

# MOLECULES

CHEM 2430

## SCF equations

$$\hat{F}\phi_i = \sum_{j=1}^N \lambda_{ij}\phi_j, i = 1, \dots, N$$

For closed-shell SCF we can find a unique choice of orbitals for which  $\lambda_{ij} = \varepsilon_i \delta_{ij}$

The resulting canonical orbitals are delocalized

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The usefulness of electronic structure methods is greatly extended by the availability of analytical gradients and Hessians

Grid searches only viable for a small number of degrees of freedom

Suppose you needed 10 energy evaluations for one degree of freedom, and your molecule has 30 degrees of freedom

Would need  $(10)^{30}$  energy evaluations

Analytical geometry gradients  $\frac{\partial E}{\partial q_i}$

$N$  atoms:  $3N$  coordinates,  $q_i$

Available for a wide range of methods

HF, DFT, MP2, CASSCF, CCSD, etc.

HF level gradient CPU time roughly the same as that for the SCF integral and energy calculations.

Need to combine with an algorithm that determines the step size. (E.g., steepest descent)

More rapid convergence can be achieved if we also have second derivatives

The matrix of the second derivatives  $\frac{\partial^2 U}{\partial q_i \partial q_j}$  is the Hessian matrix

Lets consider the use of the Hessian when there re two degrees of freedom

$$E = E_0 + \frac{\partial E}{\partial q_1} \Big|_{q_1^\circ} (q_1 - q_1^\circ) + \frac{\partial E}{\partial q_2} \Big|_{q_1^\circ} (q_2 - q_2^\circ) \\ + \frac{1}{2} \frac{\partial^2 E}{\partial q_1^2} \Big|_{q_1^\circ} (q_1 - q_1^\circ)^2 + \frac{1}{2} \frac{\partial^2 E}{\partial q_2^2} \Big|_{q_2^\circ} (q_2 - q_2^\circ)^2 + \frac{\partial^2 E}{\partial q_1 \partial q_2} \Big|_{q_1^\circ, q_2^\circ} (q_1 - q_1^\circ) (q_2 - q_2^\circ)$$

Now at the minimum

$$\frac{\partial E}{\partial q_1} = 0 = \frac{\partial E}{\partial q_1} \Big|_{q_1^\circ} + \frac{\partial^2 E}{\partial q_1^2} \Big|_{q_1^\circ} (q_1 - q_1^\circ) + \frac{\partial^2 E}{\partial q_1 \partial q_2} \Big|_{q_1^\circ, q_2^\circ} (q_2 - q_2^\circ)$$

$$\frac{\partial E}{\partial q_2} = 0 = \frac{\partial E}{\partial q_2} \Big|_{q_2^\circ} + \frac{\partial^2 E}{\partial q_2^2} \Big|_{q_2^\circ} (q_2 - q_2^\circ) + \frac{\partial^2 E}{\partial q_1 \partial q_2} \Big|_{q_1^\circ, q_2^\circ} (q_1 - q_1^\circ)$$

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} q_1 - q_1^\circ \\ q_2 - q_2^\circ \end{pmatrix} = - \begin{pmatrix} \left( \frac{\partial E}{\partial q_1} \right)_{q_1^\circ} \\ \left( \frac{\partial E}{\partial q_2} \right)_{q_2^\circ} \end{pmatrix}$$

Where  $H_{ij}$  indicates a particular component of the Hessian matrix

$$H \Delta q = -g$$

$$\Delta q = -H^{-1} g$$

$g$  is the vector of gradients

This is the Newton Raphson Method

For large molecules, evaluating the analytical Hessian at every step is very computationally demanding

The quasi-Newton method uses approximate second derivatives, and thus takes less computer time.

In this approach an approximate Hessian is formed as one moves along the potential energy surface.

Steepest descents uses only first derivatives: guaranteed to converge,

Newton methods obviously fail problem if  $H^{-1}$  blows up or if one starts off on the “wrong” side of an inflection point.

Can start with steepest descents and then switch to Newton or quasi-Newton when near convergence

In addition one can re-express the NR and quasi-Newton methods in terms of the eigenmodes and eigenvalues if the Hessian

Improved radius of convergence. Also can be used to locate transition states.

