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Bonding/antibonding Character of “lone Pair” Molecular Orbitals from their Energy Derivatives; Consequences for experimental Data

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Abstract

The derivative of molecular orbitals (MO) energies with respect to a bond length (dynamic orbital force, DOF) is used to estimate the bonding/antibonding character of valence MOs along this bond, with a focus on lone pair MOs, in a series of small molecules: AH (A = F, Cl, Br), AH₂ (A = O, S, Se) AX₃ (A = N, P, As; X = H, F) and H₂CO. The HOMO DOF agrees with the calculated variation of bond length and force constant in the corresponding ground state cation, and of bond length variation by protonation. These results also agree with available experimental data. It is worthy to note that the p-type HOMOs in AH and AH₂ are found bonding. The lone pair MO is bonding in NH₃, while it is antibonding in PH₃, AsH₃, and AF₃.

Introduction

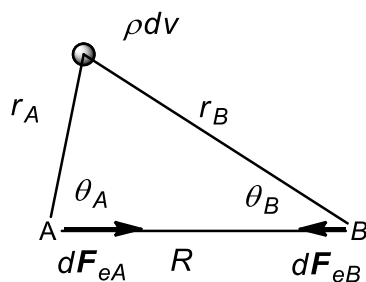
How to define the bonding/antibonding character of a MO ?

The bonding/antibonding character can be based on essentially two criteria, energy or force, with different possible definitions on these criteria.

The IUPAC Gold Book¹ prefers the energy point of view, a bonding MO being characterized by “an increase in the total bonding”. This generally corresponds also to a MO energy lower than the mean energy of the AOs constituting this MO. These definitions involve the whole molecule. Nevertheless, for the chemist, it is important to characterize local MO properties, i.e. their bonding/antibonding character along a bond, or more generally with respect to geometrical parameters. From this point of view one can consider that a MO is bonding along a given bond if its occupancy increases the bond dissociation energy.

Other definitions are based on force concepts. A MO will be said bonding if its electrons exert an attractive force on the nuclei of concern. For this purpose, a useful guideline is provided by the “Berlin function” $f(x, y, z)$ which performs a partition of the space into bonding and antibonding areas.² With the notations of Scheme 1, for a diatomic molecule AB, the forces F_{eA} and F_{eB} exerted by an electron density ρ on nuclei A and B are (Eq. 1) :

$$F_{eA} = F_{eB} = -\frac{1}{2} \int \left[\frac{z_A}{r_A^2} \cos \theta_A + \frac{z_B}{r_B^2} \cos \theta_B \right] \rho dv = -\frac{1}{2} \int f(x, y, z) \rho(x, y, z) dv \quad (1)$$



Scheme 1. Forces acting in a diatomic molecule AB

The bonding/antibonding zones are thus characterized by a positive/negative value of the function f . They are separated by a non-bonding surface given in Fig. 1 for a symmetrical A_2 molecules and the unsymmetrical HF one.

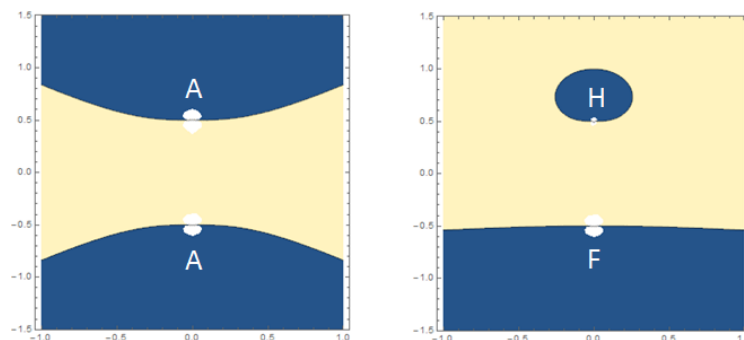


Figure 1. Bonding ($f > 0$, yellow) and antibonding ($f < 0$ dark blue) zones for diatomic A_2 and HF molecules.

On this basis, the total electron density is decomposed into MO densities and thus into additive orbital forces which quantify their bonding character.^{3,4,5}

Another concept of “orbital forces” was proposed by Tal and Katriel⁶. It is built up from the MO energy derivatives with respect to nuclear coordinates. According to the Koopmans theorem⁷, the MO energy can be expressed as Eq. 2:

$$\varepsilon_i = E^0 - E_i^+ \quad (2)$$

where E^0 is the Hartree-Fock (H-F) energy of a neutral species and E_i^+ the energy of the frozen orbital cation resulting from the removal of one electron from the i^{th} spin-orbital ϕ_i . For a diatomic molecule, the derivative with respect to the internuclear distance R yields (Eq. 3):

$$\frac{d\varepsilon_i}{dR} = \frac{dE^0}{dR} - \frac{dE_i^+}{dR} \quad (3)$$

At the equilibrium value R_e of the neutral species, $dE^0/dR = 0$ and (Eq. 4):

$$\left(\frac{d\varepsilon_i}{dR} \right)_{R=R_e} = - \left(\frac{dE_i^+}{dR} \right)_{R=R_e} \quad (4)$$

Eq. 4 means that if $\varepsilon_i = d\varepsilon_i/dR$ is positive, the ion energy E_i^+ tends to decrease by lengthening R which characterizes a bonding ϕ_i MO.

