

## 28.1: The Chemical Bond in the Water Molecule Using a Minimal Basis

For a minimal representation of the two hydrogen atoms, we need two  $1s$  functions, one centered on each atom. Oxygen has electrons in the second principal quantum level, so we will need one  $1s$ , one  $2s$ , and three  $2p$  functions (one each of  $p_x$ ,  $p_y$ , and  $p_z$ ). Summarizing, for a minimal representation of the water wave function we need five orbitals on oxygen, plus one each on the hydrogen atoms, for a total of 7 functions. From these atomic functions, we can build a total wave function using the LCAO method of [chapter 27](#), and then we can use the variational principle, in conjunction with the Hartree—Fock (HF) method, to build and solve a secular determinant that looks is similar to that in [Equation 27.3.4](#), with  $m = 7$  being the total number of basis functions. The approximated Hamiltonian operator in the HF method is called the Fock operator, and it can be divided into one-electron integrals, comprising the kinetic and potential energy contributions:

$$\begin{aligned} K_{ij} &= \int \phi_i^* \hat{K} \phi_j d\tau = \int \phi_i^* \left( -\frac{1}{2} \nabla^2 \right) \phi_j d\tau \\ V_{ij} &= \int \phi_i^* \hat{V} \phi_j d\tau = \int \phi_i^* \left( - \sum_k^{\text{nuclei}} \frac{Z_k}{r_k} \right) \phi_j d\tau, \end{aligned} \quad (28.1.1)$$

as well as two-electron integrals describing the coulomb repulsion between electrons:

$$V_{ijkl} = \iint \phi_i^* \phi_j^* \hat{r}_{12} \phi_k \phi_l d\tau_1 d\tau_2 = \iint \phi_i^* \phi_j^* \left( \frac{1}{r_{12}} \right) \phi_k \phi_l d\tau_1 d\tau_2. \quad (28.1.2)$$

Despite the minimal basis set, the total number of integrals that need to be calculated for water is large, since  $i$ ,  $j$ ,  $k$ , and  $l$  can be any one of the 7 basis functions. Hence there are  $7 \times 7 = 49$  kinetic energy integrals, and the same number of potential energy integrals for each nucleus, resulting in  $7 \times 7 \times 3 = 147$ . The grand total of one-electron integrals is thus 196. For the two-electron integrals, we have  $7 \times 7 \times 7 \times 7 = 2,401$  integrals to calculate. Overall for this simple calculation on water, we need almost 2,600 integrals.<sup>1</sup>

All this to find 5 occupied molecular orbitals from which to form a final Slater determinant (10 electrons, two to an orbital, so 5 orbitals). The situation sounds horrible, but it should be recognized that the solutions to all of the integrals are known to be analytic formulae involving only interatomic distances, cartesian exponents, and the values of a single exponent in the atomic functions. If we use slightly simpler gaussian functions instead of the more complicated hydrogenic solutions, the total number of floating-point operations to solve the integrals is roughly 1,000,000. In computer speak that's one megaflop (megaflop = million FLoating-point OPerations). A modern digital computer processor can achieve gigaflop per second performance, so the computer can accomplish all these calculations in under one second. An additional way in which things can be improved is to recognize that the molecule has symmetries that can be exploited to reduce the number of total integrals that needs to be calculated.

1. The numbers computed here involve the minimum amount of uncontracted "hydrogenic" functions that can be used for calculation on water. In real-life calculations a linear combination of simpler primitive functions (gaussians) is used to describe a single uncontracted function. For example in the simplest case, the STO-3G basis set, each uncontracted function is composed of 3 primitive gaussian functions. Thus, for any individual one-electron integral, there will be  $3 \times 3 = 9$  separate integrals involving the primitives. There are thus  $9 \times 196 = 1,764$  individual primitive one-electron integrals. As for the two-electron integrals, again, every individual integral will require considering every possible combination of constituent primitives which is  $3 \times 3 \times 3 \times 3 = 81$ . Thus, the total number of primitive two-electron integrals is  $81 \times 2,401 = 194,481$  (gulp!) Notice that even for this small molecule the number of two-electron integrals totally dominates the number of one-electron integrals. The disparity only increases with molecular size. Notice: Portions of this section are based on Prof. C.J. Cramer's lecture notes available (here)[[http://pollux.chem.umn.edu/4502/3502\\_lecture\\_29.pdf](http://pollux.chem.umn.edu/4502/3502_lecture_29.pdf)]

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