Some aspects of many bodies theories

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Atomic and Molecular properties

Dipole, Quadruple moment, Oscillator strengths, Hyperfine coupling constants

Geometry and Vibrational frequencies, Dissociation / bond breaking energy

Transition energies

Ionization potentials, Electron affinities (Feshbach resonance) , Excitation energies

Double ionization potential (Auger)

Potential energy curves /surfaces to study reaction path.

$$H(R,r)\,\Psi(R,r) = E(R)\,\Psi(R,r)$$

$$\langle O \rangle = \langle \Psi | O | \Psi \rangle / \langle \Psi | \Psi \rangle$$

$$\delta/\delta R \{ \langle \Psi(R,r) | [H(R,r) - E(R)] | \Psi(R,r) \rangle \} = 0$$

$$H = H_0 + V$$
$$\Psi = \Psi_0 + X$$
$$E = E_0 + \Delta$$

Approximate theories should satisfy

Flexible to handle closed and open-shell atomic and molecular systems

Maintain proper scaling of the computed quantities (size-extensivity)

Capable of providing reliable and accurate estimate of the computed quantities

Rapidly convergent (for perturbative approaches)

Variational

Configuration interaction

Perturbative

Many-body Perturbation Theory and its variants

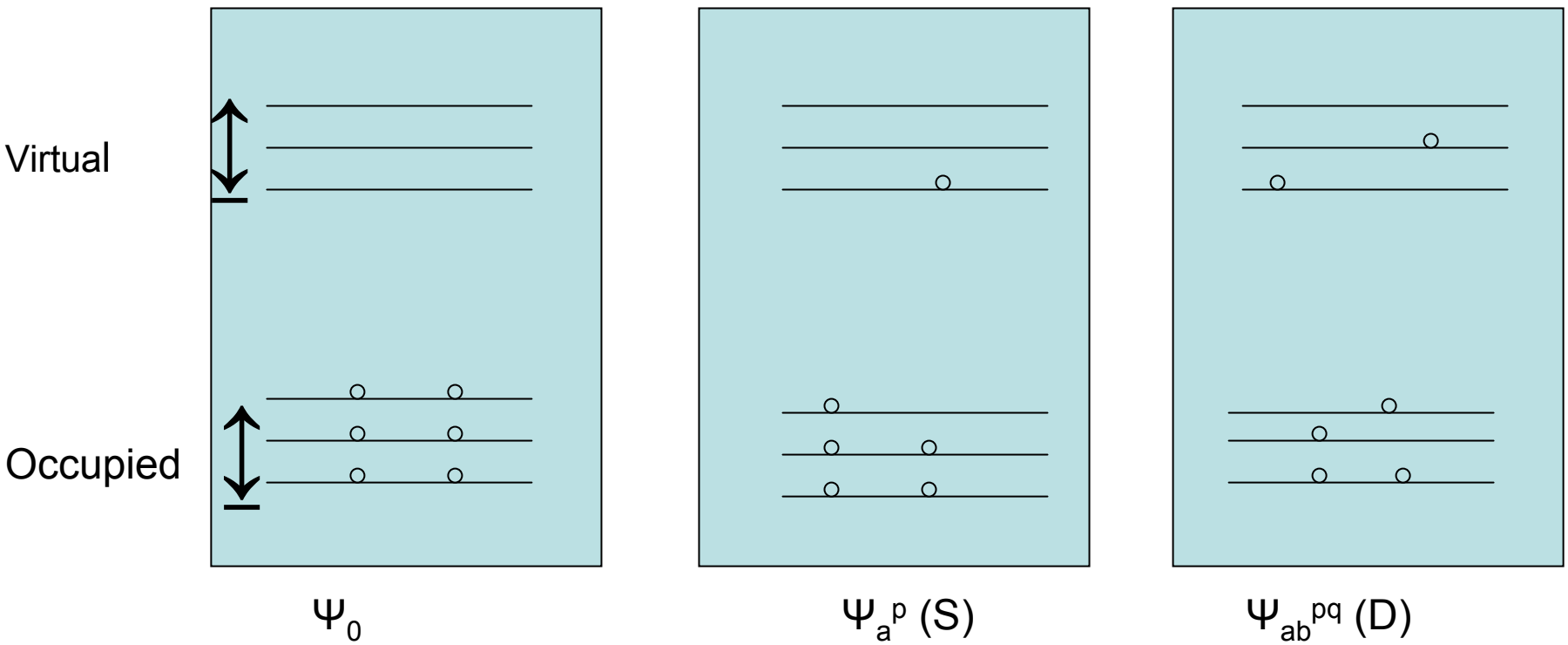
Non-perturbative

Coupled cluster, Green's function

Coupled Cluster Method

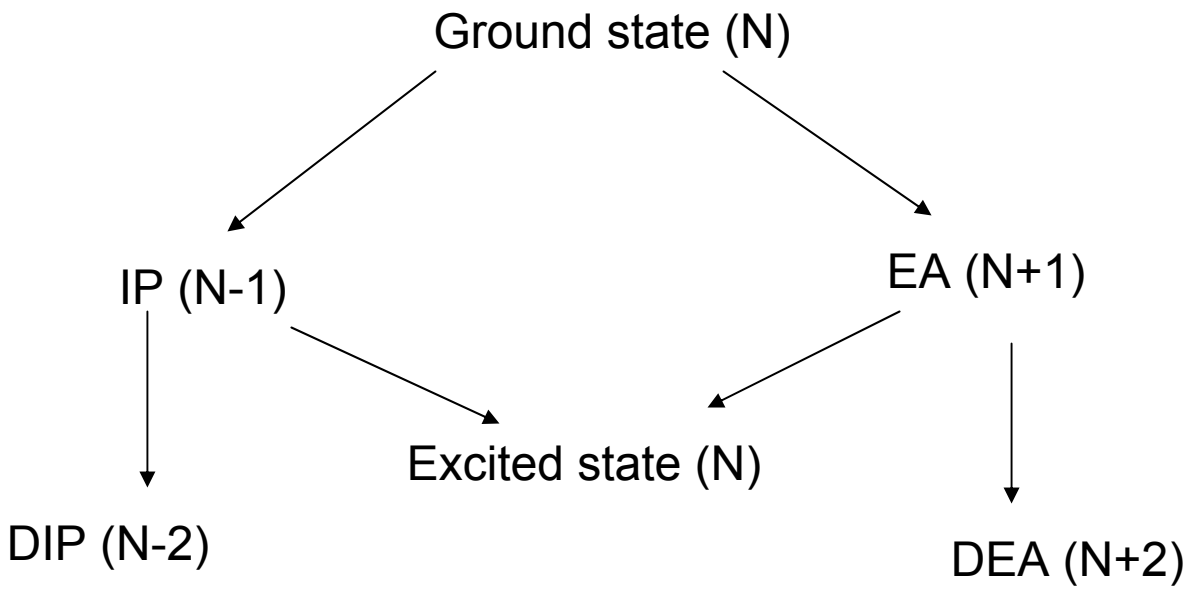
$$\Psi = \exp(S)\,\Psi_0 = \Psi_0 + X$$

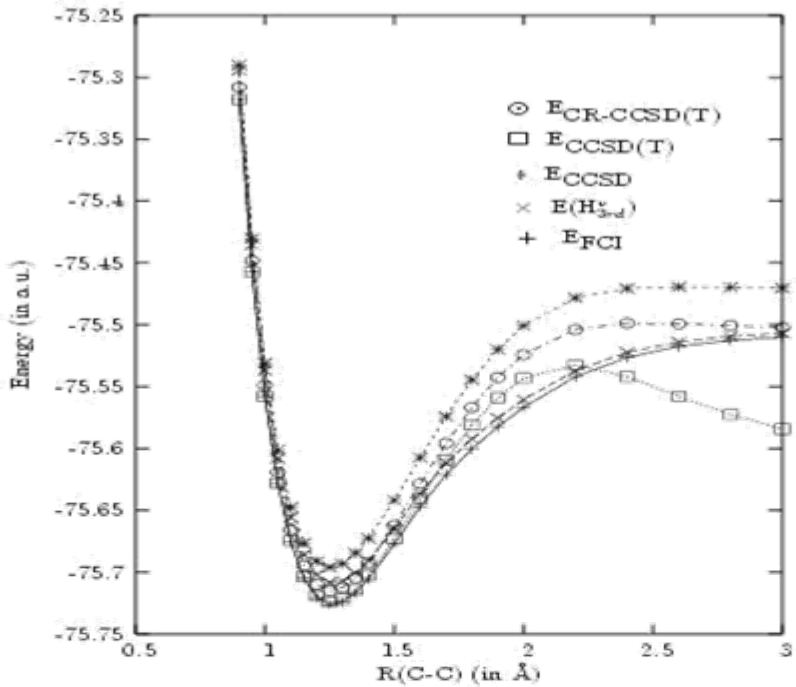
$$S = \Sigma_n S_n$$



For n=2, CCM (iterated once) is equivalent to Traditional Perturbation Theory (2^{nd} order)

It is size-extensive and capable of providing highly accurate properties.