These orbital forces are not additive since the total H-F energy is not the sum of occupied MO energies. The term of “dynamical orbital forces” (DOF) was proposed by Averill and Painter for these derivatives because they arise from electron removing (whereas the additive Bader orbital forces appear as “static orbital forces”).⁸ These forces are closely related to the Mulliken’s criterion of the “bonding power” of an electron.⁹

Because canonical MOs are delocalized on the whole molecule, a given MO can be more or less bonding along a given bond and antibonding along another one. These characters can be evaluated by calculating the energy derivative (DOF) with respect to each bond by a finite difference of length. In most of cases, a small variation of one bond length, typically a few 10^{-3} Å, has a negligible effect on the other internal coordinates and the resulting DOF can be regarded as a reliable measure of the local (on a given bond) bonding/antibonding character.

Because Eq. 4 involves the neglect of MO relaxation and correlation energy, the question arises if the DOF correctly predicts the variation of geometry (and eventually of other properties) following the ionization. At least, one can expect that this quantity reflects a trend which indicates the sign of this variation. As a matter of fact, this assumption has been fully validated in a recent work¹⁰, in which were reported the DOFs of the valence shell MOs of a panel of 19 diatomic species and of HCN, HNC and CH₃CN, focusing our attention on the “lone pairs” MOs of some coordinating species.

Very few works have been devoted to the study of canonical MO derivatives^{11,12,13}. Tal and Katriel⁶ have determined the bonding/antibonding character of the MOs of diatomic homonuclear molecules of the Li-F period. Also, the variation of the DOFs of selected MOs along a reaction coordinate (RC) highlights the nature of the reorganization of these MOs and what stage of the RC it occurs. Moreover, the shape of the DOF curves reveals the existence and precise location of MO avoided crossings.¹⁴ Because Kohn-Sham MO energy also approximate ionisation energy¹⁵, its derivative was used successfully by several authors as a criterion of bonding character.^{8, 16,17}

In this work, we will focus on the MOs associated to “lone pairs” of small molecules AH (A = F, Cl, Br), AH₂ (A = O, S, Se), AH₃, AF₃ (A = N, P, As) and H₂CO. It has been already pointed out that “lone pair” and “non-bonding pair” are not synonymous and, using the localization procedure of Ciolkowski, Chesnut¹⁸ showed that the participation to bonding in some of the preceding molecules is approximately 10-15%. From a qualitative point of view, most of time no “visual” criterion, based on the presence or not of nodal surfaces cutting the bond, can be used to decide whether such MOs are more or less bonding or antibonding. The results will be compared with the variation of observable physical data upon ionization and protonation involving these lone pairs: bond lengths, vibration frequencies and forces constants, computed at a reliable level, and experimental available results.

Calculation details

Calculations of MO energy derivatives (Dynamic Orbital Forces, DOF) have been performed at the HF/6-311G** level, and for sake of comparison, at the B3LYP/6-311G** level, after optimization of geometrical parameters at the same level. The derivatives are computed by finite difference of the length of equivalent bonds by $2-3 \cdot 10^{-3}$ Å. In a previous work¹⁰ it was stated that that higher level basis sets do not improve significantly the DOF values. The DOFs have been visualized using red (antibonding)/blue (bonding) arrows, whose thickness is proportional to their value in percent of the maximum DOF of the occupied MOs.

The geometry of neutral molecules, positive ions and protonated species were computed at the CCSD(T)/cc-pVTZ level. Vibration frequencies and force constants were computed at the B3LYP/cc-pVTZ level. The GAUSSIAN 09 series of program¹⁹ was used.

Results and discussion

Molecules HF, HCl and HBr

The results are gathered in Table 1. The DOFs of the valence shell are visualized in Figure 2 in the case of HF.

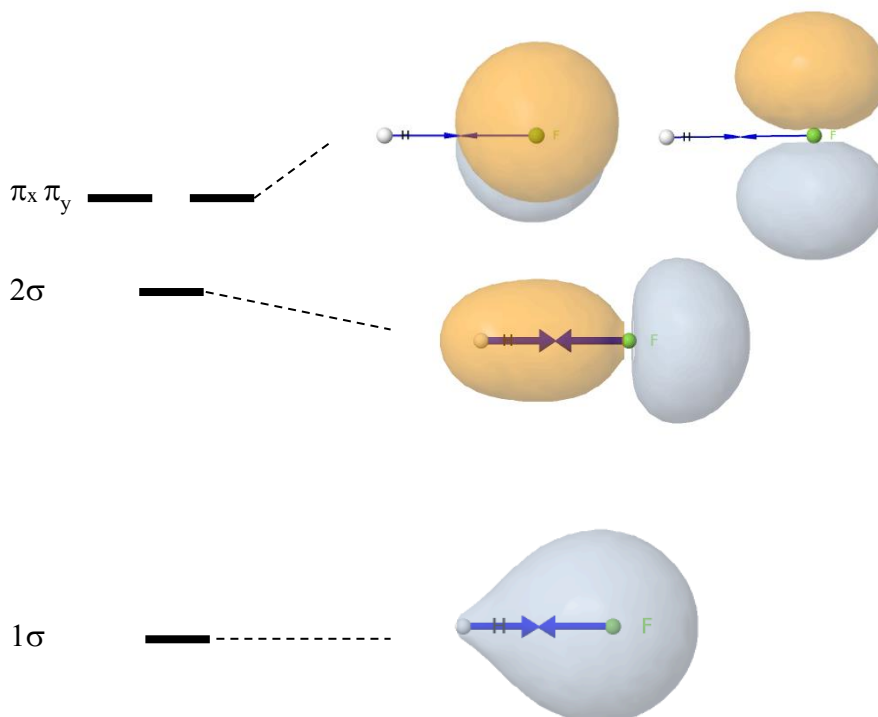


Figure 2. *DOF of valence shell MOs of HF. Blue/red arrows indicate a bonding/antibonding character, with a thickness proportional to the % of maximum DOF*

