Effects of higher order triples in Coupled cluster method

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# Plan of the talk

❖ **Brief introduction to Coupled Cluster Theory**

❖ **Inclusion of higher order effects in CC**

❖ **Applications**

- ❖ **Single and double Ionization (related Auger) potentials**
- ❖ **Electron affinities**
- ❖ **Transition energies**
- ❖ **Allowed as well as forbidden transitions**
- ❖ **Dissociation energies**
- ❖ **Geometrical parameter and Structure**
- ❖ **Vibrational frequencies and stability etc**

Criteria that the theory should satisfy

- ➢ **Predictibility**
- ➢ **Maintain size-extensivity of the energy over the entire of PES.**
- ➢ **Rapid perturbative convergence i.e., Intruder free**
- ➢ **General applicability**

Triplet

~ 4 eV (32844 cm^{-1})

Triplet

~ 4.5 eV

X^1A_1
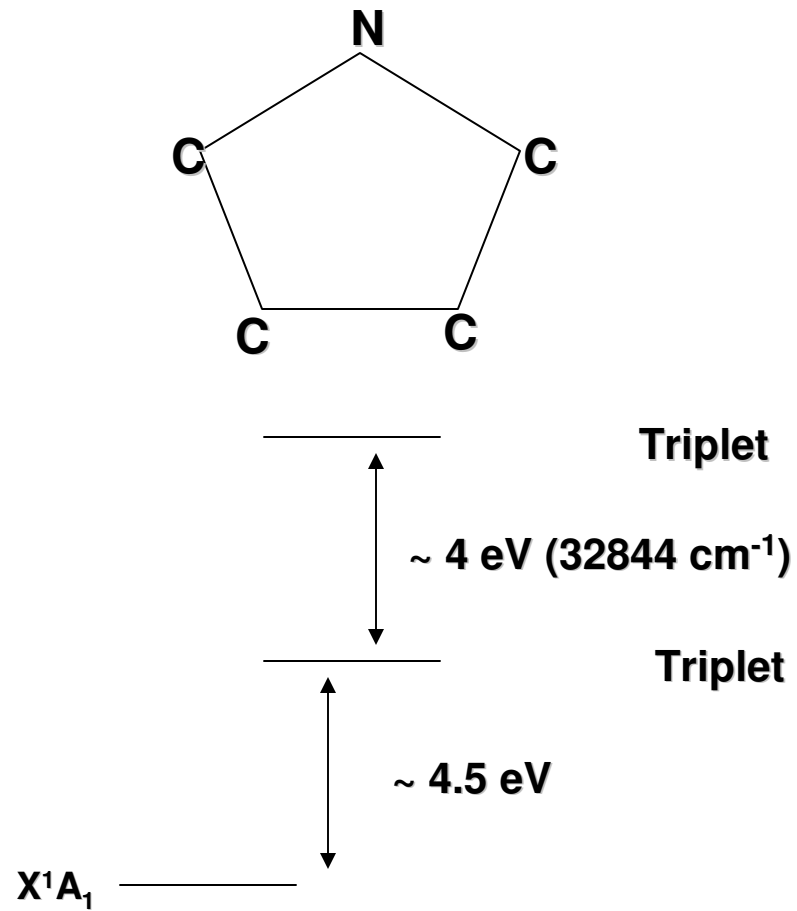
Some well known problems

Energy levels of Pt atom

$6s^2$ ($^1S_0$) → $5d6s$ ($^3D_1$) M1 transition amplitude

Basic formalism of Coupled Cluster Theory (CCT)

The starting point of CCT

$$H = H_0 + V$$

The full many electron space of dimension N is then partitioned into a reference space of dimension M. defined by the projector P and its orthogonal complement associate with the projector $Q=1-P$.

