CHEM3023: Spins, Atoms and Molecules

Lecture 7

Hartee-Fock calculations in practice

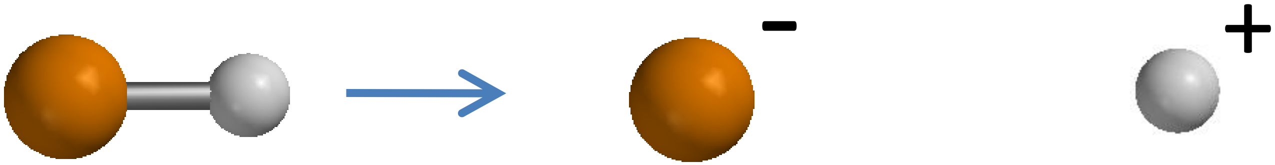
C.-K. Skylaris

Learning outcomes

- Be able to set up and run Hartree-Fock calculations
- Be able to construct formulas for the calculation of experimental observables from the Hartree-Fock molecular orbitals or the density

Hartree Fock calculations example

Calculate the deprotonation energy of HCl



Compare the results obtained with the following basis sets:

1) STO-3G (very simple, low-quality basis)
2) 6-31+G* (medium quality basis)

Basis sets

STO-3G

```
 H  (Hydrogen)
  ------------
            Exponent   Coefficients
       -------------- -------------
  1  S   3.42525091E+00   0.154329
  1  S   6.23913730E-01   0.535328
  1  S   1.68855400E-01   0.444635

  Cl  (Chlorine)
  -------------
            Exponent   Coefficients
       -------------- -------------
  1  S   6.01345614E+02   0.154329
  1  S   1.09535854E+02   0.535328
  1  S   2.96446769E+01   0.444635

  2  S   3.89604189E+01  -0.099967
  2  S   9.05356348E+00   0.399513
  2  S   2.94449983E+00   0.700115

  3  P   3.89604189E+01   0.155916
  3  P   9.05356348E+00   0.607684
  3  P   2.94449983E+00   0.391957

  4  S   2.12938650E+00  -0.219620
  4  S   5.94093427E-01   0.225595
  4  S   2.32524141E-01   0.900398

  5  P   2.12938650E+00   0.010588
  5  P   5.94093427E-01   0.595167
  5  P   2.32524141E-01   0.462001
```

6-31+G*

```
 H  (Hydrogen)
  ------------
Exponent   Coefficients
       -------------- -----------
  1  S   1.87311370E+01   0.033495
  1  S   2.82539370E+00   0.234727
  1  S   6.40121700E-01   0.813757

  2  S   1.61277800E-01   1.000000

  Cl  (Chlorine)
  -------------
            Exponent   Coefficients
       -------------- -------------
  1  S   2.51801000E+04   0.001833
  1  S   3.78035000E+03   0.014034
  1  S   8.60474000E+02   0.069097
  1  S   2.42145000E+02   0.237452
  1  S   7.73349000E+01   0.483034
  1  S   2.62470000E+01   0.339856

  2  S   4.91765000E+02  -0.002297
  2  S   1.16984000E+02  -0.030714
  2  S   3.74153000E+01  -0.112528
  2  S   1.37834000E+01   0.045016
  2  S   5.45215000E+00   0.589353
  2  S   2.22588000E+00   0.465206
```

```
  3  P   4.91765000E+02   0.003989
  3  P   1.16984000E+02   0.030318
  3  P   3.74153000E+01   0.129880
  3  P   1.37834000E+01   0.327951
  3  P   5.45215000E+00   0.453527
  3  P   2.22588000E+00   0.252154

  4  S   3.18649000E+00  -0.251830
  4  S   1.14427000E+00   0.061589
  4  S   4.20377000E-01   1.060180

  5  P   3.18649000E+00  -0.014299
  5  P   1.14427000E+00   0.323572
  5  P   4.20377000E-01   0.743507

  6  S   1.42657000E-01   1.000000

  7  P   1.42657000E-01   1.000000

  8  S   4.83000000E-02   1.000000

  9  P   4.83000000E-02   1.000000

 10  D   7.50000000E-01   1.000000
```

