Structure électronique de la molécule LiH

1. voir cours.

2. La molécule est parallèle à l'axe x et orientée de Li vers H. La distance interatomique est égale à 1,3761 Å.

3. Fonction d'onde de l'état fondamental :

$$\Psi_0 = \frac{1}{\sqrt{2}}\phi(1)\phi(2)\big(\alpha(1)\beta(2) - \beta(1)\alpha(2)\big)$$

4. Expression LCAO de l'OM doublement occupée :

$$\phi = 0{,}4141 \times 2s_{Li} + 0{,}3307 \times 2px_{Li} + 0{,}8480 \times 1s_{H}$$

5. Populations orbitalaires et charges partielles.

$$Q_{2s_{Li}} = 2 \times (0{,}4141)^2 = 0{,}34305$$
$$Q_{2px_{Li}} = 2 \times (0{,}3307)^2 = 0{,}21875$$
$$Q_{2px_{Li}} = 2 \times (0{,}8480)^2 = 1{,}4382$$
$$n_{Li} = 0{,}34305 + 0{,}21875 = 0{,}5618$$
$$n_{H} = 1{,}4382$$
$$\delta_{Li} = 1 - 0{,}5618 = 0{,}4382$$
$$\delta_{H} = 1 - 1{,}4382 = -0{,}4382$$

6. Moment dipolaire de LiH :

$$\vec{\mu}_0 = \frac{1}{2}\left\langle \phi(1)\phi(2)\big(\alpha(1)\beta(2) - \beta(1)\alpha(2)\big) \middle| -e\vec{r}_1 + -e\vec{r}_2 + Ze\vec{R}_{Li} + Ze\vec{R}_{H} \middle| \phi(1)\phi(2)\big(\alpha(1)\beta(2) - \beta(1)\alpha(2)\big) \right\rangle$$

L'opérateur ne portant pas sur le spin, on peut sortir les fonctions de spin du bra-ket. D'après l'orthonormalité des fonctions de spin, on a :

$$\big\langle \alpha(1)\beta(2) - \beta(1)\alpha(2) \big| \alpha(1)\beta(2) - \beta(1)\alpha(2) \big\rangle = 2$$

d'où :

$$\vec{\mu}_0 = \langle\phi(1)\phi(2)|-e\vec{r}_1|\phi(1)\phi(2)\rangle + \langle\phi(1)\phi(2)|-e\vec{r}_2|\phi(1)\phi(2)\rangle$$
$$+\langle\phi(1)\phi(2)|+Ze\vec{R}_{Li}|\phi(1)\phi(2)\rangle + \langle\phi(1)\phi(2)|Ze\vec{R}_H|\phi(1)\phi(2)\rangle$$
$$\vec{\mu}_0 = -e\langle\phi(1)|\vec{r}_1|\phi(1)\rangle - e\langle\phi(2)|\vec{r}_2|\phi(2)\rangle$$
$$+Ze\vec{R}_{Li}\langle\phi(1)\phi(2)|\phi(1)\phi(2)\rangle + Ze\vec{R}_H\langle\phi(1)\phi(2)|\phi(1)\phi(2)\rangle$$
$$\vec{\mu}_0 = -2e\langle\phi|\vec{r}|\phi\rangle + Ze\vec{R}_{Li} + Ze\vec{R}_H$$

7. En utilisant le développement LCAO de l'OM ϕ :

$$\phi = 0{,}4141 \times 2s_{Li} + 0{,}3307 \times 2px_{Li} + 0{,}8480 \times 1s_H$$

on obtient :

$$\vec{\mu}_0 = -2e\langle 0{,}4141 \times 2s_{Li} + 0{,}3307 \times 2px_{Li} + 0{,}8480 \times 1s_H|\vec{r}|0{,}4141 \times 2s_{Li} + 0{,}3307 \times 2px_{Li} + 0{,}8480 \times 1s_H\rangle$$
$$+Z_{Li}e\vec{R}_{Li} + Z_He\vec{R}_H$$
$$\vec{\mu}_0 = -2e \times 0{,}4141^2\langle 2s_{Li}|\vec{r}|2s_{Li}\rangle$$
$$-2e \times 0{,}3307^2\langle 2px_{Li}|\vec{r}|2px_{Li}\rangle$$
$$-2e \times 0{,}8480^2\langle 1s_H|\vec{r}|1s_H\rangle$$
$$-4e \times 0{,}8480 \times 0{,}3307\langle 2s_{Li}|\vec{r}|2px_{Li}\rangle$$
$$+Z_{Li}e\vec{R}_{Li} + Z_He\vec{R}_H$$

