

CHM 673

Lecture 19: Electronic excited states, part 1

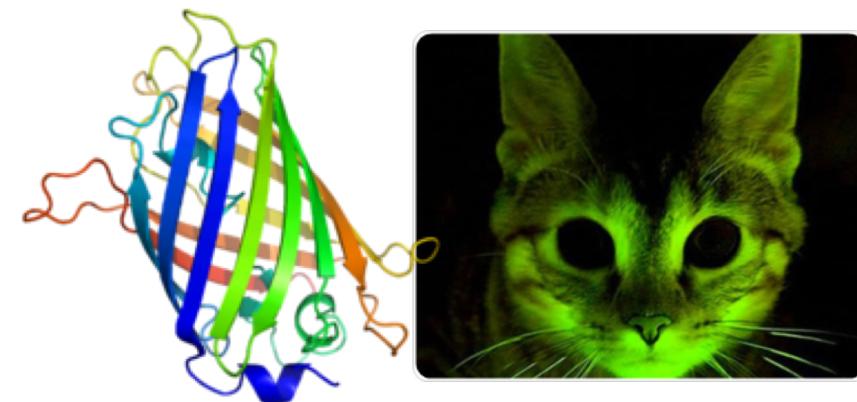
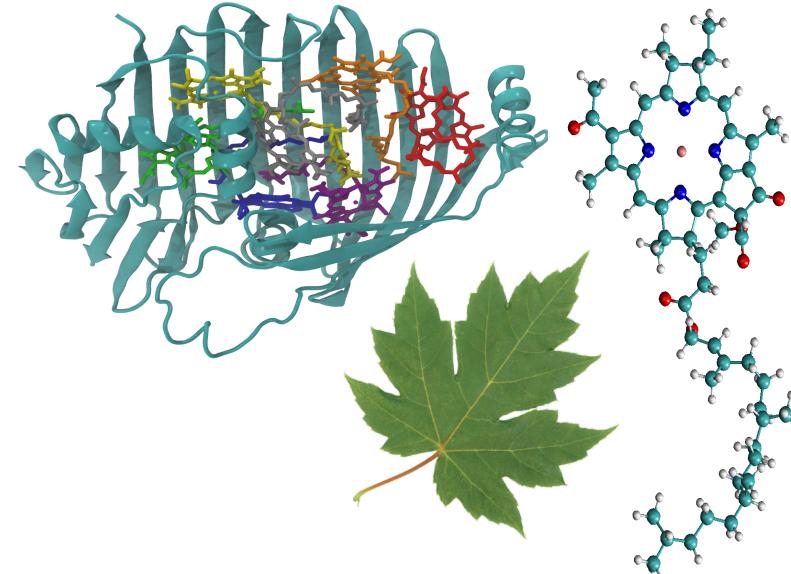
Suggested reading:

Chapter 4.14 from Jensen

Electronic excited states in chemistry

Natural and artificial photo-induced processes:

- Photosynthesis
- Photoactive proteins (GFP, rhodopsin, etc)
- Applications in photovoltaics
- Photo-induced catalysis
- Optical spectroscopy
- ...



Electronic excited states

- Ultraviolet / visible (UV/vis) spectra are dominated by electronic transitions
- Electronic transitions: 1-12 eV ($10,000\text{-}100,000\text{ cm}^{-1}$)
- 1-6 eV: rearrangements of valence electrons; lower-energy range – transitions in molecules with double bonds and aromaticity
- 6-12 eV: valence and Rydberg transitions
Rydberg transition: excitation from a valence orbital to a very diffuse orbital, final state: cation + a lone electron
- >12 eV: high-energy transitions often leading to electron ionization
- X-ray spectra (>100 eV): excitations of core electrons