The Table 1 indicates that 1σ and 2σ usually referred as σ bonding MO and sp lone pair MO respectively are almost equally bonding. The π MOs, usually described as “purely non-bonding” have in fact a marked bonding character. This character is partly due to the presence of empty p MOs of hydrogen in an extended basis set. Nevertheless, even at the STO-3G level, this character remains (0.011 au for HF), though the overlap with the 1s AO of hydrogen is zero. It means that the pure atomic p density on atom A is intrinsically bonding, i.e. exerts an attractive force on the H nucleus. It can be understood qualitatively from Figure 1: the non-bonding surface does not divide equally the 2p density which can be seen slightly more localized in the bonding region.

Table 1. Molecules HF, HCl and HBr: DOFs (au) of valence MOs at the H-F(B3LYP) levels; bond lengths (Å) of neutral R(AH), cationic R(AH⁺) and protonated R(AH₂⁺) species; vibration frequency (cm⁻¹) and force constant of neutral ν (AH) and cationic ν (AH⁺) species.^a 6-311 G** ^b CCSD(T)/cc-pVTZ; ^c B3LYP/ cc-pVTZ; ^d experimental values from the NIST database (ref. 20)

| | HF | HCl | HBr |
|--|-----------------------------------|---------------|---------------|
| MO | DOF H-F(B3LYP)^a | | |
| 1 σ | 0.201 (0.167) | 0.103 (0.082) | 0.085 (0.063) |
| 2 σ | 0.212 (0.118) | 0.111 (0.067) | 0.093 (0.058) |
| π (HOMO) | 0.056 (0.047) | 0.013 (0.013) | 0.008 (0.008) |
| Bond lengths^b | | | |
| R(AH) | 0.9173 | 1.2772 | 1.4129 |
| R(AH ⁺) | 1.0023 | 1.3175 | 1.4451 |
| ΔR_{ion} (calc) | 0.0850 | 0.0403 | 0.0322 |
| ΔR_{ion} (exp) ^d | 0.097 | 0.040 | 0.034 |
| R(AH ₂ ⁺) | 0.9617 | 1.3068 | 1.4370 |
| ΔR_{prot} | 0.0444 | 0.0296 | 0.0241 |
| Stretching vibration frequency (force constant)^c | | | |
| ν (AH) | 4088.0 (10.42) | 2936.8 (5.26) | 2620.5 (4.13) |
| ν (AH ⁺) | 2992.3 (5.58) | 2616.8 (4.18) | 2372.9 (3.39) |
| $\Delta \nu_{\text{ion}}$ (calc) | -1095.7 | -320 | -247.6 |
| $\Delta \nu_{\text{ion}}$ (exp) ^d | -1225. | -318. | -207. |

The bonding character of π MOs agrees with the calculated bond lengths of neutral and cationic ($^2\pi$) species: in each case the cation HF⁺, HCl⁺, HBr⁺ exhibit a bond lengthening ($\Delta R_{\text{ion}} > 0$) with respect to the neutral molecule. As also expected, the ionization results in a decrease of the vibration frequency and force constant. The protonation results also in a bond lengthening, but less marked than in ionization: it can be viewed essentially as a partial electron removing from one π MO because the HAH⁺ angle is close to 90° (111° for A= F, 94° for A = Cl and 92° for A = Br). Experimental results available in the NIST database²⁰, reported in Table 1, agree with the bonding character of the HOMO, with an increase of the bond length and a decrease of the vibration frequency, close to calculated values. Also, an increase of the bond length from 0.917 Å to 0.961 Å has been observed in H₂F⁺.²¹

We can note that the B3LYP DOF values are in qualitative agreement with H-F ones and close to them for the HOMO, but may differ significantly in some other cases.

Molecules H₂O, H₂S and H₂Se

The results are gathered in Table 2. The DOFs are visualized for H₂O in Figure 3.

