

Excited states

UV/VIs 1-12 eV

$$1 \text{ eV} = 8065 \text{ cm}^{-1}, \quad 1 \text{ eV} = 1240 \text{ nm}$$

$$2 \text{ eV} = 620 \text{ nm}$$

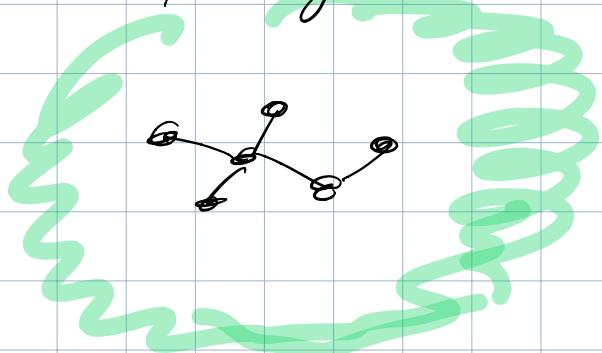
1-5 eV - valence transitions

$$\pi \rightarrow \pi^*, \quad n \rightarrow \pi^*$$

5-12 eV - valence & Rydberg exc.

Rydberg excitations \rightarrow electron goes
to higher n values

cation + diffuse
electron

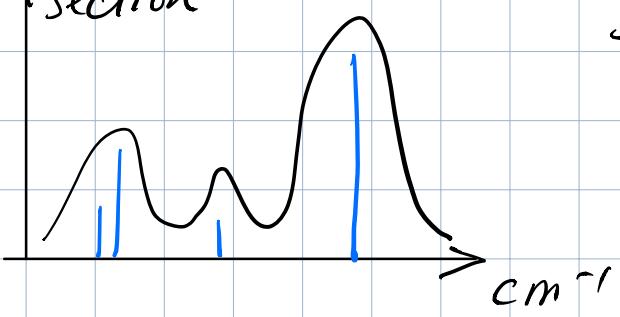


$> 12 \text{ eV}$ - excitation
 \rightarrow lead to ionization

$\sim \text{keV}$ - core excitations

$1s \rightarrow \text{Rydberg}$

