

# Molecular Orbitals of Water

Eric Zhou

PS 10 Final Project

# Molecular Orbitals: LCAO

$$\Psi_{H_2O} = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4 + c_5\phi_5 + c_6\phi_6 + c_7\phi_7$$

Atomic Orbitals:  $O_{1s}$        $O_{2s}$        $O_{2p_x}$        $O_{2p_y}$        $O_{2p_z}$        $H_{1s}$        $H_{1s}$

**Objective:** Solve the time-independent Schrödinger equation  $\hat{H}|\Psi_{H_2O}\rangle = E_n|\Psi_{H_2O}\rangle$  where  $\hat{H} =$

$$\underbrace{\sum_{i=1}^{10} \left( -\frac{1}{2} \nabla_i^2 \right)}_{\text{KE of } e^-} + \underbrace{\sum_{i=1}^{10} \sum_{A=1}^3 \left( -\frac{Z_A}{r_{iA}} \right)}_{e^- \text{ nuclear attraction}} + \underbrace{\sum_{i=1}^{10} \sum_{j>i}^{10} \left( \frac{1}{r_{ij}} \right)}_{e^- e^- \text{ repulsion}} + \underbrace{\sum_{A=1}^3 \sum_{B>A}^3 \left( \frac{Z_A Z_B}{R_{AB}} \right)}_{\text{nuclear repulsion}} + \underbrace{\sum_{A=1}^3 \left( -\frac{1}{2M_A} \nabla_A^2 \right)}_{\text{KE of nuclei}}$$

## One-Electron Hamiltonian

Each electron has an energy that can be considered independent from other electrons

## The Hartree-Fock method

approximates this as each independent electron interacting with a fixed, spherically symmetric mean charge distribution

## Born-Oppenheimer theory

approximates the nuclei to be fixed (KE = 0). Therefore, the nuclear repulsion energy becomes a constant

**\*\*NOTE\*\*** atomic units:  $\hbar = 1$ ,  $m_e$  (mass of  $e^-$ ) = 1,  $e$  (charge of  $e^-$ ) = 1,  $k_e = 1$

# *STO-3G Basis Set*

$$\Psi_{H_2O} = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4 + c_5\phi_5 + c_6\phi_6 + c_7\phi_7$$

Atomic Orbitals:    $O_{1s}$              $O_{2s}$              $O_{2px}$              $O_{2py}$              $O_{2pz}$              $H1_{1s}$              $H2_{1s}$

In this project, I calculated the MOs of **minimal basis water**. That means I used the minimum number of basis wavefunctions (seven, one for each atomic orbital) to describe the MOs of water. If I had used a more complicated basis set with more wavefunctions, my calculations would have been more accurate.

Basically, the STO-3G basis wavefunctions approximate each Slater-type atomic orbital as a linear combination of 3 Gaussians. The STO-3G wavefunctions were initially calculated using Hartree-Fock as well, but I used pre-calculated constants<sup>[2,3,4]</sup> to make this project much less cumbersome.

In addition, I took one-electron integral, two-electron integral, and overlap integral data from an open-source *ab initio* electronic structure package<sup>[5]</sup> that also used the STO-3G basis set to make its calculations

[2,3,4] – STO-3G basis set orbitals obtained from an online open-source database/library (Feller 1996) (Schuchardt, et al. 2007) basis set first calculated in 1969 (Hehre, et al. 1969)

[5] – (Crawford, et al. 2007)

# Calculating the Energies and Coefficients

$$\langle E \rangle = \frac{\int d\vec{r}^3 \Psi_{H_2O}^* \hat{H} \Psi_{H_2O}}{\int d\vec{r}^3 \Psi_{H_2O}^* \Psi_{H_2O}}$$

From our work in PS10, we know that by expanding the variational principle and taking the partial derivative of  $\langle E \rangle$  with respect to each of the coefficients  $\{c_1, c_2, \dots, c_7\}$ , we get our **secular equations**, which we can represent as a matrix equation

$$\begin{pmatrix} H_{11} - E_n S_{11} & H_{12} - E_n S_{12} & \cdots & H_{17} - E_n S_{17} \\ H_{21} - E_n S_{21} & H_{22} - E_n S_{22} & \ddots & \vdots \\ \vdots & \ddots & \ddots & \vdots \\ H_{71} - E_n S_{71} & \cdots & \cdots & H_{77} - E_n S_{77} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_7 \end{pmatrix} = 0$$

where  $H_{\mu\nu} = \langle \phi_\mu | \hat{H} | \phi_\nu \rangle$  and  $S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$