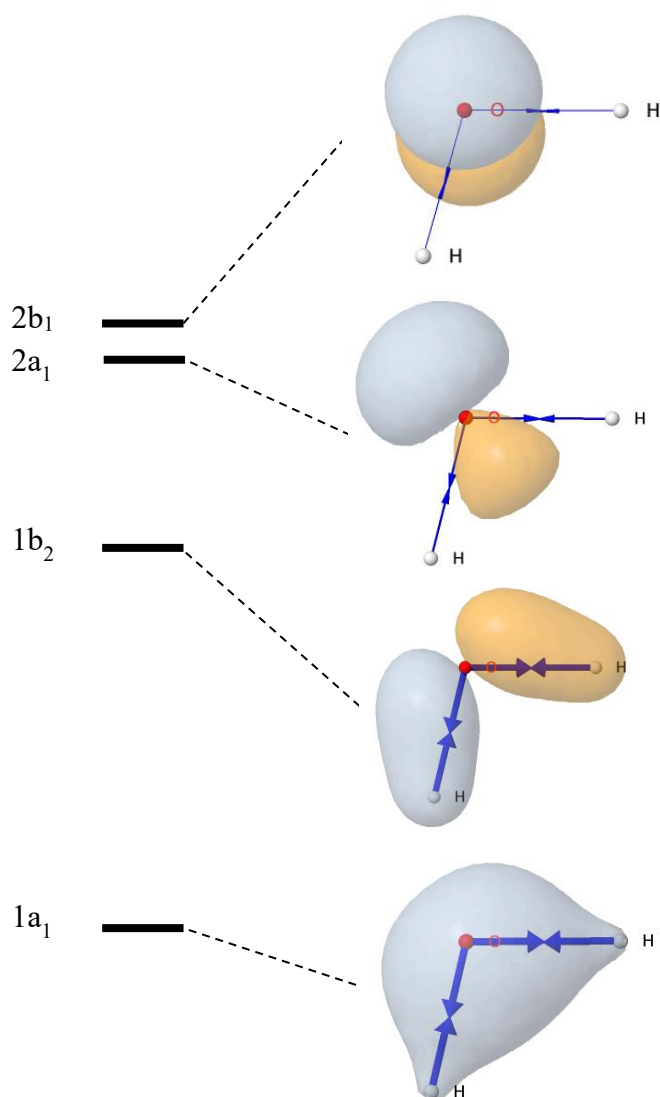


Figure 3. Molecule H_2O . Graphical representation of H-F DOFs of valence shell MOs. Blue/red arrows indicate a bonding/antibonding character, with a thickness proportional to the % of maximum DOF

The $1a_1$ and $1b_2$ MOs correspond to the σ bonds of AH_2 ; they appear with almost equal bonding character. The $2a_1$ MO is associated to the sp lone pair and is also bonding, but significantly less than the corresponding ones in AH molecules. Like in the AH species, the HOMO is essentially a p AO of atom A, nevertheless slightly bonding in H_2O and very slightly bonding in H_2S and H_2Se . This character agrees with the lengthening of the A-H bonds in cations AH_2^+ (${}^2\text{B}_1$) and protonated AH_3^+ species as well as a decrease of both (in-phase and out-of-phase) stretching vibrations frequencies and of corresponding force constants. Experimental results for some vibration frequencies agree with the bonding character of the HOMO of these species: the a_1 and b_2 modes of H_2O at respectively 3652 cm^{-1} and 3757 cm^{-1} drops to 3213 cm^{-1} and 3259 cm^{-1} in H_2O^+ ;²⁰ similarly the a_1 mode of H_2S (2615 cm^{-1}) and H_2Se (2345 cm^{-1}) slightly decreases in H_2S^+ (2496 cm^{-1}) and H_2Se^+ (2267 cm^{-1}) respectively²⁰.

Also, an increase of the bond lengths is observed by protonation of H₂O (from 0.958 Å to 0.974 Å)²² and of H₂S (from 1.336 Å to 1.359 Å)²³.

Table 2. Molecules H₂O, H₂S and H₂Se: DOFs (au) with respect to A-H length of valence MOs at the H-F(B3LYP) levels; bond lengths (Å) of neutral R(AH₂), cationic R(AH₂⁺) and protonated R(AH₃⁺) species; vibration frequencies (cm⁻¹) and force constants of neutral ν (AH₂) and cationic ν (AH₂⁺) species ^a 6-311 G** ^b CCSD(T)/cc-pVTZ; ^c B3LYP/cc-pVTZ.

| | H ₂ O | H ₂ S | H ₂ Se |
|--------------------------------------|--|------------------|-------------------|
| MO | DOF HF(B3LYP)^a | | |
| 1a₁ | 0.283 (0.224) | 0.146 (0.111) | 0.127 (0.091) |
| 1b₂ | 0.294 (0.195) | 0.156 (0.107) | 0.132 (0.091) |
| 2a₁ | 0.098 (0.038) | 0.040 (0.015) | 0.032 (0.014) |
| 1b₁(HOMO) | 0.042 (0.038) | 0.003 (0.007) | 0.003 (0.005) |
| | Bond lengths^b | | |
| R(AH₂) | 0.9595 | 1.3406 | 1.4583 |
| R(AH₂⁺) | 1.0012 | 1.3607 | 1.4747 |
| ΔR_{ion} | 0.0417 | 0.0201 | 0.0164 |
| R(AH₃⁺) | 0.9778 | 1.3549 | 1.4688 |
| ΔR_{prot} | 0.0183 | 0.0143 | 0.0105 |
| | Stretching vibration frequency (force constant)^c | | |
| | AH₂ | | |
| ν(a₁) | 3801.0 (8.89) | 2685.3 (4.40) | 2391.7 (3.44) |
| ν(b₂) | 3901.3 (9.70) | 2699.4 (4.46) | 2406.2 (3.48) |
| | AH₂⁺ | | |
| ν(a₁) | 3326.4 (6.80) | 2562.8 (4.01) | 2324.2 (3.24) |
| ν(b₂) | 3372.3 (7.28) | 2565.3 (4.033) | 2331.8 (3.27) |

Molecules NH₃, PH₃ and AsH₃

The results are gathered in Table 3.