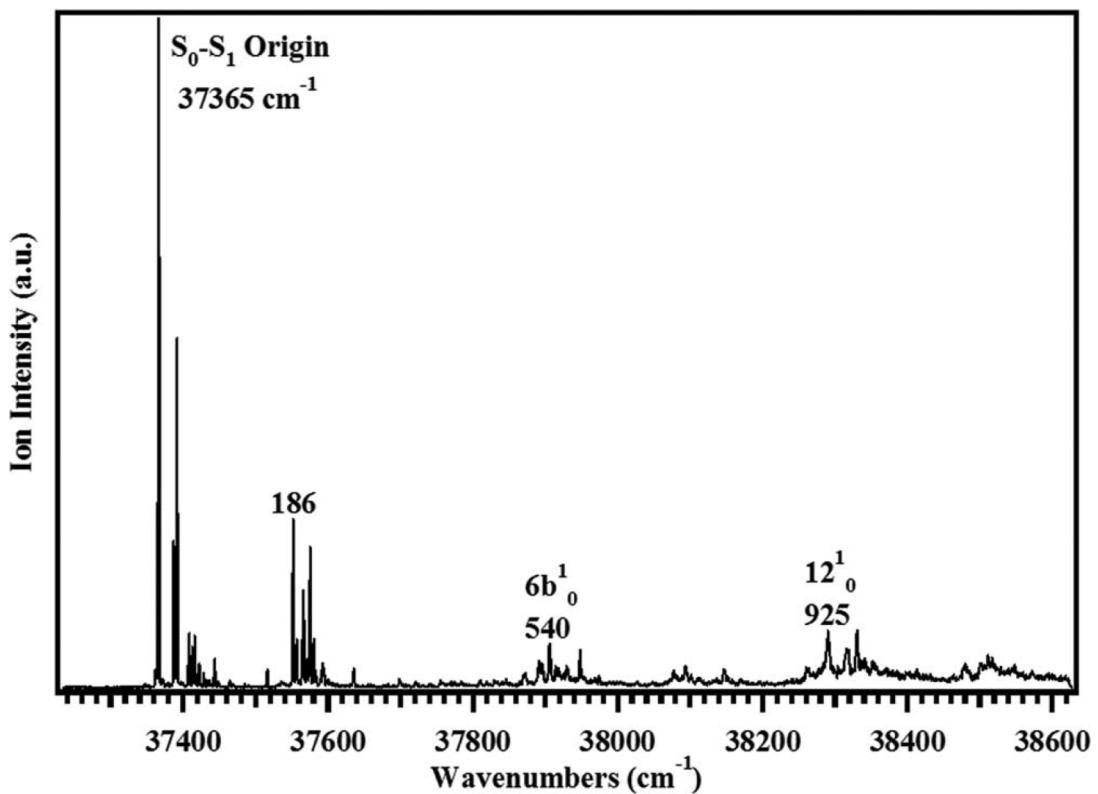
$$1 \text{ eV} = 8065.5 \text{ cm}^{-1}$$