SCF calculations: Hartree-Fock energies of HCl

STO-3G

```
  -----------------------------------------------
        Tag         Shells   Functions and Types
  ----------------  ------  ---------------------
  H                    1        1   1s
  Cl                   5        9   3s2p


   iter       energy          gnorm     gmax
  ----- ------------------- --------- ---------
    1     -455.1125956242  3.94D-01  3.78D-01
    2     -455.1346340394  3.50D-02  3.42D-02
    3     -455.1348033282  1.37D-04  1.11D-04
    4     -455.1348033301  5.13D-06  5.00D-06


      Final RHF  results
      ------------------

        Total SCF energy =   -455.134803330094
     One-electron energy =   -644.157134414045
     Two-electron energy =    181.963866405257
Nuclear repulsion energy =      7.058464678694

       Time for solution =      0.0s
```

6-31+G*

```
------------------------------------------------
       Tag          Shells   Functions and Types
 ----------------  ------  ---------------------
 H                     2        2   2s
 Cl                   10       23   5s4p1d


  iter       energy          gnorm     gmax
 ----- ------------------- --------- ---------
   1     -460.0441394765  4.05D-01  2.19D-01
   2     -460.0598340681  1.23D-01  4.60D-02
   3     -460.0609809568  4.51D-03  2.38D-03
   4     -460.0609823850  4.53D-06  2.03D-06


  Final RHF  results
  ------------------

          Total SCF energy =   -460.060982384978
       One-electron energy =   -649.755049084147
       Two-electron energy =    182.635602020475
  Nuclear repulsion energy =      7.058464678694

         Time for solution =      0.2s
```

Calculated deprotonation energies

	E (STO-3G) in Hartrees	E (STO-3G) in kJ/mol	E (6-31+G*) in Hartrees	E (6-31+G*) in kJ/mol
HCl	-455.13480	-1194956.4	-460.06098	-1207890.1
Cl^-	-454.48042	-1193238.3	-459.53966	-1206521.4
Proton affinity $E(Cl^-) - E(HCl)$	0.65438	1718.1	0.52132	1368.7

The experimentally measured proton affinity is 1395 kJ/mol

Molecular Orbital energies, Koopmans' theorem

```
STO-3G
Eigenvalues

     1 -103.7226
     2  -10.4041
     3   -7.8489
     4   -7.8422
     5   -7.8422
     6   -1.0437
     7   -0.5646
     8   -0.4232
     9   -0.4232
    10    0.4043
```

→ 11.5 eV

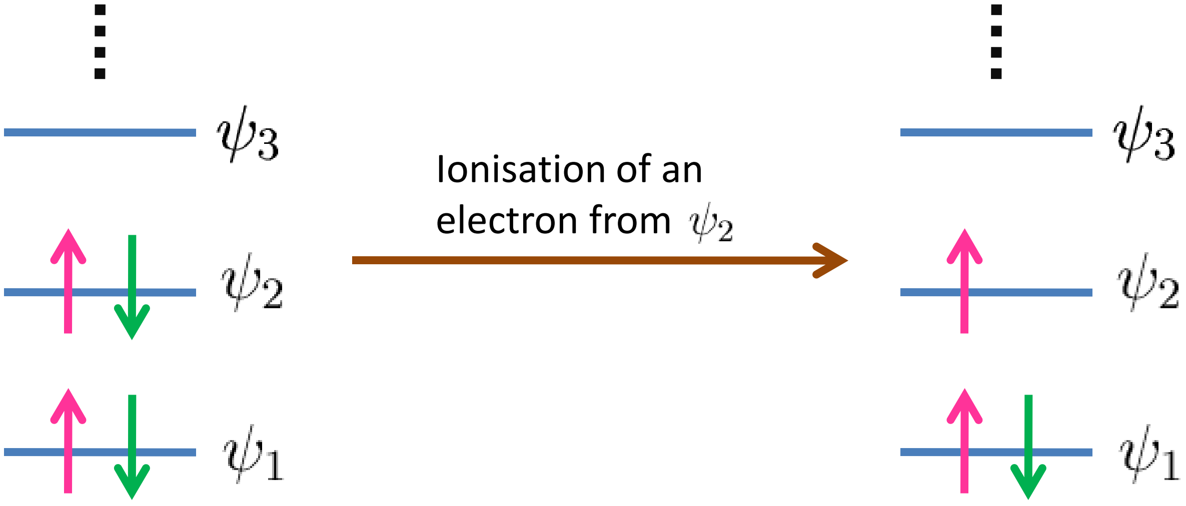
```
6-31+G*
Eigenvalues

     1 -104.8395
     2  -10.5737
     3   -8.0437
     4   -8.0395
     5   -8.0395
     6   -1.1220
     7   -0.6295
     8   -0.4773
     9   -0.4773
    10    0.0867
    11    0.1296
    12    0.1388
    13    0.1388
    14    0.1994
    15    0.7255
    16    0.7707
    17    0.7926
    18    0.7926
    19    0.9489
```