**Solve for Energies:**  $\det|H - E_n S| = 0$

**Solve for Coefficients** by plugging the energies back into the secular equations

## **Two Big Questions:**

- 1) How do we build this matrix equation in MATLAB?
- 2) How can we incorporate electron-electron repulsion integrals into the matrix?

# *The Fock Matrix*

$$\begin{aligned}
 \langle \phi_\mu | \hat{H} | \phi_\nu \rangle = H_{\mu\nu} \approx F_{\mu\nu} &= \underbrace{\text{one-electron integrals}}_{\text{KE + V}} + \underbrace{\text{two-electron integrals}}_{\text{double summation}} \\
 &= \left\langle \phi_\mu \left| -\frac{1}{2} \nabla^2 + \sum_{A=1}^3 \left( -\frac{Z_A}{r_A} \right) \right| \phi_\nu \right\rangle + \underbrace{\sum_{\lambda=1}^7 \sum_{\sigma=1}^7 P_{\lambda\sigma} [(\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma)]}_{\text{double summation}}
 \end{aligned}$$

This double summation of two-electron integrals evaluates to a **constant** for every element of the Fock matrix  $(\mu, \nu)$ . In Hartree-Fock theory, the approximation is that each electron interacts with a spherically symmetric charge distribution, which is the sum of all double-electron interactions.

# Two Electron Integrals

$$\sum_{\lambda=1}^7 \sum_{\sigma=1}^7 P_{\lambda\sigma} [(\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma)]$$

$$P_{\lambda\sigma} = 2 \sum_{i=1}^7 c_{\lambda i}^* c_{\sigma i}$$

$$(\mu\nu | \lambda\sigma) = \underbrace{\left\langle \phi_{\mu}(1)\phi_{\nu}(2) \left| \frac{1}{r_{12}} \right| \phi_{\lambda}(1)\phi_{\sigma}(2) \right\rangle}_{\text{Integral over all space, average potential energy created by electron-electron repulsion}}$$

The **density matrix** P is entirely dependent on the coefficients of the atomic orbitals. This makes intuitive sense because the average electron charge distribution should be dependent on the coefficients of the LCAO

## Two-electron Integrals

For  $\mu, \nu, \lambda, \sigma = 1, 2, 3 \dots 7$ , there are **406** possible combinations of two-electron exchange interactions.

( 0 0   0 0 ) =	4.785065404705502
( 1 0   0 0 ) =	0.741380351973408
( 1 1   0 0 ) =	1.118946866342470
( 1 0   1 0 ) =	0.136873385354388
( 1 1   1 0 ) =	0.256633394730974
( 1 1   1 1 ) =	0.817206321526058
( 2 0   0 0 ) =	0.000000000000000
( 3 0   0 0 ) =	0.000000000000000
( 4 0   0 0 ) =	-0.000000000000000
( 2 1   0 0 ) =	0.000000000000000
( 3 1   0 0 ) =	0.000000000000000

The first 11 two-electron integrals<sup>[5]</sup>

# *Solving for Energies and Coefficients*

Solve for Energies:

**Original**  $\Rightarrow \det|H - E_n S| = 0$

**Hartree-Fock-Roothan**  $\Rightarrow \det|F - E_n S| = 0$

Solve for Coefficients:

plug energies back into secular equations:

$$(F - E_n S)(c) = 0$$

where  $c$  is a column vector made of coefficients of LCAO

# *Hartree Fock Self Consistent Field (SCF) Method*

$$\Psi_{H_2O} = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4 + c_5\phi_5 + c_6\phi_6 + c_7\phi_7$$