$$1 \text{ eV} = 1240 \text{ nm} \text{ (reciprocal scale!)}$$

Visible range: 1.63 – 3.26 eV

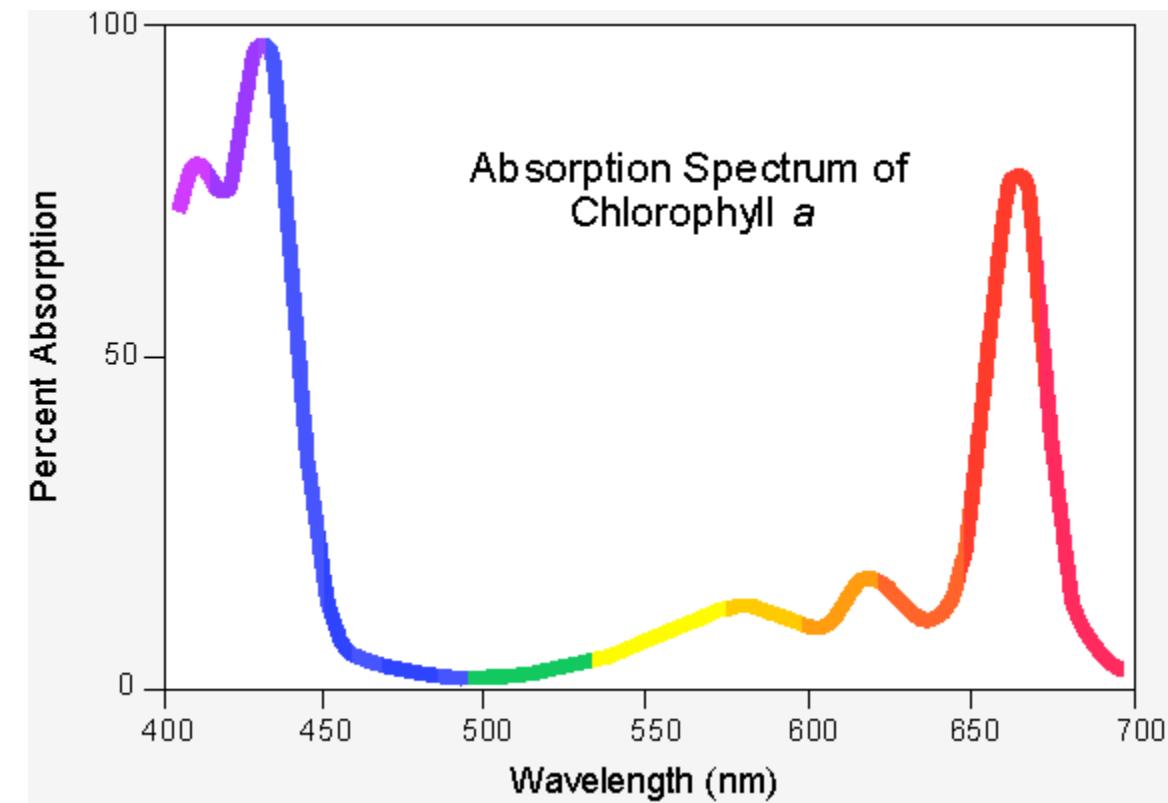
Shape of UV-vis spectra

In gas phase or frozen matrix:



a series of narrow vibronic bands

In solution / soft matrix:

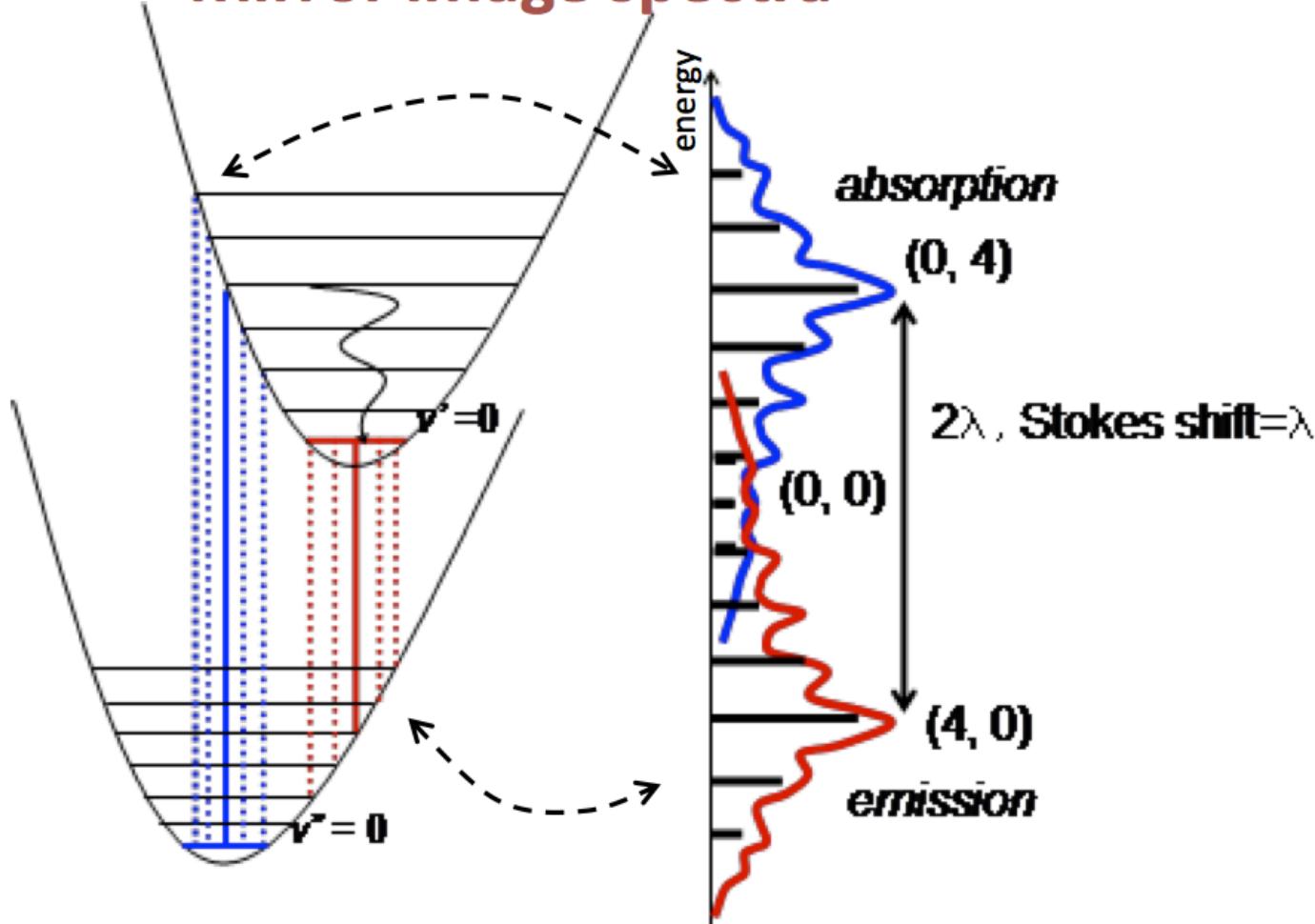


Broadened bands due to solvent motion

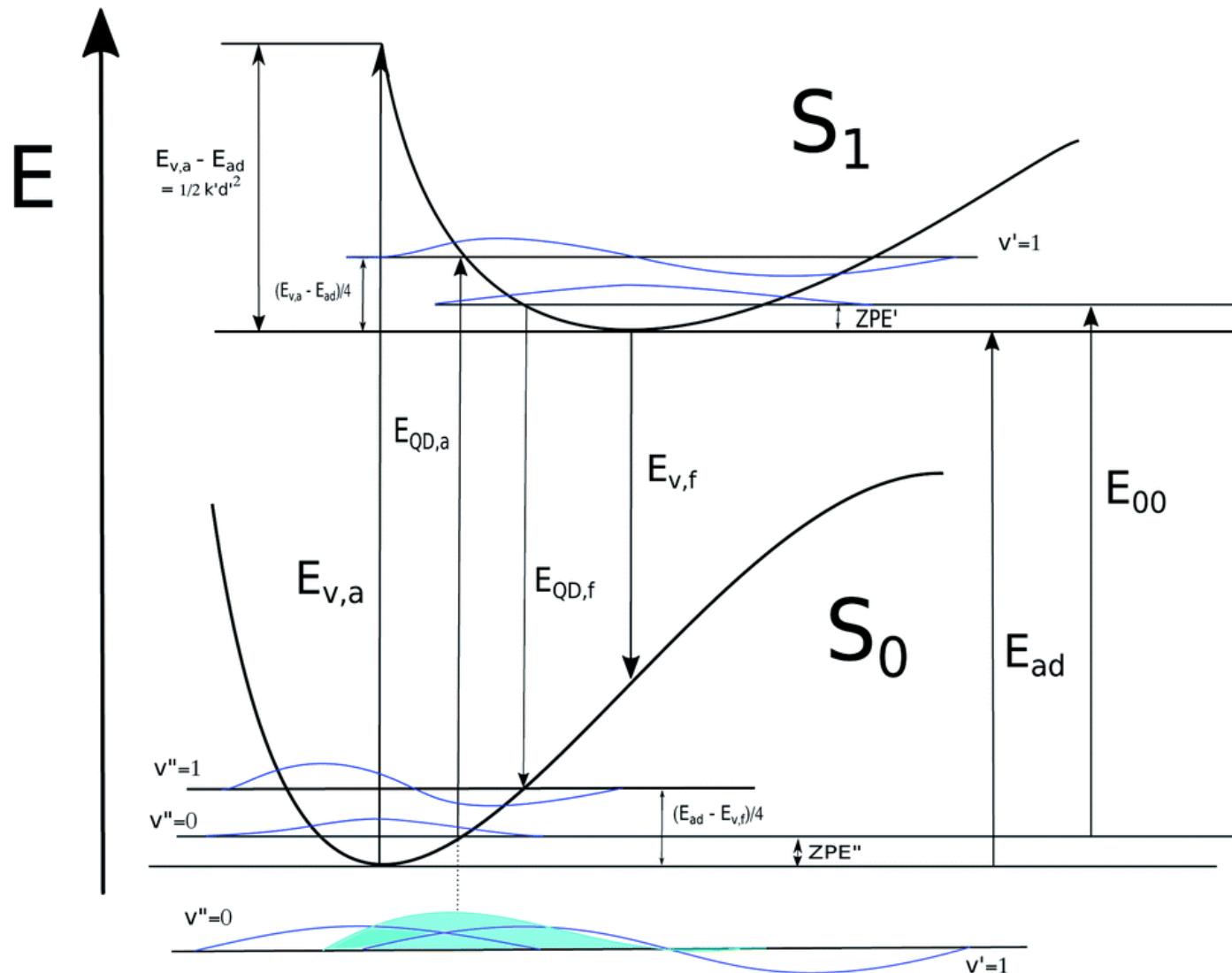
calculations provide stick spectra
(energy of S₀ → S₁ transition and intensity)

Absorption and emission spectra

Mirror image spectra



Vertical vs adiabatic transition



Transition intensities