Ethylene  $(1a_g)^2 (1b_{1u})^2 (2a_g)^2 (2b_{1u})^2 (3a_g)^2 (1b_{3g})^2 (1b_{3u})^2$

the HOMO  $1b_{3u}$  is a " $\pi$ " orbital

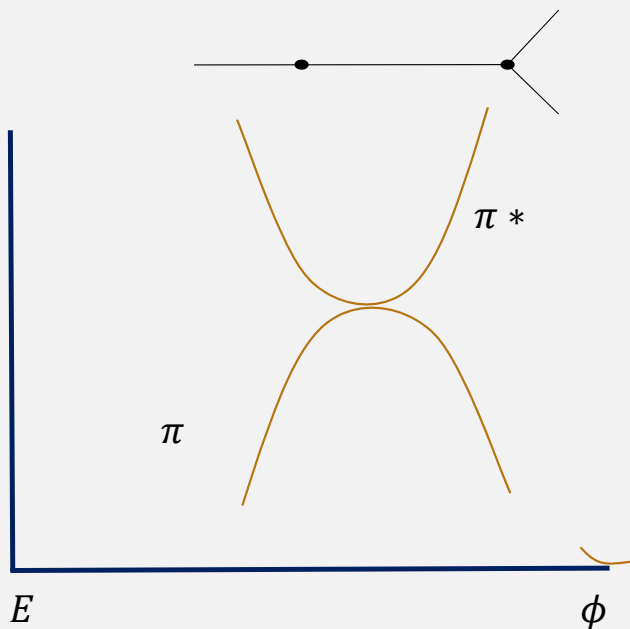
the LUMO  $1b_{2g}$  is a " $\pi^*$ " orbital

Excited  $\pi \rightarrow \pi^*$  singlet and triplet states

Expect these to be twisted with a twist angle of  $90^\circ$

Note that the  $90^\circ$  structure has  $D_{2d}$  symmetry

$D_{2d}$	$E$	$2S_4$	$C_2$	$2C_2'$	$2\sigma_d$		
$A_1$	1	1	1	1	1		$x^2 + y^2, z^2$
$A_2$	1	1	1	-1	-1		
$B_1$	1	-1	1	1	-1		$x^2 - y^2$
$B_2$	1	-1	1	-1	0	$z$	$xy$
$E$	2	0	-2	0	0	$(x, y)$	$(xz, yz)$



Although there is no  $C_4$  rotation axis, there is a improper rotation, hence the degeneracy.

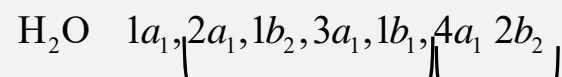
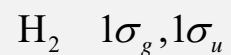
The  $\pi$  and  $\pi^*$  orbitals are degenerate in the perpendicular structure, making it important to use a two configurational wave function

$$\psi = c_1\pi^2 + c_2\pi^{*2}$$

These can be viewed as “atomic like” bound to the core

## Valence vs Rydberg orbitals

Valence space results from minimum basis set.



Occupied  
valence

valence virtual  
orbitals

Ethylene : 6 valence virtual orbitals ( $CH\sigma^*, CC\sigma, CC\pi^*$ )

Excited states involving other virtual orbitals are best classified as Rydberg in nature with an electron in an atomic-like orbital bound to a  $\text{C}_2\text{H}_4^+$  core

E.g., for ethylene  $\dots\pi(3s)$

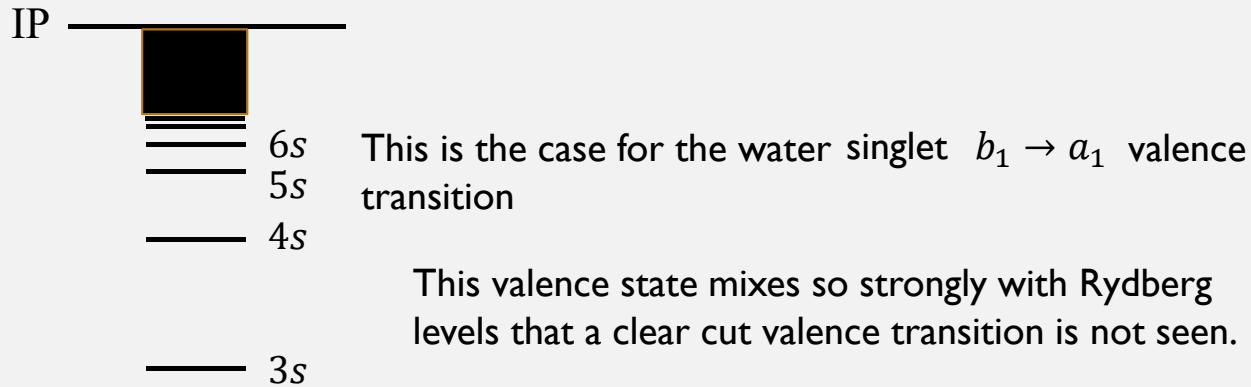
$\dots\pi(3p)$

$\dots\pi(3d)$

etc.



It is possible for Rydberg states to drop below valence excited states in energy



The situation is different in the triplet manifold, in which case the valence state is well below the Rydberg state in energy.

What is the nature of the various transitions?