Sachant que les intégrales dipolaires monocentriques faisant intervenir une seule OA sont égales à la position du noyau sur laquelle l'OA est centrée :

$$\vec{\mu}_0 = -2e \times 0{,}4141^2\vec{R}_{Li} - 2e \times 0{,}3307^2\vec{R}_{Li} - 2e \times 0{,}8480^2\vec{R}_H$$
$$-4e \times 0{,}8480 \times 0{,}3307\langle 2s_{Li}|\vec{r}|2px_{Li}\rangle + Ze\vec{R}_{Li} + Ze\vec{R}_H$$
$$\vec{\mu}_0 = -e \times n_{Li}\vec{R}_{Li} - e \times n_H\vec{R}_H + Z_{Li}e\vec{R}_{Li} + Z_He\vec{R}_H - 2e \times D_{2s/2px}\langle 2s_{Li}|\vec{r}|2px_{Li}\rangle$$
$$\vec{\mu}_0 = e \times \underbrace{(Z_{Li} - n_{Li})}_{\delta_{Li}=\delta}\vec{R}_{Li} + e \times \underbrace{(Z_H - n_H)}_{\delta_H=-\delta_{Li}=-\delta}\vec{R}_H - 2e \times D_{2s/2px}\langle 2s_{Li}|\vec{r}|2px_{Li}\rangle$$
$$\vec{\mu}_0 = e\delta(\vec{R}_{Li} - \vec{R}_H) - 2e \times D_{2s/2px}\langle 2s_{Li}|\vec{r}|2px_{Li}\rangle$$

Soit,

$$\vec{\mu}_0 = e\delta(\vec{\ell}_{Li-H}) - 2e \times D_{2s/2px}\langle 2s_{Li}|\vec{r}|2px_{Li}\rangle$$

avec

$$\vec{\mu}_{charge} = e\delta(\vec{\ell}_{Li-H})$$

et

$$\vec{\mu}_{\text{hybrid}} = -2eD_{2s/2px}\left\langle 2s_{\text{Li}}|\vec{r}|2p_{x\,\text{Li}}\right\rangle$$

8. Valeur numérique de la contribution des charges ponctuelles.

$$\left\|\vec{\mu}_{\text{charge}}\right\| = 1{,}602.10^{-19} \times 0{,}4382 \times 1{,}3761.10^{-10}$$
$$= 9{,}6602.10^{-30}\ \text{C.m.}$$
$$= 2{,}896\ \text{D}$$

Le dipôle est orienté du pôle (–) (H) vers le pôle (+) (Li). $\vec{\mu}_{\text{charge}} = -2{,}896\vec{x}$

9. Valeur numérique de la contribution d'hybridation.

$$\vec{\mu}_{\text{hybrid}} = -2eD_{2s/2px}\left\langle 2s_{\text{Li}}|\vec{r}|2p_{x\,\text{Li}}\right\rangle$$

$$\left\langle 2s_{\text{Li}}|\vec{r}|2p_{x\,\text{Li}}\right\rangle = \frac{5}{\sqrt{3}} \times \sqrt{2 \times 0{,}70238} \times \sqrt{2 \times 0{,}70238} \times \frac{(4 \times 0{,}70238)^2}{(0{,}70238 + 0{,}70238)^6}$$
$$= 2{,}0550\ \text{Bohrs} = 1{,}0875.10^{-10}\ \text{m}$$

$$\left\|\vec{\mu}_{\text{hybrid}}\right\| = 2 \times 1{,}602.10^{-19} \times 2 \times 0{,}4141 \times 0{,}3307 \times 1{,}0875.10^{-10}$$
$$= 9{,}5427.10^{-30}\ \text{C.m.}$$
$$= 2{,}861\ \text{D}$$

Attention au signe (–) dans l'expression de $\vec{\mu}_{\text{hybrid}}$:
$\vec{\mu}_{\text{hybrid}} = -\left\|\vec{\mu}_{\text{hybrid}}\right\|\vec{x}$, donc $\vec{\mu}_{\text{hybrid}}$ est orienté de H vers Li.

Dipôle total :

$$\vec{\mu}_{\text{total}} = \vec{\mu}_{\text{charge}} + \vec{\mu}_{\text{hybrid}} = -2{,}896\vec{x} - 2{,}861\vec{x} = -5{,}757\vec{x}$$

10. L'approximation des charges ponctuelles sous-estime le moment dipolaire de 50%, et ne peut pas être utilisée pour évaluer précisément le dipôle moléculaire.