The intensity of a transition between electronic states p and q is proportional to the “oscillator strength”:

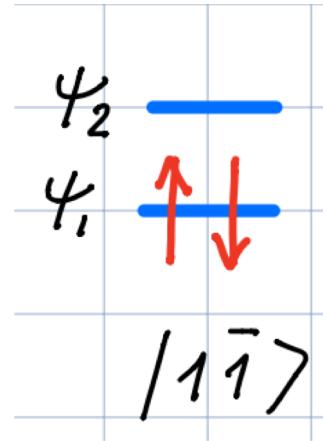
$$f_{pq} = \frac{2m_e}{3\hbar^2} (E_q - E_p) \sum_{\alpha=x,y,z} |\langle \Psi_p | \hat{\mu}_\alpha | \Psi_q \rangle|^2$$

transition dipole moment

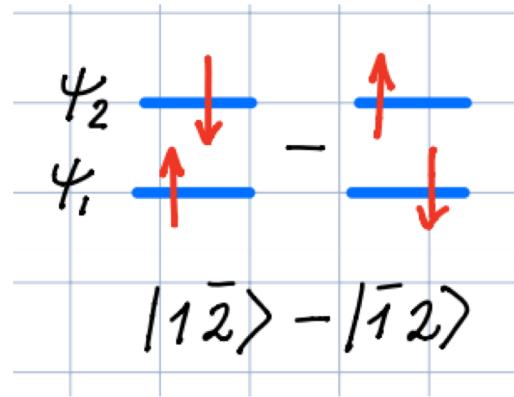
Modeling excited states

Will HF & DFT work for the excited states?