1. Guess coefficients  $\{c_1, c_2, \dots c_7\}$  for each of the 5 occupied MOs

- This gives us our initial guess of the **charge density field**

→ 2. Calculate new energies and coefficients

- Are the new coefficients  $\{c_1, c_2, \dots c_7\}$  the same as the initial coefficients  $\{c_1, c_2, \dots c_7\}$  ?
  - If NO, it means that our final calculated charge density field is different from our initial charge density field. We must REPEAT the calculation using our new coefficients
  - If YES, it means that the new charge density field is self-consistent with the initial charge density field. At this point, we can STOP repeating our calculations, and we've reached our final answer



# Computational Method

1. Given: one-electron integrals, two-electron integrals, and overlap integrals (Crawford, et al. 2007)
2. I imported this data into MATLAB and calculated my Fock matrix

F =

-19.6393	-5.0218	0.0000	0.0000	-0.0225	-1.0780	-1.0780
-5.0218	-2.0810	-0.0000	0.0000	-0.0945	-0.8390	-0.8390
0.0000	-0.0000	0.0750	0.0000	0.0000	0.0000	0.0000
0.0000	0.0000	0.0000	0.0908	-0.0000	-0.3066	0.3066
-0.0225	-0.0945	0.0000	-0.0000	0.2186	-0.2548	-0.2548
-1.0780	-0.8390	0.0000	-0.3066	-0.2548	-0.2203	-0.2896
-1.0780	-0.8390	0.0000	0.3066	-0.2548	-0.2896	-0.2203

3. I calculated my energies and coefficients using the Hartree-Fock-Roothan equations  $(F - E_n S)(c) = 0$
4. I calculated the Hartree-Fock energy,  $E_{tot} = \sum_{i=1}^5 (E_i + H_{ii}) + V_{nn}$ , where  $V_{nn}$  is the nuclear repulsion energy.<sup>[6]</sup>
5. I checked to see if  $new E_{tot} - old E_{tot} < 10^{-8} \text{ hartrees}$ , which was my tolerance parameter. If not, I repeated the loop.

# Results

Final energies and coefficients 😊

	MO 1	MO 2	MO 3	MO 4	MO 5	MO 6	MO 7
Energy (hartrees)	-19.64807	-0.9212478	-0.2768517	0.02433165	0.07496861	1.0432692	1.13615086
Energy (eV)	-534.6515	-25.068443	-7.5335235	0.66209827	2.04000091	28.3888155	30.9162556
O 1s	0.99961632	-0.2582905	0	0.10320274	-5.50E-16	-0.0806617	1.38E-16
O 2s	0.02627022	0.92307858	-7.65E-16	-0.5545061	2.89E-15	0.5171351	-8.24E-16
O 2px	-3.58E-18	-5.85E-15	-6.66E-16	-5.30E-15	-1	-3.38E-16	4.71E-19
O 2py	-1.96E-18	-2.86E-15	0.65525755	-1.74E-15	-2.16E-16	8.42E-15	-0.6541021
O 2pz	0.00382902	0.08114816	-3.65E-15	0.66680507	-3.47E-15	0.52856725	-3.70E-16
H1 1s	-0.0055865	0.19316697	0.53415239	0.34441483	-1.94E-15	-0.4725895	0.53486
H2 1s	-0.0055865	0.19316697	-0.5341524	0.34441483	-1.50E-15	-0.4725895	-0.53486

$$\Psi_{H_2O} = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4 + c_5\phi_5 + c_6\phi_6 + c_7\phi_7$$

It took 26 iterations of the Hartree-Fock method before my values converged below 1e-08

Iterations	1	2	3	4	5	6	7	8	9
Hartree-Fock Energy (hartrees)	-82.12641363	-74.0655038	-74.89106138	-75.42780736	-75.50319404	-75.51443639	-75.52013396	-75.5230115	-75.52440218
Iterations	10	11	12	13	14	15	16	17	18
Hartree-Fock Energy (hartrees)	-75.52508848	-75.52542822	-75.52559646	-75.52567982	-75.52572113	-75.52574161	-75.52575176	-75.52575679	-75.52575928
Iterations	19	20	21	22	23	24	25	26	
Hartree-Fock Energy (hartrees)	-75.52576051	-75.52576113	-75.52576143	-75.52576158	-75.52576166	-75.52576169	-75.52576171	-75.52576172	