Table 3. Molecules NH_3 , PH_3 and AsH_3 : DOF (au) of valence MOs with respect to A-H length at the H-F(B3LYP) levels; bond lengths (Å) of neutral $\text{R}(\text{AH}_3)$, cationic $\text{R}(\text{AH}_3^+)$ and protonated $\text{R}(\text{AH}_4^+)$ species; vibration frequencies (cm^{-1}) and force constant of neutral and cationic species. ^a 6-311 G** ^b CCSD(T)/ccpv-TZ; ^c B3LYP/ccpv-TZ

| | NH_3 | PH_3 | AsH_3 |
|--------------------------------------|--|-----------------|-----------------|
| MO | DOF HF (B3LYP)^a | | |
| 1a₁ | 0.280 (0.213) | 0.146 (0.106) | 0.135 (0.096) |
| 1e | 0.223 (0.146) | 0.114 (0.074) | 0.098 (0.065) |
| 2a₁ | 0.024 (0.009) | -0.013 (-0.020) | -0.013 (-0.019) |
| | Bond lengths^b | | |
| R(AH₃) | 1.0141 | 1.4185 | 1.5098 |
| R(AH₃⁺) | 1.0223 | 1.4003 | 1.4833 |
| ΔR_{ion} | 0.0082 | -0.0182 | -0.0265 |
| | Bond lengths^b | | |
| R(AH₄⁺) | 1.0226 | 1.3966 | 1.4776 |
| ΔR_{prot} | 0.0085 | -0.0219 | -0.0322 |
| | Stretching vibration frequency (force constant)^c | | |
| | AH₃ | | |
| v(a₁) | 3462.5 (7.25) | 2384.8(3.46) | 2178.9(2.85) |
| v(e) | 3578.9(8.22) | 2392.6(3.51) | 2193.3 (2.89) |
| | AH₃⁺ | | |
| v(a₁) | 3339.6 (6.62) | 2446.8(3.57) | 2239.1 (2.98) |
| v(e) | 3513.7 (8.06) | 2523.3(3.95) | 2311.7 (3.23) |

The MOs 1a₁ and e, associated to the σ bonds have DOFs of the same order of magnitude. A remarkable point is the fact that the 2a₁ MO associated to the lone pair is bonding for NH₃ and antibonding for PH₃ and AsH₃, which is visualized in Figure 4. Available experimental results agree with the bonding character of the HOMO of NH₃ whose vibration frequency drops in NH₃⁺ from 3444 cm⁻¹ to 3389 cm⁻¹ (e) and from 3337 cm⁻¹ to 3177 cm⁻¹ (a₁).²⁰ Protonated species NH₄⁺ in Ne matrix absorbs at 3357.5 (e)²⁴, very close to NH₃⁺.

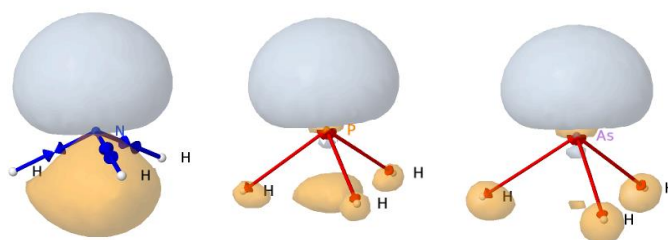


Figure 4. Molecules NH_3 , PH_3 and AsH_3 . Graphical representation of H-F DOFs of the HOMO lone pair. Blue/red arrows indicate a bonding/antibonding character, with a thickness proportional to the % of the maximum DOF

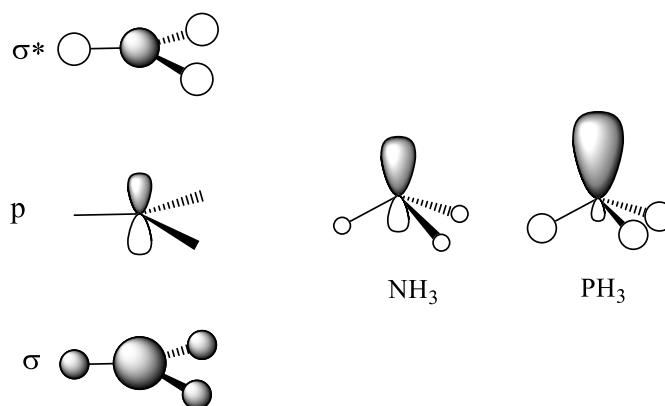
Again, B3LYP DOF values agree qualitatively with H-F ones though important differences in absolute values. All computed physical properties are consistent with DOF results : NH₃⁺ and NH₄⁺ exhibit longer bond lengths than NH₃, while PH₃⁺ and PH₄⁺ on the one hand, AsH₃⁺ and AsH₄⁺ on the other hand have shorter bonds than PH₃ and AsH₃ respectively. Similarly, ionisation and protonation result in a decrease of stretching vibration frequencies and force constants for NH₃ and an increase of the

same quantities for PH_3 and AsH_3 . To understand this difference, the corresponding planar structures were studied: the lone pair $2a_1$ MO is now pure p, and its DOF becomes positive for all three species as it can be seen in Table 4. The corresponding cations have longer bond lengths.