- Excited states are often open-shell, multideterminantal wavefunctions



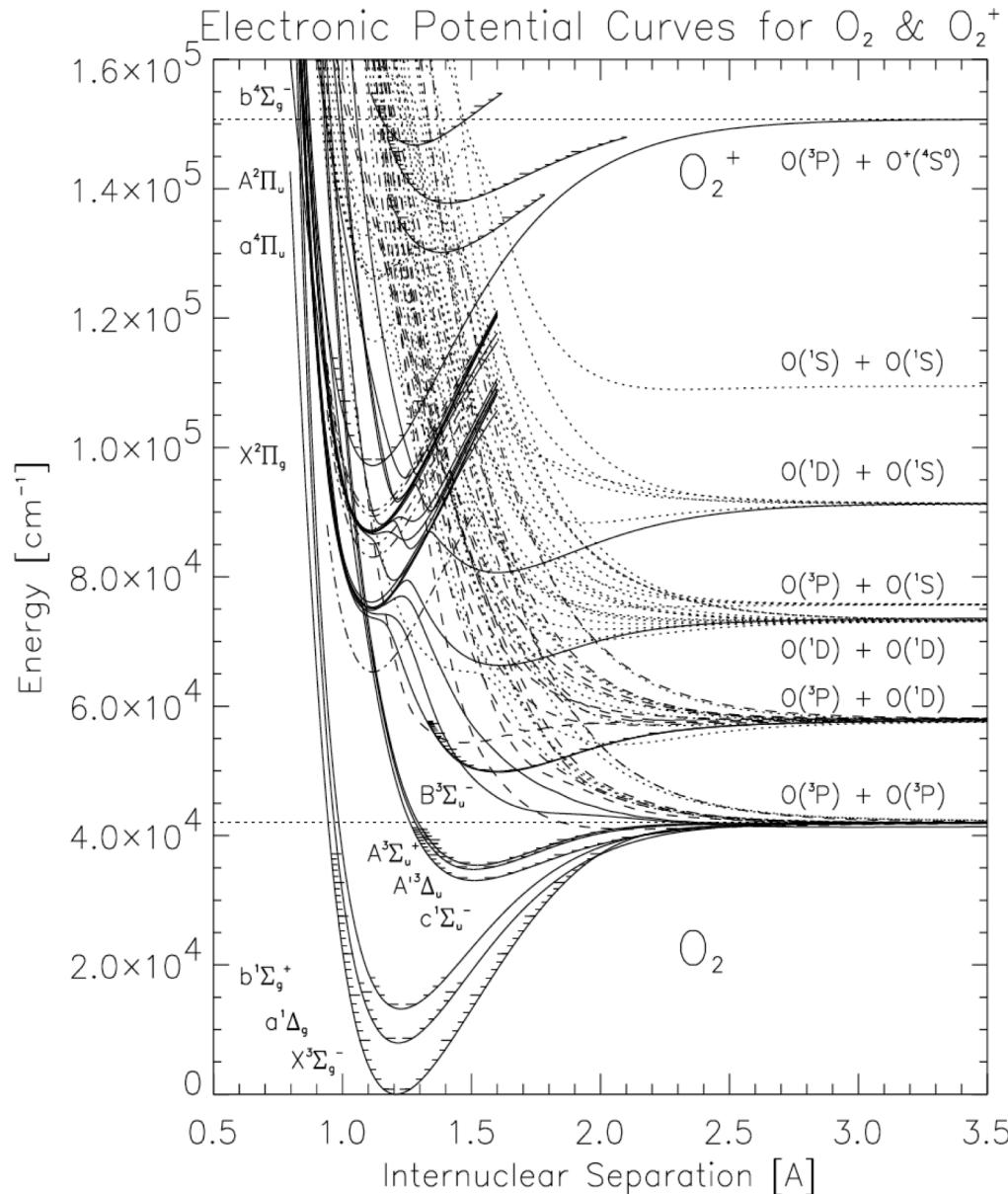
Closed-shell
ground state



Open-shell
excited state

- Ground state methods typically find the lowest state of a given symmetry (collapse to the lowest state due to variational principle)
- Multiple electronic states often cross → Born-Oppenheimer approximation fails often

Potential energy surfaces



Calculated potential energy curves of O_2 molecule.

