Etats excités de la molécule LiH

1. Fonction d'onde Ψ_e de l'état excité n°6 :

$$\Psi_e = \frac{1}{\sqrt{2}}\Phi_4 - \frac{1}{\sqrt{2}}\Phi_5$$

2. Expression des déterminants Φ_4 et Φ_5 :

$$\Phi_4 = \frac{1}{\sqrt{2}}\left|\phi(1)\alpha(1)\ \ \phi'(2)\beta(2)\right| = \frac{1}{\sqrt{2}}\begin{vmatrix}\phi(1)\alpha(1) & \phi'(1)\beta(1)\\ \phi(2)\alpha(2) & \phi'(2)\beta(2)\end{vmatrix}$$
$$= \frac{1}{\sqrt{2}}\left(\phi(1)\alpha(1)\phi'(2)\beta(2) - \phi(2)\alpha(2)\phi'(1)\beta(1)\right)$$

$$\Phi_5 = \frac{1}{\sqrt{2}}\left|\phi(1)\beta(1)\ \ \phi'(2)\alpha(2)\right| = \frac{1}{\sqrt{2}}\begin{vmatrix}\phi(1)\beta(1) & \phi'(1)\alpha(1)\\ \phi(2)\beta(2) & \phi'(2)\alpha(2)\end{vmatrix}$$
$$= \frac{1}{\sqrt{2}}\left(\phi(1)\beta(1)\phi'(2)\alpha(2) - \phi(2)\beta(2)\phi'(1)\alpha(1)\right)$$

On en déduit l'expression de Ψ_e :

$$\Psi_e = \frac{1}{2}\left(\phi(1)\phi'(2) - \phi'(1)\phi(2)\right)\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)$$

3. Expression LCAO des OM ϕ et ϕ' :

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

$$\phi' = -2py_{Li}$$

4. Moment de transition :

$$\vec{\mu}_{0e} = -e\left\langle\Psi_0\middle|\vec{r}\middle|\Psi_e\right\rangle$$
$$= -e\left\langle\frac{1}{\sqrt{2}}\phi(1)\phi(2)\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)\middle|\vec{r}\middle|\frac{1}{2}\left(\phi(1)\phi'(2) - \phi'(1)\phi(2)\right)\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)\right\rangle$$

L'opérateur ne portant pas sur le spin, on peut donc sortir les fonctions de spin du bra-ket, avec :
$\left\langle\alpha(1)\beta(2) - \beta(1)\alpha(2)\middle|\alpha(1)\beta(2) - \beta(1)\alpha(2)\right\rangle = 2$

d'où :

$$\vec{\mu}_{0e} - \frac{1}{\sqrt{2}} e\langle \phi(1)\phi(2)|\vec{r}|\phi(1)\phi'(2) - \phi'(1)\phi(2)\rangle$$
$$= -\frac{1}{\sqrt{2}} e\langle \phi(1)\phi(2)|\vec{r}|\phi(1)\phi'(2)\rangle - \frac{1}{\sqrt{2}} e\langle \phi(1)\phi(2)|\vec{r}|\phi'(1)\phi(2)\rangle$$
$$= -\frac{1}{\sqrt{2}} e\underbrace{\langle \phi(1)|\phi(1)\rangle}_{=1}\langle \phi(2)|\vec{r}|\phi'(2)\rangle - \frac{1}{\sqrt{2}} e\underbrace{\langle \phi(2)|\phi(2)\rangle}_{=1}\langle \phi(1)|\vec{r}|\phi'(1)\rangle$$
$$= -\frac{1}{\sqrt{2}} e\langle \phi(2)|\vec{r}|\phi'(2)\rangle - \frac{1}{\sqrt{2}} e\langle \phi(1)|\vec{r}|\phi'(1)\rangle$$
$$= -\sqrt{2} e\langle \phi|\vec{r}|\phi'\rangle$$