→ 13.0 eV

Experimentally measured ionisation energy of HCl: 12.8 eV

Ionisation potential (ionisation energy)

Example with 4 electrons



Ionisation of an electron from ψ_2

$$^4E = 2h_1 + 2h_2 + J_{11} + J_{22} + 4J_{12} - 2K_{12}$$

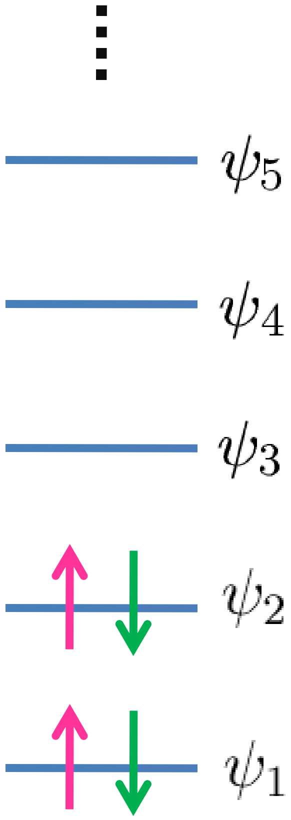
$$^3E = 2h_1 + h_2 + J_{11} + 2J_{12} - K_{12}$$

The ionisation potential (IP) is:

$$\begin{aligned} ^3E - ^4E &= -h_2 - J_{22} - 2J_{12} + K_{12} \\ &= -\varepsilon_2 \end{aligned}$$

Ionisation Potential (continued)

Example with 4 electrons



Fock operator acting on ψ_2

$$\hat{f}\psi_2(\mathbf{r}) = \hat{h}\psi_2(\mathbf{r}) + \hat{J}_2\psi_2(\mathbf{r}) + 2\hat{J}_1\psi_2(\mathbf{r}) - \hat{K}_1\psi_2(\mathbf{r})$$

$$\hat{f}\psi_2(\mathbf{r}) = \varepsilon_2\,\psi_2(\mathbf{r})$$

Fock operator acting on ψ_3

$$\hat{f}\psi_3(\mathbf{r}) = \hat{h}\psi_3(\mathbf{r}) + 2\hat{J}_1\psi_3(\mathbf{r}) - \hat{K}_1\psi_3(\mathbf{r}) + 2\hat{J}_2\psi_3(\mathbf{r}) - \hat{K}_2\psi_3(\mathbf{r})$$

$$\hat{f}\psi_3(\mathbf{r}) = \varepsilon_3\,\psi_3(\mathbf{r})$$

$$\mathrm{IP}_{\psi_2} = {}^3E - {}^4E = -\varepsilon_2$$

- This calculation of the IP is called Koopmans’ theorem
- It can also be used to compute electron affinities (EA)
- What approximations are implied in this calculation and how do they affect the computed IPs and EAs?

The electronic charge density

- Is equal to the sum of the squares of the occupied molecular orbitals

- It can be transformed to an expression involving the basis functions

$$\rho(\mathbf{r}) = 2\sum_{i=1}^{N_{elec}/2} |\psi_i(\mathbf{r})|^2 = 2\sum_{i=1}^{N_{elec}/2} \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})$$

$$= 2\sum_{i=1}^{N_{elec}/2}\left(\sum_{\alpha=1}^{N_{BF}} G_\alpha^*(\mathbf{r})c_{\alpha i}^*\right)\left(\sum_{\beta=1}^{N_{BF}} G_\beta(\mathbf{r})c_{\beta i}\right)$$

$$= \sum_{\alpha=1}^{N_{BF}}\sum_{\beta=1}^{N_{BF}}\left(2\sum_{i=1}^{N_{elec}/2} c_{\alpha i}^* c_{\beta i}\right) G_\alpha^*(\mathbf{r})G_\beta(\mathbf{r})$$

$$= \sum_{\alpha=1}^{N_{BF}}\sum_{\beta=1}^{N_{BF}} P_{\alpha\beta}G_\alpha^*(\mathbf{r})G_\beta(\mathbf{r})$$

$$= \sum_{\alpha=1}^{N_{BF}}\sum_{\beta=1}^{N_{BF}} G_\alpha^*(\mathbf{r})\underset{\uparrow}{P_{\alpha\beta}}G_\beta(\mathbf{r})$$