# Error

	MO 1	MO 2	MO 3	MO 4	MO 5	MO 6	MO 7
My Energies (hartrees)	-19.64807041	-0.9212478	-0.2768517	0.02433165	0.07496861	1.0432692	1.13615086
Theoretical E (hartrees)	-20.24094	-1.27218	-0.62173	-0.45392	-0.39176	0.61293	0.75095
Difference (hartrees)	0.592869589	0.35093219	0.34487826	0.47825165	0.46672861	0.4303392	0.38520086
Difference (eV)	16.13281154	9.54935631	9.38462026	13.013897	12.700339	11.7101321	10.4818548

Theoretical energies calculated by Dr. Jean M. Standard (2015)

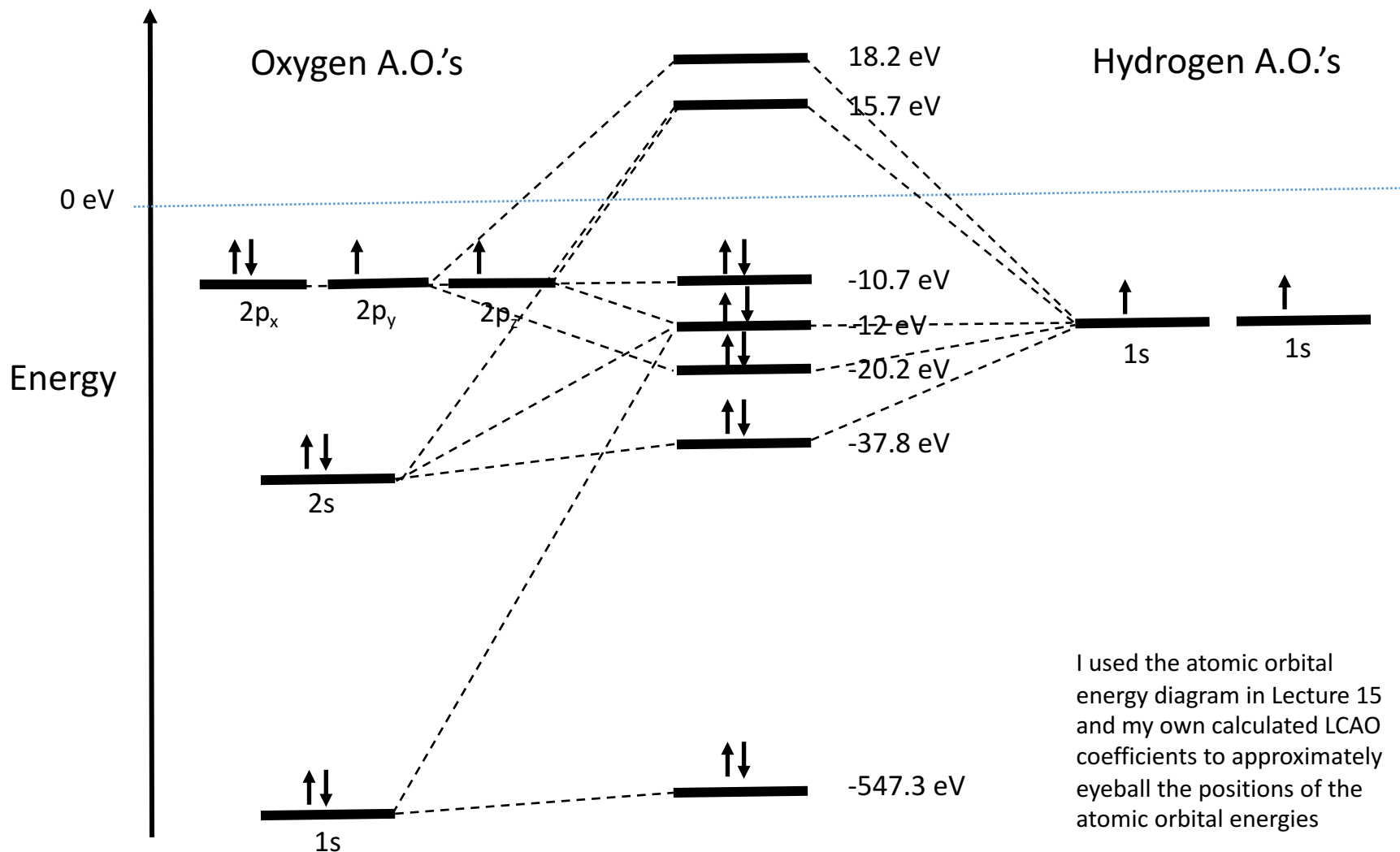
For reasons that will be further justified in the paper, this error was due to the grabbing of one-electron integrals, two-electron integrals, and overlap integrals from different sources on the internet. Although that is the main reason behind this error, I also think MATLAB might not have been precise enough in solving the Hartree-Fock-Roothan secular determinant. Plugging my energies back into the secular determinant gave me values as high as 2.6996e-08, not 0 as expected. This is significant because my tolerance parameter was 1e-08.