A wave operator Ω is introduced that satisfies,

$$\Psi_i = \Omega \Psi^0_i$$

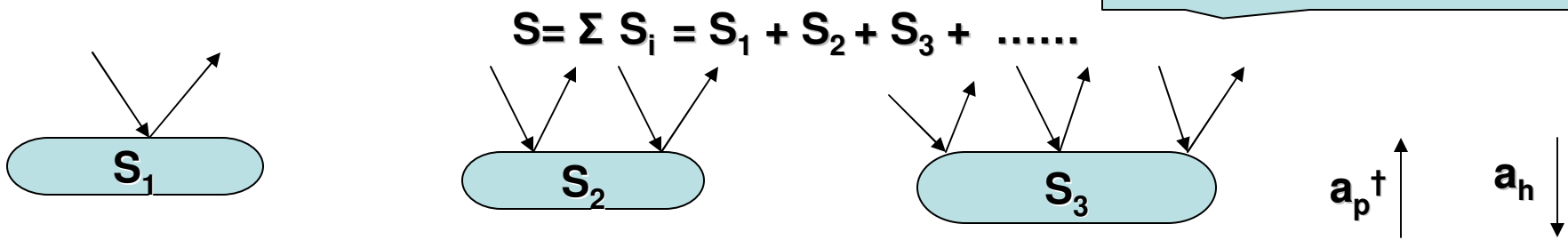**where Ψ_i and Ψ^0_i are exact and unperturbed wave functions.**

$$H_{eff} \, \Psi^0_m = E_m \, \Psi^0_m \qquad m=1,2,\ldots M$$

where $H_{eff} = PH\Omega P$.

$$\Omega = \{\exp(S)\}$$

where

$$S = \Sigma\, S_i = S_1 + S_2 + S_3 + \ldots\ldots$$

S_1

S_2

S_3

$a_p^{\dagger}$ a_h

$$H\Omega P = E\Omega P$$

Multiplying Ω^{-1} from left

$$\Omega^{-1} H\, \Omega P = EP$$

$$H'\, P = EP$$

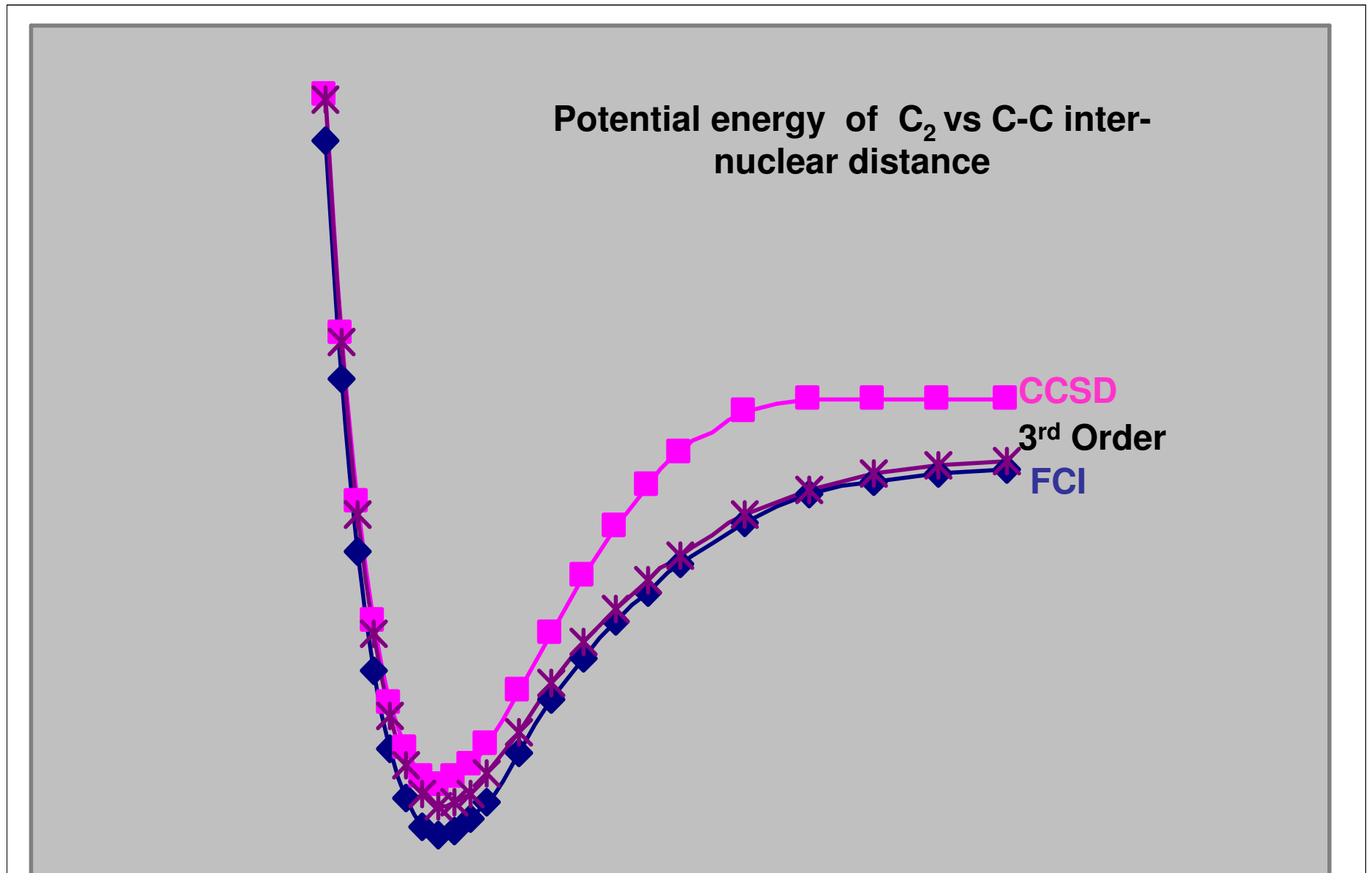**Projecting on P and Q from left, we get**