5. En utilisant l'expression LCAO des OM ϕ et ϕ', on obtient :

$$\vec{\mu}_{0e} = -\sqrt{2} e\langle \phi|\vec{r}|\phi'\rangle$$
$$= -\sqrt{2} e\langle 0{,}4141 \times 2s_{Li} + 0{,}3307 \times 2px_{Li} + 0{,}8480 \times 1s_{H}|\vec{r}| - 2py_{Li}\rangle$$
$$= \sqrt{2} e \times 0{,}4141\langle 2s_{Li}|\vec{r}|2py_{Li}\rangle + \sqrt{2} e \times 0{,}3307\langle 2px_{Li}|\vec{r}|2py_{Li}\rangle$$

6. Valeur numérique de $\vec{\mu}_{0e}$:

$$\vec{\mu}_{0e} = \sqrt{2} \times 0{,}4141 \times 2{,}0550 = 1{,}203 \text{ a.u.}$$

7. Force d'oscillateur :

$$\Delta E_{0\to e} = 6{,}0252 \text{ eV}$$

$$f_{0e} = \frac{2}{3}\Delta E|\vec{\mu}_{0e}|^2 = \frac{2}{3} \times \frac{6{,}0252}{27{,}21} \times 1{,}203^2 = 0{,}2136$$

