Chem 3502/4502 **Physical Chemistry II (Quantum Mechanics)** 3 Credits

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Answers to Homework Set 8

From lecture 29: What is the value of P_{52} for water after the first SCF step (i.e., at cycle 2)? By what percentage did it change compared to the initial guess? By what percentage did the total energy change for this same step?

We must evaluate

$$P_{\lambda\sigma} = 2 \sum_{i}^{\text{occupied}} a_{\lambda i} a_{\sigma i}$$

for $\lambda = 5$ and $\sigma = 2$ using the occupied MO coefficients after the first SCF step which were given in the lecture notes as

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Occupied MO coefficients at cycle   2.
          1            2            3            4            5
   1  .994123     -.233041      .000000     -.103527      .000000
   2  .026666      .834174      .000000      .541326      .000000
   3  .000000      .000000      .000000      .000000     1.000000
   4  .000000      .000000      .608401      .000000      .000000
   5 -.004400     -.131110      .000000      .774771      .000000
   6 -.006039      .156851      .443140     -.279656      .000000
   7 -.006039      .156851     -.443140     -.279656      .000000
```

As there are 5 occupied MOs, we will sum over all 5 the product of a_{5i} with a_{2i}. So, for MO 1 we have –0.004400 times 0.026666. For MO 2, –0.131110 times 0.834174. For MO 3, 0 times 0. For MO 4, 0.774771 times 0.541326. And, for MO 5, 0 times 0 again. If we sum the three non-zero products and multiply by 2 (see equation above) we obtain 0.620 (to 3 digits). Compared to the original value of 0.618, this is a change of about 0.3%.

The total energies for steps one and two were given in the Lecture as

E(RHF) = –74.893 002 803 A.U. after 1 cycles
E(RHF) = –74.961 289 145 A.U. after 2 cycles

which is a difference of –0.068 29 a.u. or –42.9 kcal/mol. Note that the change in energy is only about 0.1 % compared to the change in the density matrix element of 0.3%. It is

typical that the energy converges more quickly than the density matrix because the energy from the variational process represents a stationary point (so the "slope" of the energy near the minimum is very small with respect to changes in the density).

From lecture 30:

What about the radical cation generated by ionization of the least tightly held electron in water? From which orbital may it be considered to be taken? Based on that analysis, if you were to allow the geometry to relax from that of neutral water, what would you expect to happen to the OH bond lengths? What about the internal HOH bond angle?

The least tightly held electron is in the HOMO, which is the out-of-plane pure p orbital on oxygen. As this orbital is not involved in bonding in any way, our first-order analysis would be that there will be no change at all in the geometry of water upon ionization. Of course, the remaining orbitals relax a bit when an electron is taken away, but it is not obvious from looking at the neutral orbitals exactly how that will affect geometry. One would just have to do the calculation, but that's not part of the homework…

From lecture 31:

Instead of thinking about the electrons that belong to a single atom, it is sometimes interesting to ask about the electrons belonging to each basis function. It should be reasonably clear from inspection of eq. 31-4 that the population of an AO basis function *r*, as opposed to an atom, is

$$N_r = P_{rr} + \sum_{s \neq r} P_{rs} S_{rs}$$

where *r* and *s* are AO basis functions. Compute the population of each basis function for water using the **P** and **S** matrices given above. What chemical interpretation(s) can be associated with your computed values?

Using

$$\mathbf{S} = \begin{bmatrix} 1.000 & & & & & & \\ 0.237 & 1.000 & & & & & \\ 0.000 & 0.000 & 1.000 & & & & \\ 0.000 & 0.000 & 0.000 & 1.000 & & & \\ 0.000 & 0.000 & 0.000 & 0.000 & 1.000 & & \\ 0.055 & 0.479 & 0.000 & 0.313 & -0.242 & 1.000 & \\ 0.055 & 0.479 & 0.000 & -0.313 & -0.242 & 0.256 & 1.000 \end{bmatrix}$$

and

$$\mathbf{P} = \begin{bmatrix} 2.106 & & & & & & \\ -0.445 & 1.964 & & & & & \\ 0.000 & 0.000 & 2.000 & & & & \\ 0.000 & 0.000 & 0.000 & 0.736 & & & \\ -0.105 & 0.619 & 0.000 & 0.000 & 1.246 & & \\ -0.015 & -0.032 & 0.000 & 0.539 & -0.470 & 0.597 & \\ -0.015 & -0.032 & 0.000 & -0.539 & -0.470 & -0.193 & 0.597 \end{bmatrix}$$

Carrying out the indicated calculations gives:

Atomic orbital basis function	Number of electrons
O 1s	1.999
O 2s	1.828
O $2p_x$	2.000
O $2p_y$	1.073
O $2p_z$	1.473
H_a 1s	0.814
H_b 1s	0.814

Things to note include:

1) The oxygen 1s orbital is essentially completely filled, as expected given that core orbitals do not participate in bonding.

2) The atomic populations are simply the sum of the orbital populations on a given atom.

3) The oxygen $2p_x$ orbital is exactly doubly occupied, consistent with it not being able to overlap with any other basis function.

4) There are more electrons in the oxygen $2p_z$ than in the $2p_y$, which is consistent with the geometry of water. The bond angle of greater than 90 deg means that the hydrogen 1s

electrons would repel $2p_y$ electrons more than $2p_z$ electrons, so oxygen may as well put more electrons into $2p_z$.

5) The oxygen 2s orbital is not completely doubly filled because it is hybridized into bonding and antibonding orbitals, and the antibonding orbitals are empty.