This is the density matrix

Population analysis

We can partition the electronic density to net charges associated with each atom

$$\rho(\mathbf{r}) = \sum_{\alpha=1}^{N_{BF}} \sum_{\beta=1}^{N_{BF}} P_{\beta\alpha}\, \phi_\alpha^*(\mathbf{r})\phi_\beta(\mathbf{r})$$

$$\int \rho(\mathbf{r})d\mathbf{r} = \sum_{\alpha=1}^{N_{BF}} \sum_{\beta=1}^{N_{BF}} P_{\beta\alpha} \int \phi_\alpha^*(\mathbf{r})\phi_\beta(\mathbf{r})d\mathbf{r}$$

$$N_{elec} = \sum_{\beta=1}^{N_{BF}} (\mathbf{PS})_{\beta\beta} = \sum_{I=1}^{N_{at}} \sum_{\beta\, \epsilon\, I} (\mathbf{PS})_{\beta\beta}$$

$$N_{elec} = \sum_{\beta=1}^{N_{BF}} (\mathbf{PS})_{\beta\beta}$$

The net charge on atom I is

$$q_I = Z_I - \sum_{\nu\, \epsilon\, I} (\mathbf{PS})_{\nu\nu}$$

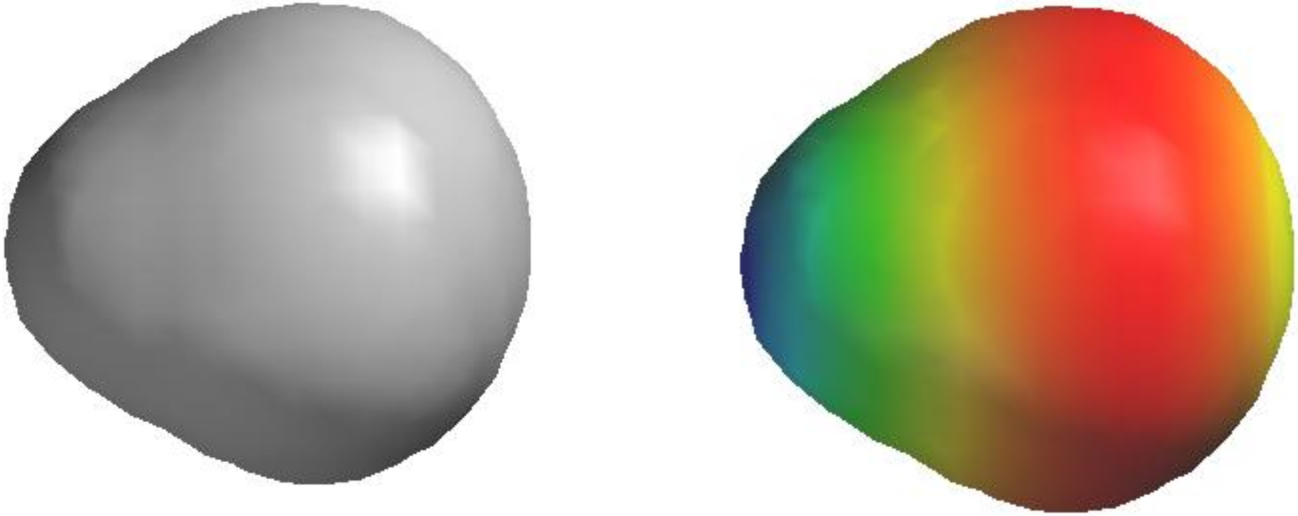
- This is called Mulliken population analysis
- It is not unique. Alternative partitions of the electronic density are possible

Mulliken population analysis of HCl

Atom	Charge (STO-3G)	Charge (6-31+G*)
Cl	-0.17	-0.23
H	+0.17	+0.23

Molecular electrostatic potential

$$V_{ES}(\mathbf{r}) = \sum_{I=1}^{N_{atom}} \frac{Z_I}{|\mathbf{r}-\mathbf{r}_I|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$$



Summary / Reading assignment

- Overview of Hartree-Fock calculations (Cramer, pages 192-201)
- Partial atomic charges - Mulliken approach (Cramer, pages 312-313)
- Molecular electrostatic potential (Cramer, pages 308-309)