Table 4. Planar NH_3 , PH_3 and AsH_3 . DOF of the HOMO a_1 at the H-F level; bond lengths of AH_3 and AH_3^+ species (CCSD(T)/cc-pVTZ.

| MO | NH_3 | PH_3 | AsH_3 |
|-------------------------|---------------|---------------|----------------|
| HOMO DOF a_1 | 0.037 | 0.005 | 0.009 |
| $R(\text{AH}_3)$ | 0.9952 | 1.3802 | 1.4595 |
| $R(\text{AH}_3^+)$ | 1.0223 | 1.3955 | 1.4752 |
| ΔR_{ion} | 0.0271 | 0.0153 | 0.0157 |

The evolution of the bonding character of the lone pair from NH_3 to PH_3 may appear paradoxical. As depicted in scheme 2, this lone pair results, by pyramidalization, from a destabilizing mixing with σ (out-of-phase) and a stabilizing mixing with σ^* (in-phase). Moreover, it has been shown there is a stronger mixing of p with σ^* in PH_3 than in NH_3 and though an increase in the in-phase participation of hydrogens²⁵. But, at the same time, due an increase of its s character, the “lone pair” density is repelled out of the A-H bond, in the antibonding force region, a phenomenon which appears in the MOs of Fig. 4.



Scheme 2. Interacting MOs in NH_3 and PH_3 lone-pairs.

A similar evolution could be expected for the $sp a_1$ “lone pair” in the series H_2O - H_2S - H_2Se . Indeed, the DOF drops from 0.098 to 0.040 and 0.032 for this MO which remains nevertheless bonding.

Molecules NF_3 , PF_3 and AsF_3

The results are gathered in Table 5. For all three molecules, the a_1 MO associated to the lone pair is strongly antibonding.

Table 5. Molecules NF_3 , PF_3 and AsF_3 : DOF (au) of the HOMO a_1 with respect to A-F length at the H-F(B3LYP) levels; bond lengths (Å), stretching vibration frequencies (cm^{-1}) and force constants for neutral $R(AF_3)$ and cationic $R(AF_3^+)$ species. ^a 6-311 G** ^b CCSD(T)/cc-pVTZ; ^c B3LYP/cc-pVTZ

| | NF_3 | PF_3 | AsF_3 |
|------------------------------------|--|-----------------------------------|-----------------|
| MO | | DOF HF (B3LYP)^a | |
| HOMO a_1 | -0.169 (-0.154) | -0.161 (-0.129) | -0.116 (-0.078) |
| | Bond lengths^b | | |
| AF_3 | 1.3717 | 1.5762 | 1.706 |
| AF_3^+ | 1.2839 | 1.5051 | 1.648 |
| ΔR_{ion} | -0.0878 | -0.071 | -0.058 |
| | Stretching vibration frequency (force constant)^c | | |
| | AF_3 | | |
| $\nu(a_1)$ | 1050.4 (9.90) | 871.2 (10.0) | 720.0 (6.77) |
| $\nu(e)$ | 895.6 (7.19) | 837.4 (9.38) | 686.3 (6.34) |
| | AF_3^+ | | |
| $\nu(a_1)$ | 988.5 (9.80) | 907.6 (10.1) | 753.8 (6.90) |
| $\nu(e)$ | 1234.8 (13.60) | 1063.2 (15.4) | 798.1(8.81) |

The graphical representation of this MO in NF_3 shows that it results from an out-of-phase mixing of the sp hybrid of the central atom with 2p AOs of fluorine atoms, *a priori* antibonding; but the density in yellow in Fig. 5, can be viewed as a bonding interaction through the N-F bonds, the balance of which is not self-evident. The antibonding nature of a_1 is clearer for PF_3 and AsF_3 .

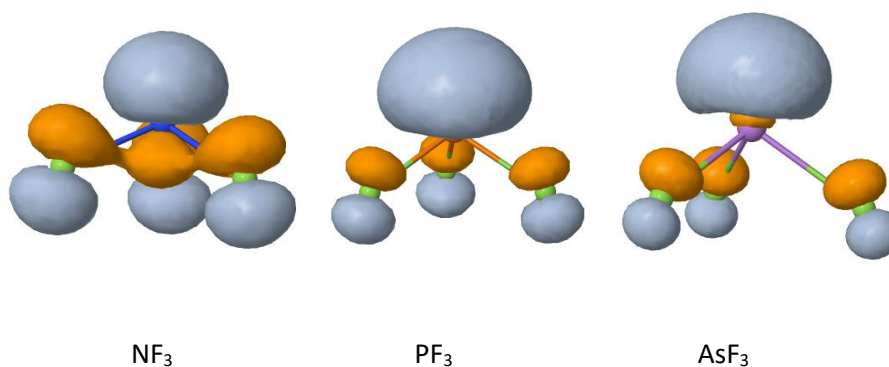


Fig. 5. a_1 HOMO lone pairs of NF_3 , PF_3 and AsF_3

Accordingly, we observe a marked shortening in bond lengths of the corresponding cations. Frequencies and force constants of the e vibration increase in cations. This effect is weak in a_1 vibrations of PF_3 and AsF_3 , and even a weak decrease is observed for NF_3 .