Consequences of Error: Unfortunately, my energies for MO 4 and MO 5 are positive, which isn't supposed to happen because they are supposed to be occupied molecular orbitals. (10 electrons from the water molecule occupy 5 molecular orbitals). Luckily, this error didn't significantly impact my coefficients for LCAO.

When I apply the correction term -12.7 eV to my MO energies...

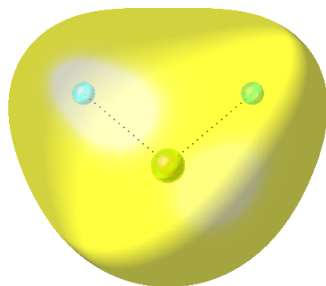
	MO 1	MO 2	MO 3	MO 4	MO 5	MO 6	MO 7
Old Energies (eV)	-534.6515032	-25.068443	-7.5335235	0.66209827	2.04000091	28.3888155	30.9162556
Corrected Energies (eV)	-547.3518421	-37.768782	-20.233862	-12.038241	-10.660338	15.6884765	18.2159167
Theoretical Energies (eV)	-550.7843147	-34.617799	-16.918144	-12.351799	-10.660338	16.6786834	20.4344008
Difference (eV)	3.43247257	-3.1509827	-3.3157187	0.31355799	0	-0.9902069	-2.2184842

# Energy Diagram of Water

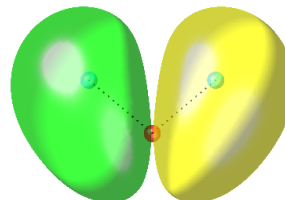


# *MOs of Water*

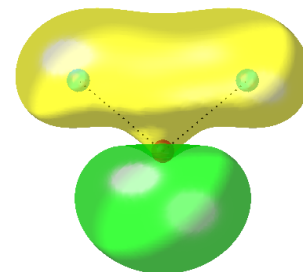
Occupied Orbital 2: Energy = -37.7688 eV



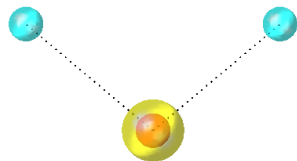
Occupied Orbital 3: Energy = -20.2339 eV



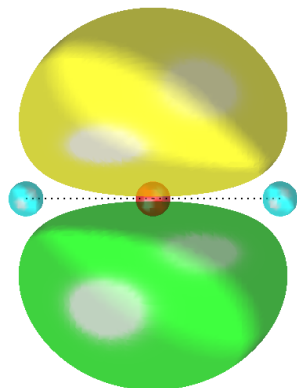
Occupied Orbital 4: Energy = -12.0382 eV



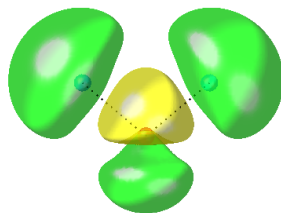
Occupied Orbital 1: Energy = -547.3518 eV



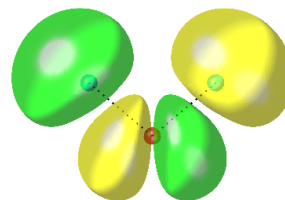
Occupied Orbital 5: Energy = -10.6603 eV



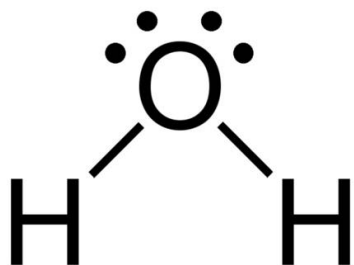
Unoccupied Orbital 6: Energy = 15.6885 eV



Unoccupied Orbital 7: Energy = 18.2159 eV



# Compare to Valence Bond Theory



2 lone pairs?