File LiH-RHF.out

```
Timestamp: 2011-04-03-21-53-38-0000006CAF-mac
User Info: castet, MacBook-Pro-de-Frederic-Castet.local
********************************************************************************
                          MNDO CALCULATION RESULTS
********************************************************************************
*                              AMPAC Version 9.2.1
*                                 Presented by:
*
*                            Semichem, Inc.
*                            12456 W 62nd Terrace - Suite D
*                            Shawnee KS 66216
*                            (913)268-3271
*                            (913)268-3445 (fax)
*
*  MNDO     - THE MNDO HAMILTONIAN TO BE USED
*  TRUSTE   - MINIMISE ENERGY USING TRUST REGION
*  T=AUTO   - AUTOMATIC DETERMINATION OF ALLOWED TIME
*  VECTORS  - SELECTED FINAL EIGENVECTORS TO BE PRINTED
*  SINGLET  - IS THE REQUIRED SPIN MULTIPLICITY
********************************************************************************
MNDO RHF SINGLET TRUSTE T=AUTO VECTORS
Title
Comment
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I     NA    NB    NC
     1     Li
     2     H          1.53000 *                                     1

  MOLECULAR POINT GROUP            SYMMETRY CRITERIA
           C*V                         0.10000000

         SINGLET STATE CALCULATION

       **  REFERENCES TO PARAMETERS  **

H  (MNDO):  M.J.S. DEWAR, W. THIEL, J. AM. CHEM. SOC., 99, 4899, (1977)
Li (MNDOC): TAKEN FROM MNDOC BY W.THIEL, QCPE NO.438, V. 2, P.63, (1982).

         CARTESIAN COORDINATES
   NO.       ATOM               X          Y          Z
      1 Li        0.00000000      0.00000000      0.00000000
      2 H         1.53000000      0.00000000      0.00000000

STANDARD DEVIATION ON ENERGY   (KCAL)       0.00000055519
STANDARD DEVIATION ON GRADIENT (KCAL/A,RD,RD)  0.00006958 0.00000000 0.00000000

MNDO RHF SINGLET TRUSTE T=AUTO VECTORS
Title
Comment

    GEOMETRY OPTIMISED : ENERGY MINIMISED
    SCF FIELD WAS ACHIEVED

                            MNDO CALCULATION
                                                      VERSION 9.2.1

                                                   Apr-03-2011

         FINAL HEAT OF FORMATION =      23.205876 kcal
                                 =      97.116591 kJ
         ELECTRONIC ENERGY       =     -28.362939 eV
         CORE-CORE REPULSION     =       8.410051 eV
         TOTAL ENERGY            =     -19.952889 eV
         GRADIENT NORM           =       0.002662
         RMS GRADIENT NORM       =       0.002662
         UNSTABLE MODE(S)        =       0 ( ESTIMATE  )
         IONIZATION POTENTIAL    =       8.865101 eV
         HOMO-LUMO GAP           =       9.738425 eV
         MOLECULAR POINT GROUP   = C*V   0.100000
         NO. OF FILLED LEVELS    =       1 (OCC = 2)
         MOLECULAR WEIGHT        =       7.948
         SCF CALCULATIONS        =       6
         COMPUTATION TIME        =       0.00     SECONDS
```

```
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I     NA    NB    NC
     1     Li
     2     H          1.37615 *                                     1

  MOLECULAR POINT GROUP            SYMMETRY CRITERIA
           C*V                        0.10000000

         RHF  EIGENVECTORS AND EIGENVALUES

ROOT NO.          1       2       3       4       5
             -8.865   0.873   2.628   2.628   5.914
             1 SI    2 SI    1 PI    1 PI    3 SI
S  Li    1  0.4141  0.7858  0.0000  0.0000 -0.4594
Px Li    1  0.3307 -0.6001  0.0000  0.0000 -0.7283
Py Li    1  0.0000  0.0000  1.0000  0.0000  0.0000
Pz Li    1  0.0000  0.0000  0.0000  1.0000  0.0000

S  H     2  0.8480 -0.1497  0.0000  0.0000  0.5084


         RHF EIGENVALUES
 -8.86510   0.87332   2.62786   2.62786   5.91387

         NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS
        ATOM NO.   TYPE          CHARGE        ATOM ELECTRON DENSITY
      1 Li           0.4382          0.5618
      2 H           -0.4382          1.4382

DIPOLE (DEBYE)   X         Y         Z       TOTAL
POINT-CHG.    -2.896     0.000     0.000     2.896
HYBRID        -2.862     0.000     0.000     2.862
SUM           -5.758     0.000     0.000     5.758


         CARTESIAN COORDINATES
   NO.       ATOM               X         Y         Z
      1 Li       0.00000000      0.00000000      0.00000000
      2 H        1.37615214      0.00000000      0.00000000


         ATOMIC ORBITAL ELECTRON POPULATIONS
  0.34303   0.21878   0.00000   0.00000   1.43819

    ELAPSED WALL CLOCK TIME :      0.04 SECONDS
    FULL COMPUTATION TIME :      0.00 SECONDS
Process Info: 0.017u 0.017s 0:00.06 33.3%  0+0k 1+8io 44pf+0w
```