Molecule H_2CO

In Table 6, we report the DOFs corresponding to derivatives with respect to the various atom distances: CO and CH bond lengths and HH distance. In the latter case, this distance variation was obtained by variation of HCH angle, i.e. keeping constant both CO and CH lengths.

Table 6. Molecule H_2CO : DOFs (au) with respect to C-O, C-H and H-H distances at the H-F(B3LYP) levels; bond lengths (\AA), stretching vibration frequency (cm^{-1}) and force constants for neutral H_2CO , cationic and protonated H_2COH^+ . ^a 6-311 G** ^b CCSD(T)/cc-pVTZ; ^c B3LYP/cc-pVTZ.

| $H_2C=O$ | | | |
|---|------------------------|--|------------------------|
| MO | DOF/R(CO) ^a | DOF/R(CH) ^a | DOF/R(HH) ^a |
| $1a_1(\sigma_{CO})$ | 0.341 (0.029) | -0.024 (-0.028) | 0.005 (0.012) |
| $2a_1(\sigma_{CH_2})$ | -0.095 (-0.077) | 0.169 (0.129) | 0.025 (0.044) |
| $1b_2(\sigma_{CH_2})$ | 0.109 (0.079) | 0.124 (0.088) | -0.031 (-0.055) |
| $3a_1(n_{sp})$ | 0.140 (0.077) | 0.008 (-0.013) | 0.025 (0.039) |
| $1b_1(\pi)$ | 0.225 (0.171) | -0.027 (-0.023) | 0.009 (0.013) |
| $2b_2(n_p)$ | -0.074 (-0.029) | 0.040 (-0.011) | -3.10^{-4} (0.015) |
| Bond lengths ^b | | | |
| | R(CO) | R(CH) | R(HH) (HCH) |
| R(H_2CO) | 1.2095 | 1.1033 | 1.8732 (116.2) |
| 2b_2 R(H_2CO^+) | 1.200 | 1.1135 | 1.9401 (121.2) |
| ΔR_{ion} | -0.0095 | 0.0102 | 0.067 (5.0) |
| R(H_2COH^+) | 1.2520 | 1.0872 1.0896 | 1.9146 (122.9) |
| ΔR_{prot} | 0.0425 | -0.0161 -0.0137 | 0.0414 (6.0) |
| Frequencies (force constant) ^c | | | |
| | $\nu(CO)$ | $\nu(CH)$ | $\gamma(HCH)$ |
| H_2CO | 1823.5 (14.41) | a_1 2878.5 (5.09) b_2 2932.6 (5.68) | a_1 1536.3 (1.54) |
| H_2CO^+ | 1708.0 (19.8) | 2758.7 (4.64) 2840.9 (5.26) | 1248.0 (0.97) |

The DOFs of the three highest MOs are graphically presented in Fig. 6.

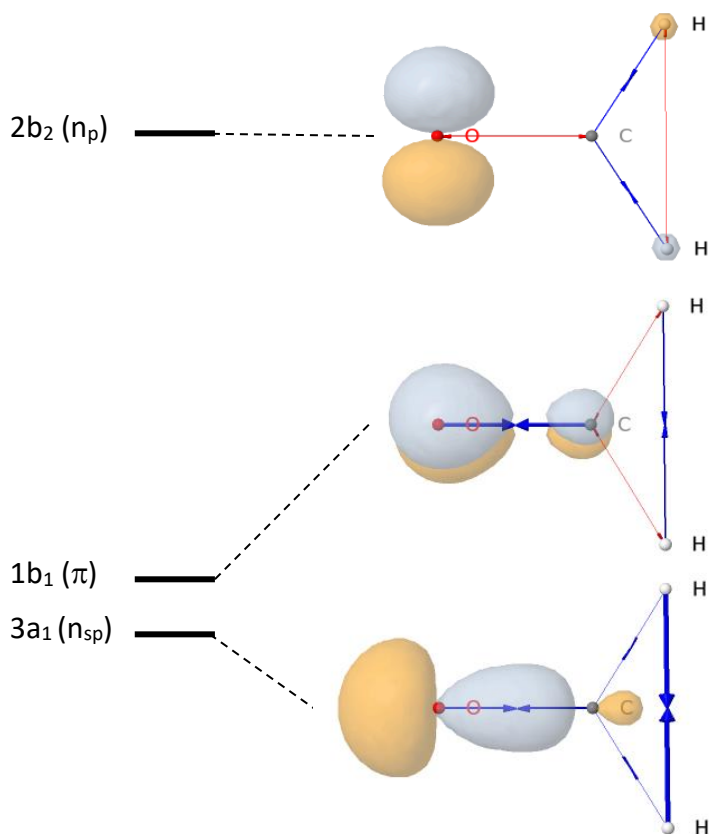


Figure 6. Molecule H_2CO . Graphical representation of H-F DOFs of valence shell MOs. Blue/red arrows indicate a bonding/antibonding character, with a thickness proportional to the % of the maximum DOF

Some discrepancies appear between HF and B3LYP calculated DOFs. For examples, the $2b_2$ and $3a_1$ MOs are found bonding along C-H at HF level and antibonding at B3LYP level.