Reproduced from Morill et al., *Review of electronic structure of molecular oxygen*.

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

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

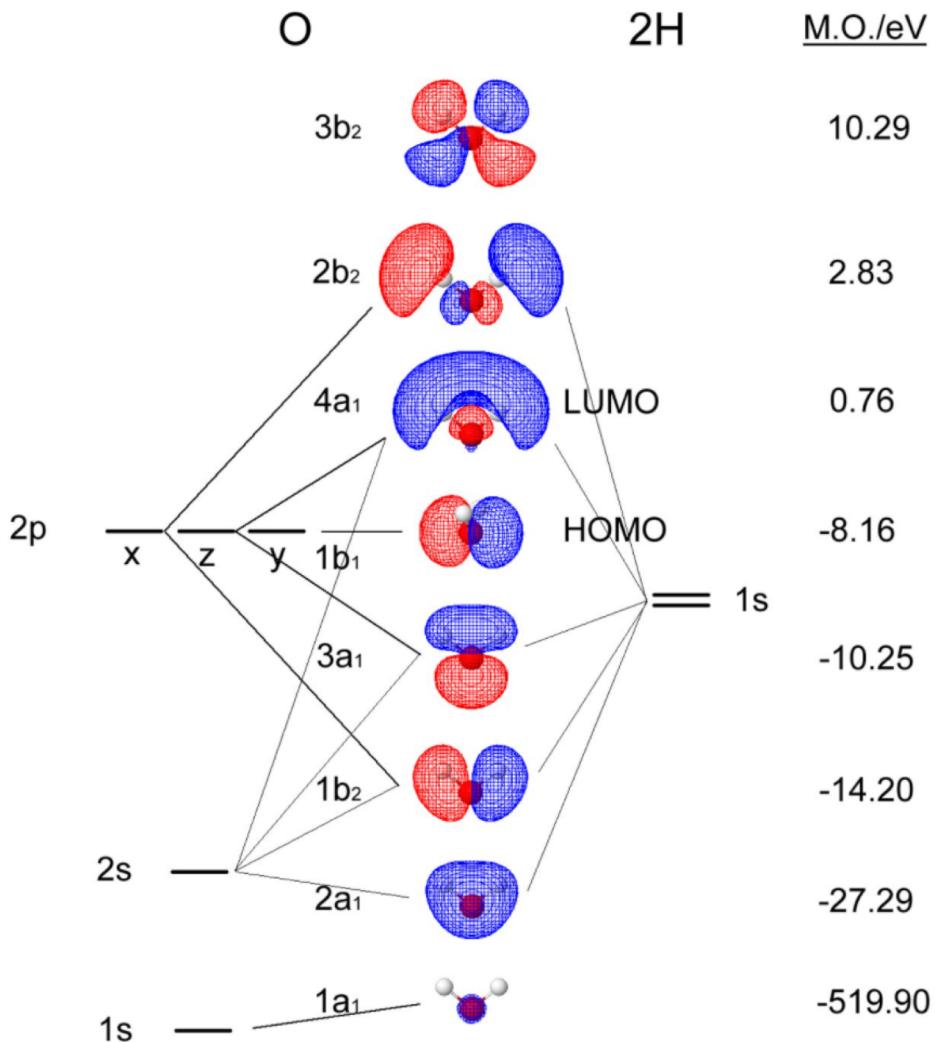
Effectively, these conditions mean that Ψ_k and $\tilde{\Psi}$ are not coupled through Hamiltonian

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}