File LiH-CIS.out

```
Timestamp: 2011-04-03-21-50-18-0000006C94-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
*  1SCF     - READ KEYWORD BUT DO 1 SCF AND THEN STOP
*  C.I.(    - SPECIFIED RANGE FOR C.I-ACTIVE MOS
*  MECI     - PRINT DETAILED RESULTS IN C.I.
*  CISTATE= 10 - EIGENSTATES CALCULATED IN CI
*  VECTORS  - SELECTED FINAL EIGENVECTORS TO BE PRINTED
*  SINGLET  - IS THE REQUIRED SPIN MULTIPLICITY
*************************************************************************
MNDO SC.I.(1,5) CISTATE=10 SINGLET 1SCF VECTORS MECI
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          1.37615 *                                    1

  MOLECULAR POINT GROUP            SYMMETRY CRITERIA
           C*V                         0.10000000

         SINGLET STATE CALCULATION

         RHF CALCULATION, No. OF DOUBLY OCCUPIED LEVELS =  1

       **  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        1.37615200      0.00000000      0.00000000


MNDO SC.I.(1,5) CISTATE=10 SINGLET 1SCF VECTORS MECI
Title
Comment

    1SCF WAS SPECIFIED, SO NO OPTIMIZATION ATTEMPTED
    SCF FIELD WAS ACHIEVED

                            MNDO CALCULATION
                                                    VERSION 9.2.1

                                                 Apr-03-2011

         FINAL HEAT OF FORMATION =      23.205876 kcal  (CI SINGLET No  1)
                                 =      97.116591 kJ
         ELECTRONIC ENERGY       =     -28.362940 eV
         CORE-CORE REPULSION     =       8.410052 eV
         TOTAL ENERGY            =     -19.952889 eV
         GRADIENT NORM           =       0.000000
         RMS GRADIENT NORM       =       0.000000
         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 + CI CALCULATIONS   =       1
         COMPUTATION TIME        =       0.01     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

         CONFIGURATION INTERACTION CALCULATION
         9 MICRO-STATES GENERATED BY     S-CI  VS         99 ROOM AVAILABLE.
    9 MICRO-STATES FINALLY KEPT.

CI-ACTIVE MOLECULAR ORBITALS:

ROOT NO.          1       2       3       4       5
             -8.865   0.873   2.628   2.628   5.914
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


DETAILED COUNT OF THE    9 CALCULATED LOWEST EIGENSTATES:
       SINGLET TRIPLET
   CSF       5       4
STATES       5       4
THE EIGENSTATE SELECTED IS No   1 (SINGLET)

ROW: MAIN MICRO-STATES OVER THE    9 SELECTED IN C.I.
COLUMN: EIGENSTATES FROM  1 TO   9

MO: 00000  1:SINGLET  2:TRIPLET  3:SINGLET  4:TRIPLET  5:TRIPLET  6:SINGLET
  : 12345 eV: 0.0000     3.8603     4.7044     5.6880     5.6880     6.0252
  1 20000       100%         0%         0%         0%         0%         0%
           ( 1.0000)  ( 0.0000)  ( 0.0000)  ( 0.0000)  ( 0.0000)  ( 0.0000)
  2 -+000         0%        41%        47%         0%         0%         0%
           ( 0.0000)  ( 0.6364)  ( 0.6864)  ( 0.0000)  ( 0.0000)  ( 0.0000)
  3 +-000         0%        41%        47%         0%         0%         0%
           ( 0.0000)  ( 0.6364)  (-0.6864)  ( 0.0000)  ( 0.0000)  ( 0.0000)
  4 -0+00         0%         0%         0%        50%         0%        50%
           ( 0.0000)  ( 0.0000)  ( 0.0000)  (-0.7071)  ( 0.0000)  ( 0.7071)
  5 +0-00         0%         0%         0%        50%         0%        50%
           ( 0.0000)  ( 0.0000)  ( 0.0000)  (-0.7071)  ( 0.0000)  (-0.7071)
  6 -00+0         0%         0%         0%         0%        50%         0%
           ( 0.0000)  ( 0.0000)  ( 0.0000)  ( 0.0000)  (-0.7071)  ( 0.0000)
  7 +00-0         0%         0%         0%         0%        50%         0%
           ( 0.0000)  ( 0.0000)  ( 0.0000)  ( 0.0000)  (-0.7071)  ( 0.0000)
  8 -000+         0%         9%         3%         0%         0%         0%
           ( 0.0000)  ( 0.3081)  ( 0.1700)  ( 0.0000)  ( 0.0000)  ( 0.0000)
  9 +000-         0%         9%         3%         0%         0%         0%
           ( 0.0000)  ( 0.3081)  (-0.1700)  ( 0.0000)  ( 0.0000)  ( 0.0000)
```

```
MO: 00000  7:SINGLET  8:TRIPLET  9:SINGLET
  : 12345 eV: 6.0252     6.5064     6.9390
  2 -+000         0%         9%         3%
           ( 0.0000)  (-0.3081)  (-0.1700)
  3 +-000         0%         9%         3%
           ( 0.0000)  (-0.3081)  ( 0.1700)
  6 -00+0        50%         0%         0%
           ( 0.7071)  ( 0.0000)  ( 0.0000)
  7 +00-0        50%         0%         0%
           (-0.7071)  ( 0.0000)  ( 0.0000)
  8 -000+         0%        41%        47%
           ( 0.0000)  ( 0.6364)  ( 0.6864)
  9 +000-         0%        41%        47%
           ( 0.0000)  ( 0.6364)  (-0.6864)

TRANSITION DIPOLE (A.U.) AND OSC. STRENGTHS FROM STATE  1 (SINGLET) TO OTHERS
STATE  eV       nm       X       Y       Z    STRENGTH
  2   3.860    321.2                                FORBIDDEN TO TRIPLET
  3   4.704    263.6 -0.4855  0.0000  0.0000  0.0272
  4   5.688    218.0                                FORBIDDEN TO TRIPLET
  5   5.688    218.0                                FORBIDDEN TO TRIPLET
  6   6.025    205.8  0.0000 -1.2036  0.0000  0.2138
  7   6.025    205.8  0.0000  0.0000  1.2036  0.2138
  8   6.506    190.6                                FORBIDDEN TO TRIPLET
  9   6.939    178.7 -0.1553  0.0000  0.0000  0.0041
SUM OF STRENGTHS:     0.0938  0.6415  0.6415

         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        1.37615200      0.00000000      0.00000000


         ATOMIC ORBITAL ELECTRON POPULATIONS
  0.34303   0.21878   0.00000   0.00000   1.43819

    ELAPSED WALL CLOCK TIME :      0.56 SECONDS
    FULL COMPUTATION TIME :      0.01 SECONDS
Process Info: 0.023u 0.032s 0:00.77 6.4%   0+0k 4+11io 663pf+0w
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