6 \rightarrow$ 3) solve EOM (CI eqns) for \bar{H}

Different versions of $EOM-CC$ methods

Photoelectron spectroscopy?



neutral

singlet
ex. state

triplet
ex. state

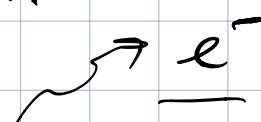


anion

$h\nu$

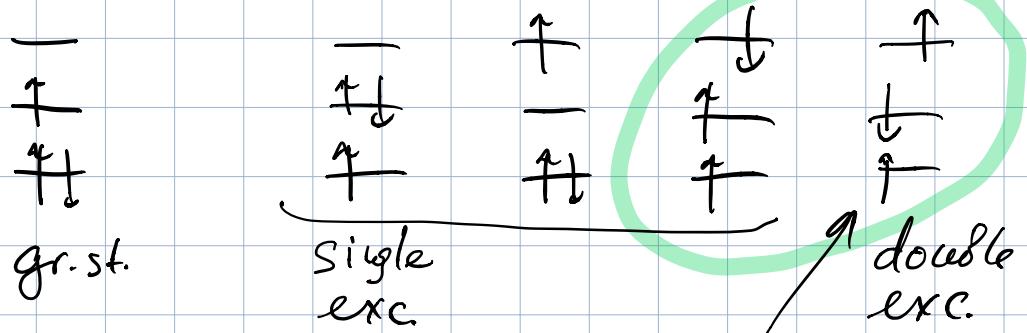


g, s.t.



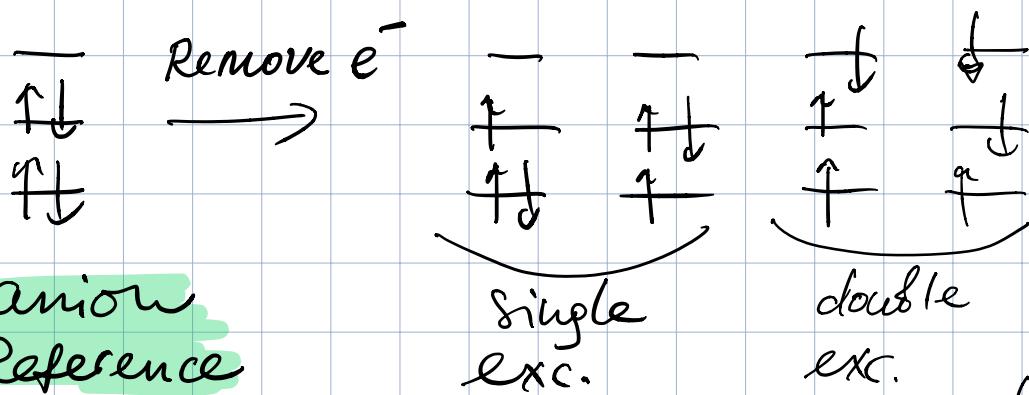
singlet triplet
ex state ex state

Want to describe radical exc. states



Radicals are often spin-contaminated

Change Reference (the starting determinant)



no spin contamination!

EOM-IP (ionization potentials)

EOM-EE $\Psi(m_s=0) = R/m_s=0 \Phi_0(m_s=0)$
(standard exc. energies)

for radicals $\Psi_r = R \Phi_r$

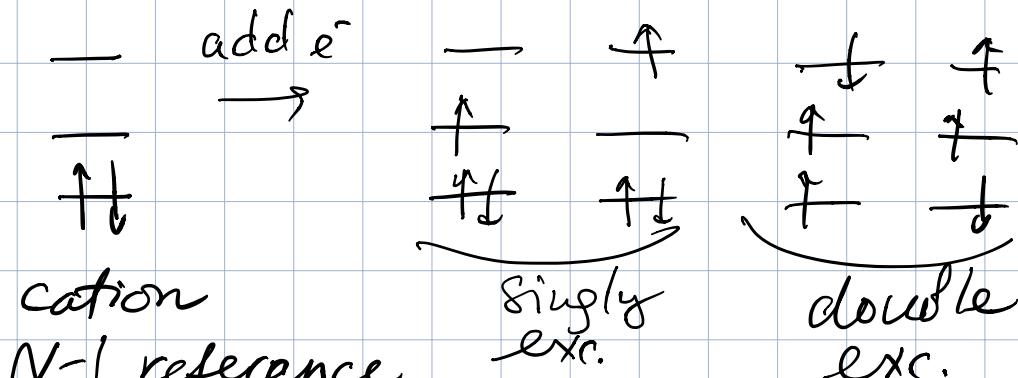
$$\text{EOM-IP} \quad \psi(N) = R(-) \Phi_0(N+1)$$

$$\hat{R}^{\text{IP}} = \sum_i r_i i + \sum_{ija} r_{ij}^a a^+ c_j$$

EOM-EA (electron affinity)

$$\psi(N) = R(+) \Phi_0(N-1)$$

$$\hat{R}^{\text{EA}} = \sum_a r^a a^+ + \sum_{abi} r_i^{ab} a^+ b^+ c_i$$



no spin contamination

EOM-SF (spin-flip)

$$\psi(m_s=0) = R(m_s=-1) \Phi_0(m_s=1)$$

diradicals and bond-breaking