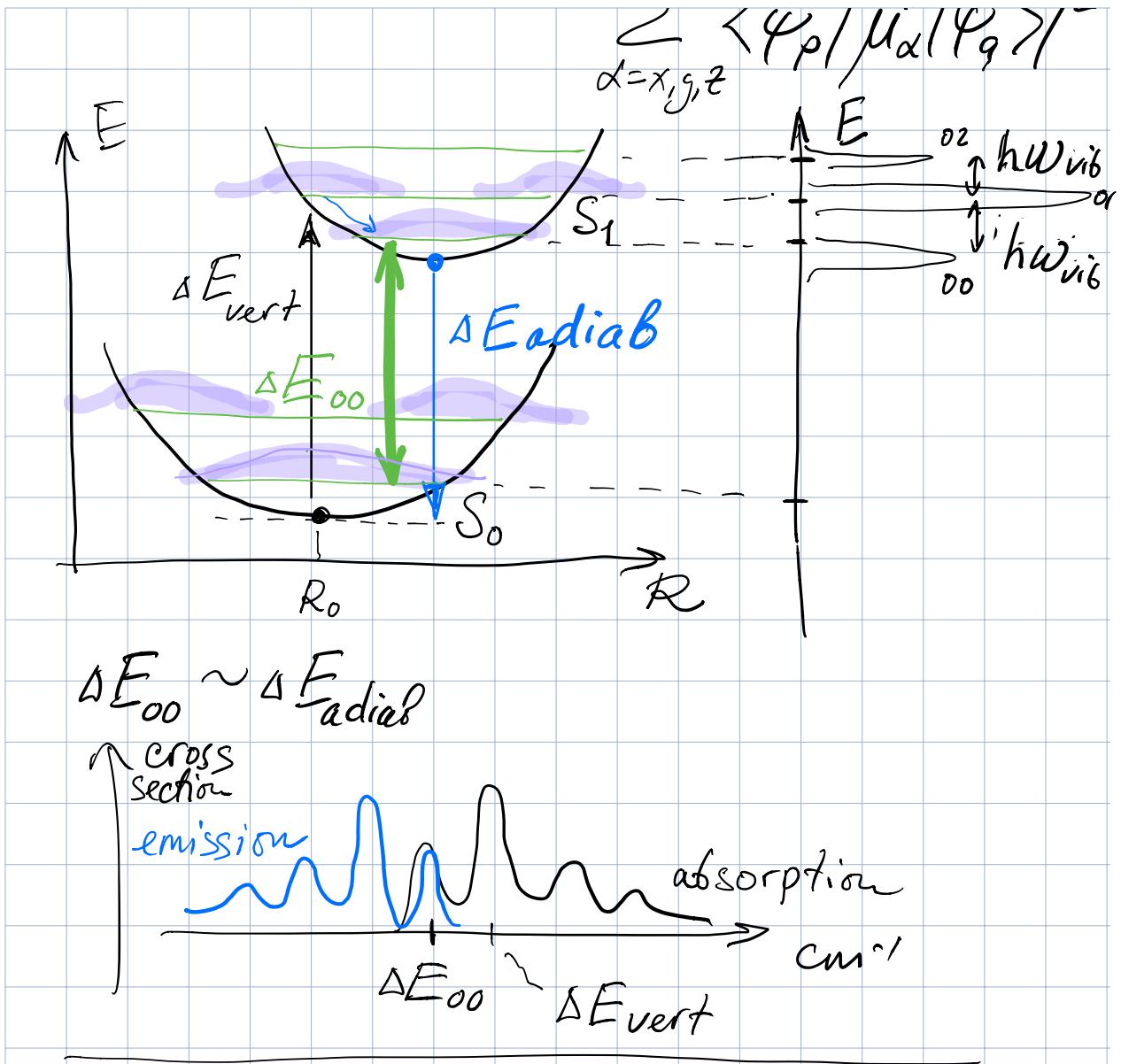
\propto cross section



Intensity of electronic transition:

$$f_{pq} = \frac{2me}{3\hbar^2} (E_q - E_p) \times$$

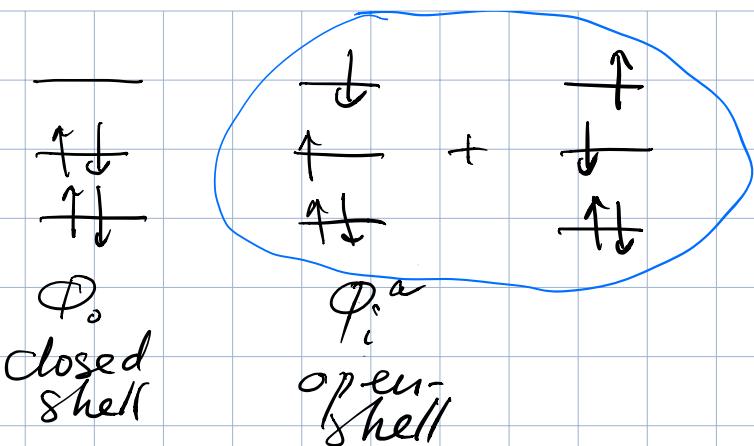
$\sim 1, 7, 1, \dots, 12$



Modeling excited states

Will HF & DFT work for excited states?

- exc. states are open-shells, multi-determinantal w.f.



- ground state methods typically find the lowest state of a given symmetry (spin, spatial) (collapse to the lowest state due to variational principle)

- multiple electronic states with crossings \rightarrow Born-Oppenheimer approximation fails often