The HOMO $2b_2$ is antibonding along CO, in agreement with the shortening of this bond and the increase of force constant upon ionization (the lowering of the frequency is due to an increase of reduced mass in the cation).

Regarding the C-H bonds, the variation by ionization of their lengths and of the force constant of the vibration in which they are involved agree with an bonding character of the HOMO along them, predicted by the B3LYP DOF (but not at the H-F level).

The calculated DOF with respect to H...H distance (i.e. with HCH angle) of the HOMO is near zero at the H-F level and positive (0.015) at the B3LYP one. By ionization, we observe an increase of this distance and a decrease of the forces constants in the $a_1 \gamma$ mode (in-plane deformation), which agrees with the bonding character found at the B3LYP level.

The effect of protonation is more difficult to discuss because several MOs are strongly perturbed. Regarding for example the variation of CO bond length, we deal with the $2b_2$ (antibonding) and $3a_1$ (bonding) associated to each "lone pair" of oxygen, but the b_1 (p) is expected to become more located on oxygen and thus less bonding along CO.

Concluding remarks

The dynamic orbital force (DOF) appears as a good criterion of the bonding/antibonding character of MOs along a given bond. For canonical H-F MOs, this quantity is the force exerted by electrons on nuclei if one electron occupying a given MO is removed, all other electrons being frozen. Indeed, it allows the prediction, with very few exceptions, of the bond length variation upon ionization and protonation, as summarized in Fig. 7. The relative bond lengths variations by ionization, $\Delta R/R_e$, are plotted as a function of the H-F (7a) and B3LYP (7b) DOFs. In the blue areas, both DOF and $\Delta R/R_e$ are positive, corresponding to a lengthening of bonds by removing an electron from a bonding MO. In the red areas both DOF and $\Delta R/R_e$ are negative, corresponding to a shortening of bonds by removing an electron from an antibonding MO. A very rough relation appears between $\Delta R/R_e$ and the Hartree-Fock DOFs. It means that, though these DOFs involve the neglect of MO relaxation and of correlation energy, they provide a reliable predictive index for the variation of experimental data upon ionisation, in confirmation to a previous work mainly devoted to diatomic species¹⁰. The same relation between $\Delta R/R_e$ and DOF is observed from B3LYP DOFs, with even a better linear correlation.

From a practical point of view, the DOFs are easy to compute and are stable with respect to the basis set, provided double zeta or higher levels are used.¹⁰ Generally, it is no more the case with the classical overlap population which can be strongly dependant on the basis set, especially with extended ones or when diffuse OAs are included. Another criterion for the MO bonding/antibonding character along a bond A-B consists in comparing the MO energy of the mean energy of the AOs of A and B fragments involved in this MO, which is not straightforward in the practice.

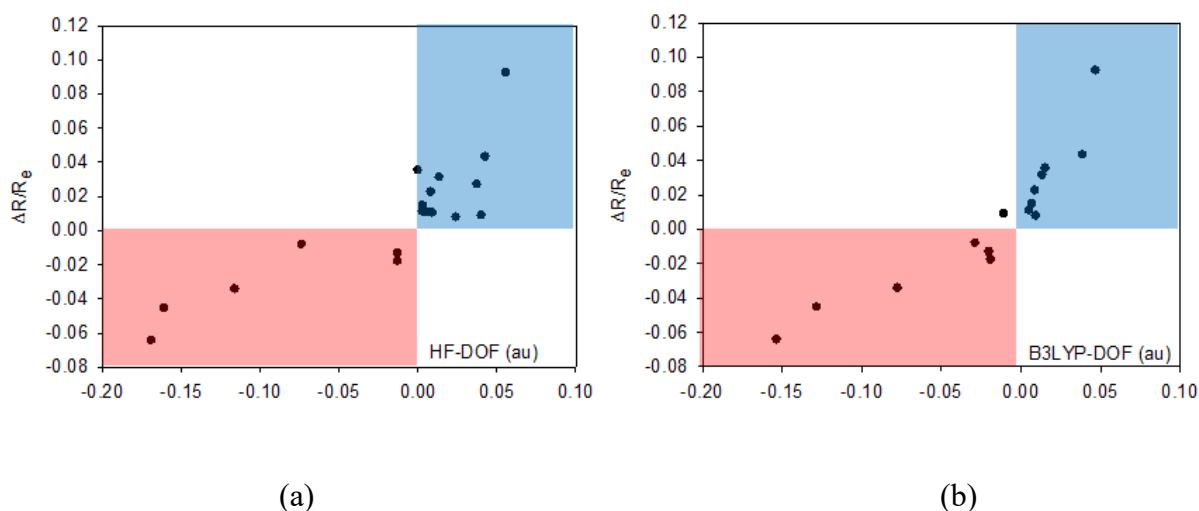


Figure 7. Relative bond length variation upon ionization as function of DOF of the removed electron; (a) DOF at the HF level; (b) DOF at the B3LYP level.

The DOFs are also in qualitative agreement with the variation of forces constants in vibration normal coordinates when the molecule is ionized. It is worthy to note that the relatively important bonding character found for the p MOs of halogen hydride is somewhat counterintuitive. Also, it can be surprising at first glance that the “lone pair” of NH_3 is bonding, while those of PH_3 and AsH_3 are antibonding.

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