Location of electrons?

$sp^3$  hybridization?

- MO calculations seem to only show 1 obvious lone pair, which is oxygen's  $p_x$  orbital (MO 5)
- Even if we consider the other possible non-bonding pair lone pair, the O 2s orbital (MO 2), it is  $\sim 30\text{eV}$  lower than the other non-bonding pair (MO 5). There certainly are not 2 lone pairs sitting in *equal*  $sp^3$  orbitals. A tetrahedral geometry of orbitals is simply not the case.
- VSEPR  $sp^3$  model only considers two types of orbitals for water, which would result in two spectrum peaks, not three peaks as seen on the figure at the right<sup>[6]</sup>

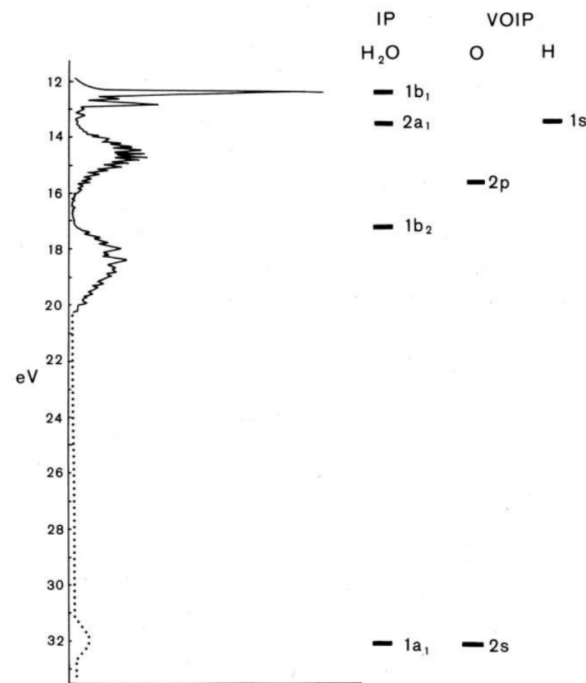


Figure 6. Photoelectron spectrum of the H<sub>2</sub>O molecule with the ionization energies of the various molecular orbitals and atomic orbitals of the H and O atoms on the same energy scale.

# References

- [1] - Szabo, A., and N. S. Ostlund. *Modern quantum chemistry: Introduction to advanced electronic structure theory*. McGraw-Hill, 1989.
- [2] - Feller, D. "The role of databases in support of computational chemistry calculations." *Journal of Computational Chemistry*, vol. 17, no. 13, 1996, pp. 1571-1586, doi:10.1002/jcc.9.
- [3] - Schuchardt, K. L., et al. "Basis Set Exchange: A Community Database for Computational Sciences." *Journal of Chemical Information and Modeling*, vol. 47, no. 3, 2007, pp. 1045-1052, doi:10.1021/ci600510j.
- [4] - Hehre, W. J. "Self-Consistent Molecular-Orbital Methods. I. Use of Gaussian Expansions of Slater-Type Atomic Orbitals." *The Journal of Chemical Physics*, vol. 51, no. 6, 1969, p. 2657, doi:10.1063/1.1672392.
- [5] - Crawford, T. D., et al. "PSI3: An open-source Ab Initio electronic structure package." *Journal of Computational Chemistry*, vol. 28, no. 9, 2007, pp. 1610-1616.
- [6] - Standard, Jean M. "A Hartree-Fock Calculation of the Water Molecule." *Department of Chemistry - Illinois State University*, 22 Apr. 2015, chemistry.illinoisstate.edu/standard/che460/handouts/460water.pdf.
- [7] - Laing, Michael. "No rabbit ears on water. The structure of the water molecule: What should we tell the students?" *Journal of Chemical Education*, vol. 64, no. 2, 1987, p. 124.

With thanks to Michael Mavros for his guidance and support throughout this project, Victor Zhao for his patience and willingness to help, Adam Cohen for his fascinating lectures and office hours, and Lu Wang for her clear explanations to my questions 😊