X, A, B, C, \dots	low-spin states
a, b, c, \dots	high-spin states

Π, Σ, Δ	- symmetry repr.
$X^2 \Pi \sim$	Cash
	multiplicity

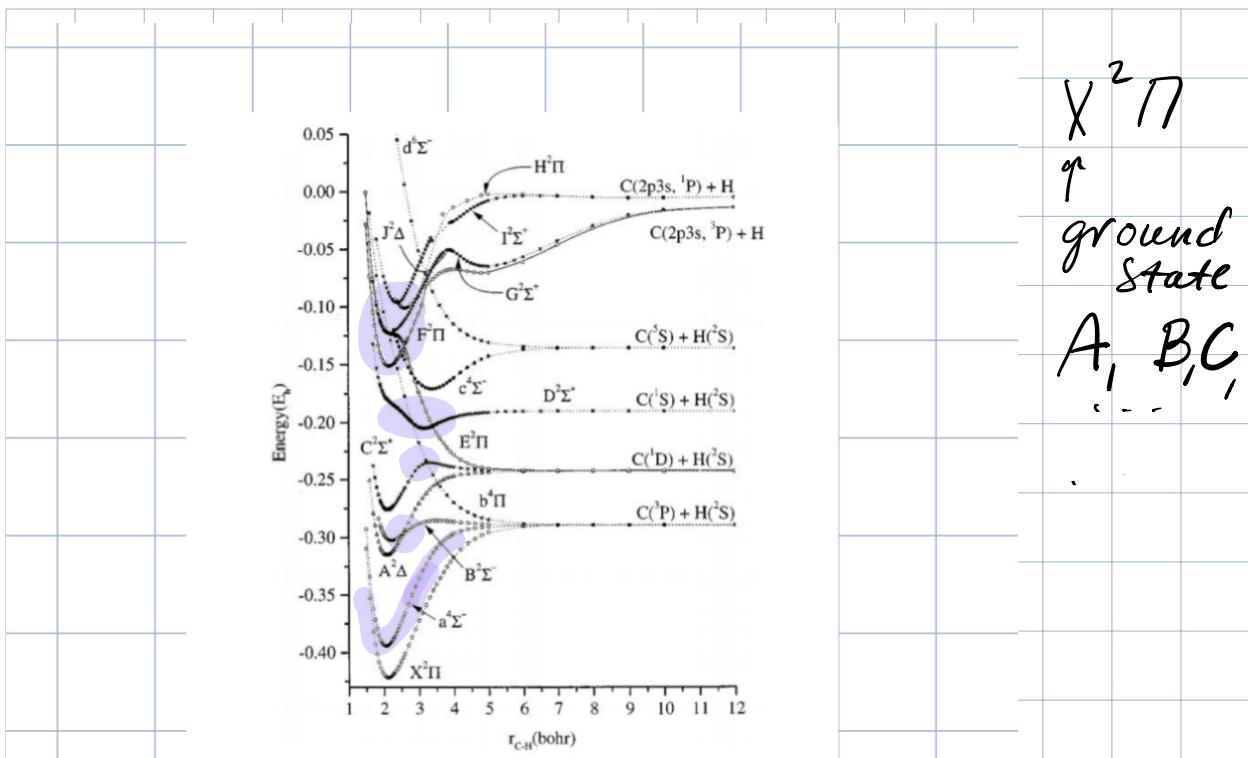


FIG. 1. Potential energy curves of the lowest 11 valence and 4 Rydberg states of CH. All energies have been shifted by +38.00 hartree.

$S_0, S_1, S_2, S_3 \dots$
 T_1, T_2, T_3

Modeling:

- using excited determinants

CI..., EOM-CC...

equation-of-motion

ADC(2), (3)

MCSCF, ...

— use response theory
 TD-DFT, LR-CC, ...
 molecule is subjected to oscillating electric field $E = E_0 \cos(\omega t)$

$$\langle \alpha \rangle_\omega = \sum_{i=0}^{\text{states}} \frac{|\langle \psi_0 | \hat{\mu} | \psi_i \rangle|^2}{\omega - (E_i - E_0)}$$

freq.-dependent polarizability

find poles of $\langle \alpha \rangle_\omega$
 $\omega = (E_i - E_0)$

Variational principle for excited states

i) if $\psi_0, \psi_1, \dots, \psi_N$ - exact eigenstates of \hat{H}

build trial w.f. $\tilde{\psi} : \langle \tilde{\psi} | \tilde{\psi} \rangle = 1$

$$\langle \tilde{\psi} | \psi_k \rangle = 0, \quad k = 0, \dots, N$$

$\tilde{\psi}$ is orthogonal to the lowest N eigenstates

$$\Rightarrow \langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle \geq E_{N+1}$$

	$\psi_0 \dots \psi_N$	$\tilde{\psi}$
ψ_0		0
\vdots		0
ψ_N		0
$\tilde{\psi}$	$0 \ 0 \ 0 \ 0$	

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

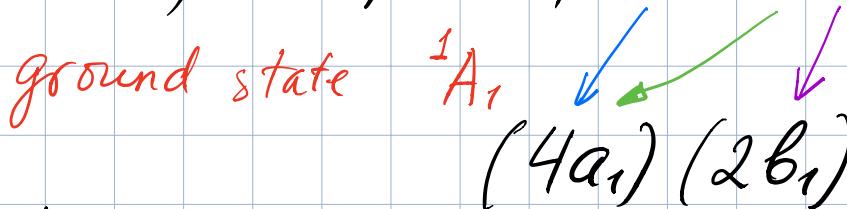
ψ_k & $\tilde{\psi}$ are not coupled through \hat{H}
 \Rightarrow separate H matrix

$\langle \hat{F} | \hat{H} | \hat{F} \rangle$ - can solve separately

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

water

$$(1a_1)^2 (2a_1)^2 (1b_1)^2 (3a_1)^2 (1b_2)^2 \rightarrow$$



which states can be described
using „gr. state“ technique?



3B_2 yes

1B_2 yes



3A_1 yes

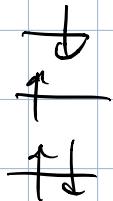
1A_1 no



3A_2 yes

1A_2 yes

Singlets : only one component
 is described



„fishy“ description

Triplets: just fine



$$a \times a \rightarrow a$$

$$1 \times 1 \rightarrow 1$$

$$b \times b \rightarrow a$$

$$2 \times 2 \rightarrow 1$$

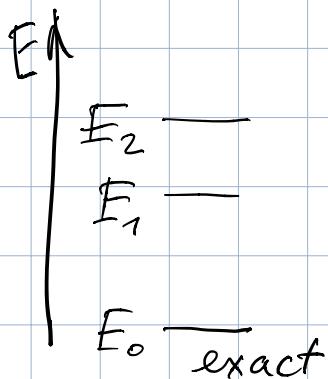
$$a \times b \rightarrow b$$

$$1 \times 2 \rightarrow 2$$

Ritz variational principle

In a linear subspace of w.f.)

$$\tilde{E}_i \geq E_i^{\text{exact}}$$



$$E_2$$

$$E_1$$

$$E_0$$

variations

$$E_2$$

$$E_0$$

$$E_1$$

variations

Tuesday presentations

Michael

Gabriel

Mingxin

Ankita

Vibha

Apr. 28

Reports due May 1