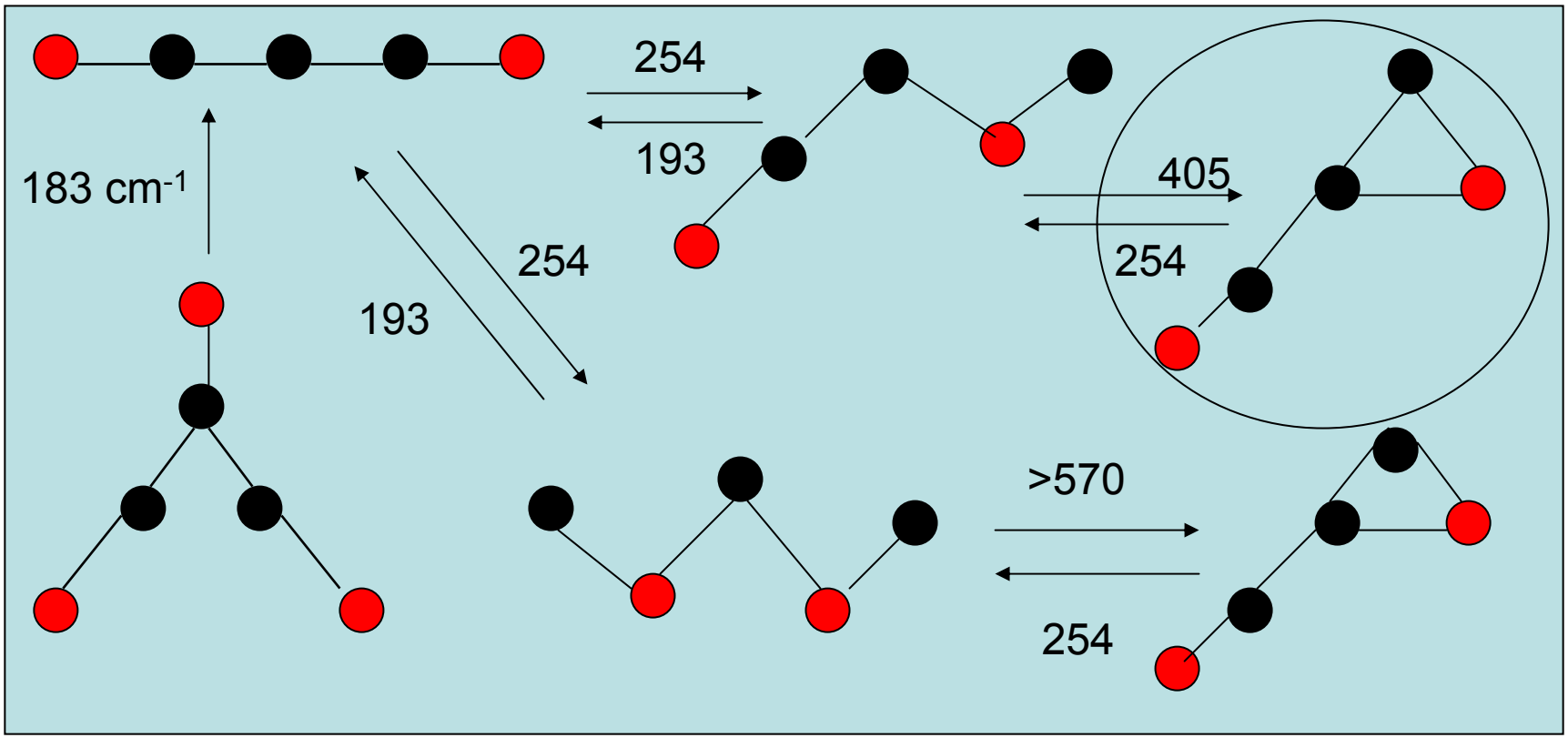


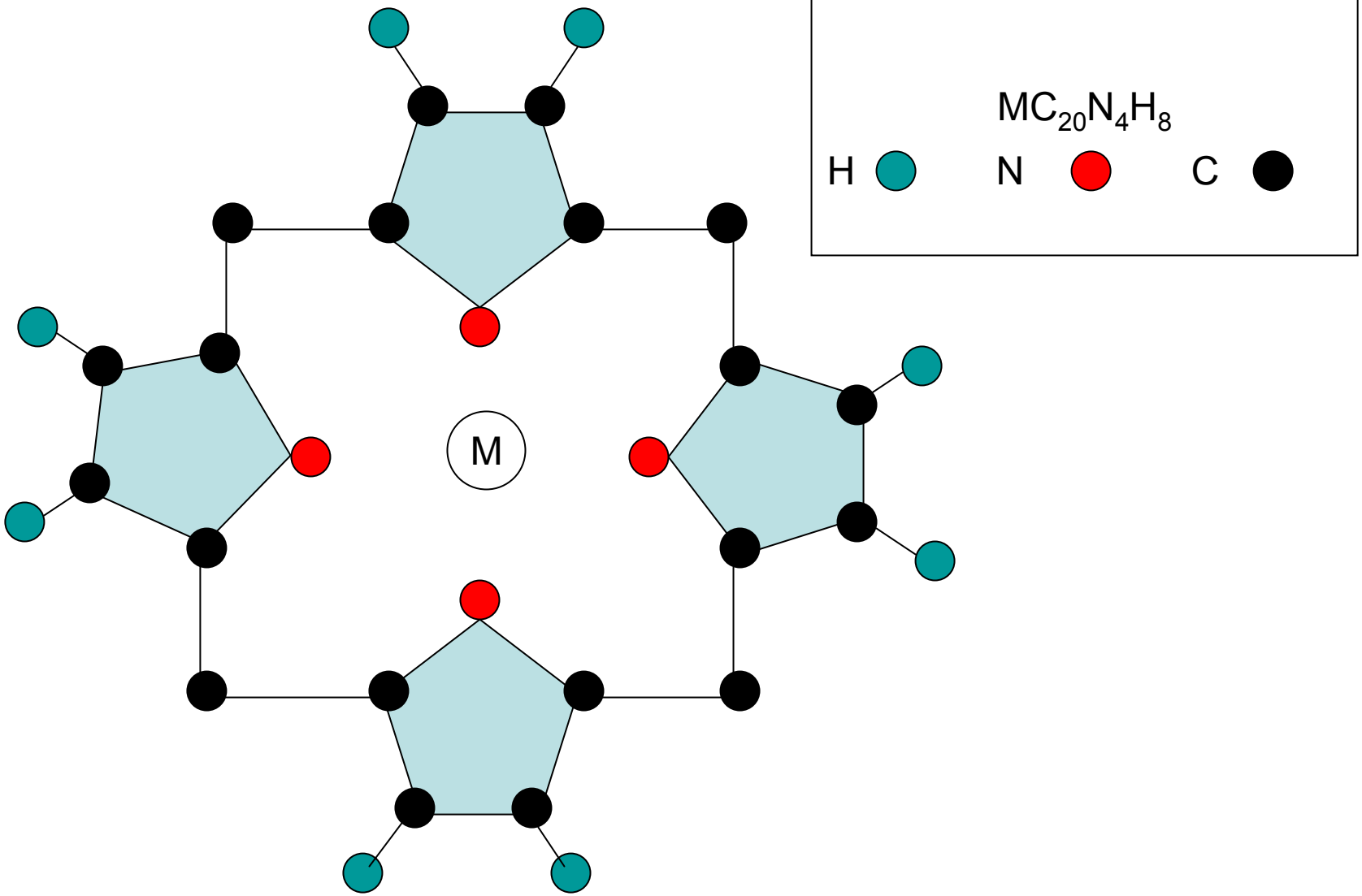

-75.25
-75.3
-75.35
-75.4
-75.45
-75.5
-75.55
-75.6
-75.65
-75.7
-75.75
Energy (in a.u.)
0.5
1
1.5
2
2.5
3
R(C-C) (in Å)
E_CR-CCSD(T)
E_CCSD(T)
E_CCSD
E(H^s_3+d)
E_FCI

Microwave discharge of mixtures of N_2 and C_2H_2 condensed to 20K shows two emission bands between 3000 and 4900 Å. It also shows a progression of 22 broad and diffuse band with a mean interval 670 cm^{-1} with 0-0 band at 2895Å (4.28 eV)

Question : What is the emitter?

Matrix Photolysis of Dicyanodicarbene




$MC_{20}N_4H_8$
H
N
C
M