$$PH'P = EP$$

$$QH'P = 0$$

where

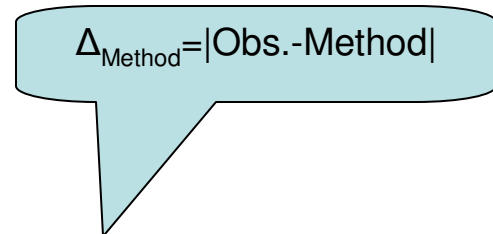$$H' = \Omega^{-1} H\Omega = H + [H,S] + \tfrac{1}{2}[[H,S],S] + \ldots\ldots$$

This series terrminates at the fourth power of S !!!

- ❖ For S=S1 + S2,, CCT is called CCSD.
- ❖ CCSD is size-extensivity as its wave- function is multiplicatively separable

Potential energy of C$_2$ vs C-C inter-nuclear distance

CCSD

3rd Order

FCI

For $S = S_1 + S_2 + S_3,$ the scheme is called CCSDT

$S = S_1 + S_2 + S_3 + S_4$ the scheme is called CCSDTQ

$\Delta_{Method} = |Obs.-Method|$

Equilibrium bond length (Å)

	State	Observed	Δ_{CCSD}	Δ_{CCSDT}
N_2	$X^1\Sigma_g^+$	1.0977	0.0078	0.0004
CO	$X^1\Sigma$	1.1283	0.0067	0.0001
C_2	$X^1\Sigma_g^+$	1.2422	0.0028	0.0001

Harmonic frequency (cm^{-1})

	State	Observed	Δ_{CCSD}	Δ_{CCSDT}
N_2	$X^1\Sigma_g^+$	2359	86	25
CO	$X^1\Sigma$	2170	73	5
C_2	$X^1\Sigma_g^+$	1856	46	14

Straight forward inclusion of higher order cluster is, however, computationally expensive and that is why CCSDT , CCSDTQ schemes applications are very limited.

How to include higher order excitation at CCSD framework?

We introduce the unitary CC ansatz of the form

$$\Omega = \{\exp(S - S^\dagger)\} = \{\exp(\sigma)\} \qquad \sigma^\dagger = -\sigma$$

Instead of

$$\Omega = \{\exp(S)\}$$

$$H' = \Omega^{-1} H \Omega = H + [H,\sigma] + \tfrac{1}{2}[[H,\sigma],\sigma] + \ldots\ldots$$

This is a non-terminating series !!!

But it contains higher order clusters (S_3 and S_4 even at CCSD level. This CC variant is called UCC.

UCC is variationally bound !!!

Excitation energies of C II (in cm⁻¹)

Term	Observed	ΔE_{ccsd}	ΔE_{UCCSD}
2p $^2P_{1/2}$	0	0	0
2p $^2P_{3/2}$	63	10	18
3p $^2P_{1/2}$	116537	100	42
3p $^2P_{3/2}$	131724	100	45

ΔE_{Method} = | Obs. − E(Method) |

Thank you