

# CHEM3023: Spins, Atoms and Molecules

## Lecture 8

### Experimental observables / Unpaired electrons

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#### Learning outcomes

- Develop and work with expressions to calculate experimental observables from Hartree-Fock wavefunctions
- Be able to select and use suitable Hartree-Fock approaches for molecules with unpaired electrons

# Expectation values

- The operators for many experimental observables are sums of one-electron operators

$$\hat{O} = \sum_{i=1}^{N_{elec}} \hat{o}(\mathbf{r}_i)$$

- The expectation value of such operators, when the wavefunction is a Slater determinant (as in Hartree-Fock theory), is simply a sum over the occupied molecular orbitals

$$\begin{aligned} \langle O \rangle &= \frac{\langle \Psi_{SD} | \hat{O} | \Psi_{SD} \rangle}{\langle \Psi_{SD} | \Psi_{SD} \rangle} = \langle \Psi_{SD} | \hat{O} | \Psi_{SD} \rangle = \langle \Psi_{SD} | \sum_{i=1}^{N_{elec}} \hat{o}(\mathbf{r}_i) | \Psi_{SD} \rangle \\ &= 2 \sum_{i=1}^{N_{elec}/2} \langle \psi_i | \hat{o} | \psi_i \rangle \end{aligned}$$

## Example: Dipole moment

$$\hat{\boldsymbol{\mu}}_{elec} = \sum_{i=1}^{N_{elec}} -\mathbf{r}_i$$

$$\langle \hat{\boldsymbol{\mu}}_{elec} \rangle = \langle \Psi_0 | \hat{\boldsymbol{\mu}}_{elec} | \Psi_0 \rangle = \langle \Psi_0 | \sum_{i=1}^{N_{elec}} -\mathbf{r}_i | \Psi_0 \rangle = \sum_{i=1}^{N_{elec}} \langle \psi_i | -\mathbf{r} | \psi_i \rangle \quad (\text{in terms of MOs})$$

$$= \sum_{\alpha=1}^{N_{BF}} \sum_{\beta=1}^{N_{BF}} P_{\beta\alpha} \langle G_{\alpha} | -\mathbf{r} | G_{\beta} \rangle \quad (\text{in terms of the basis set})$$

The total dipole moment is the sum of electronic and nuclear dipole moments

$$\langle \hat{\boldsymbol{\mu}}_{total} \rangle = \langle \hat{\boldsymbol{\mu}}_{elec} \rangle + \langle \hat{\boldsymbol{\mu}}_{nuc} \rangle = \sum_{\alpha=1}^{N_{BF}} \sum_{\beta=1}^{N_{BF}} P_{\beta\alpha} \langle G_{\alpha} | -\mathbf{r} | G_{\beta} \rangle + \sum_{I=1}^{N_{nuc}} Z_I \mathbf{R}_I$$

## Dipole moment of HCl

Basis	$N_{BF}$	Dipole moment (D)
STO-3G	10	1.73
6-31+G*	25	1.53
aug-cc_pVTZ	84	1.20
aug-cc_pVQZ	164	1.19
aug-cc_pV5Z	291	1.18

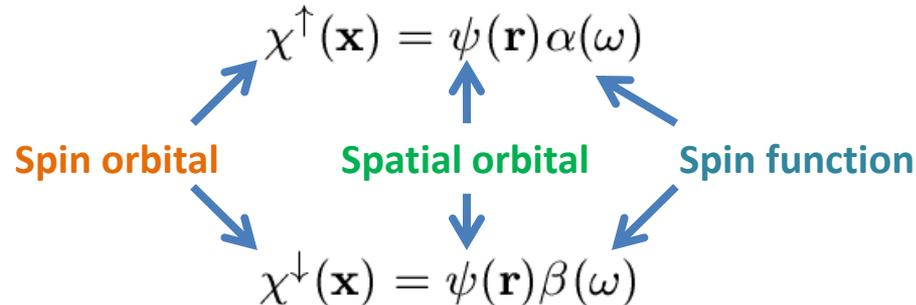
The experimentally measured dipole moment of HCl is 1.08D (Atkins' Physical Chemistry)

# Unpaired electrons

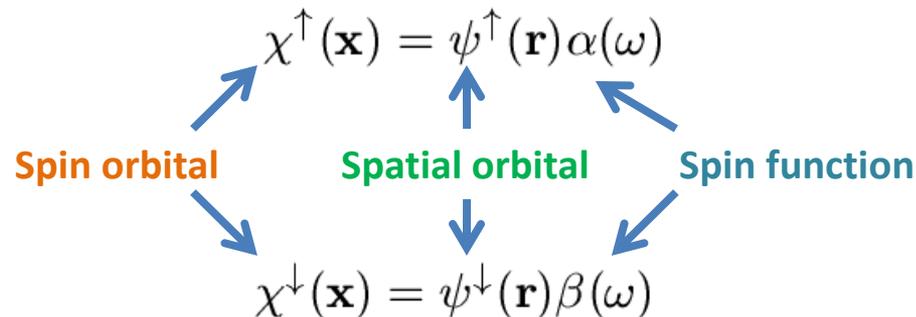
- So far we have developed Hartree-Fock theory for the case of paired electrons in doubly-occupied molecular orbitals
- Such calculations are called “restricted closed-shell” and are represented simply by the abbreviation **RHF** (Restricted Hartree Fock)
  - Restricted because pairs of alpha (“up”) and beta (“down”) spin orbitals are restricted to have the same spatial part
  - Closed shell because each spatial orbital (a “shell”) is closed, i.e. doubly occupied
- Can not work on molecules with unpaired electrons, such as free radicals
- Another failure is in the description of homolytic bond breaking. For example with RHF calculations a  $H_2$  molecule can only be dissociated to  $H^-$  and  $H^+$  and not to two H atoms

## Unrestricted spin orbitals

- So far we have been working with restricted spin orbitals where the up (“alpha”) and down (“beta”) spins have the same spatial orbital  $\psi(\mathbf{r})$



- In the unrestricted formalism the up and down spins are free to have **different** spatial orbitals  $\psi^\uparrow(\mathbf{r})$  and  $\psi^\downarrow(\mathbf{r})$  ,

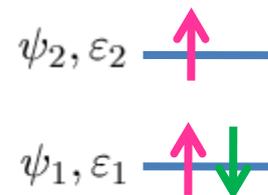


and hence different energies

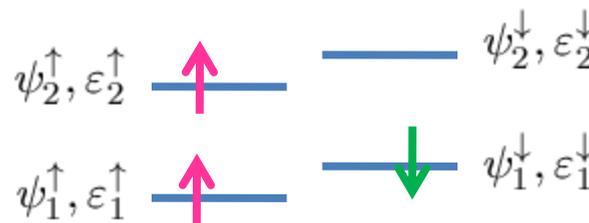
# ROHF and UHF calculations

To deal with unpaired electrons

- **Restricted Open shell Hartree-Fock (ROHF)**  
Spatial orbitals restricted to be the same for opposite spins but allowed to be partly occupied

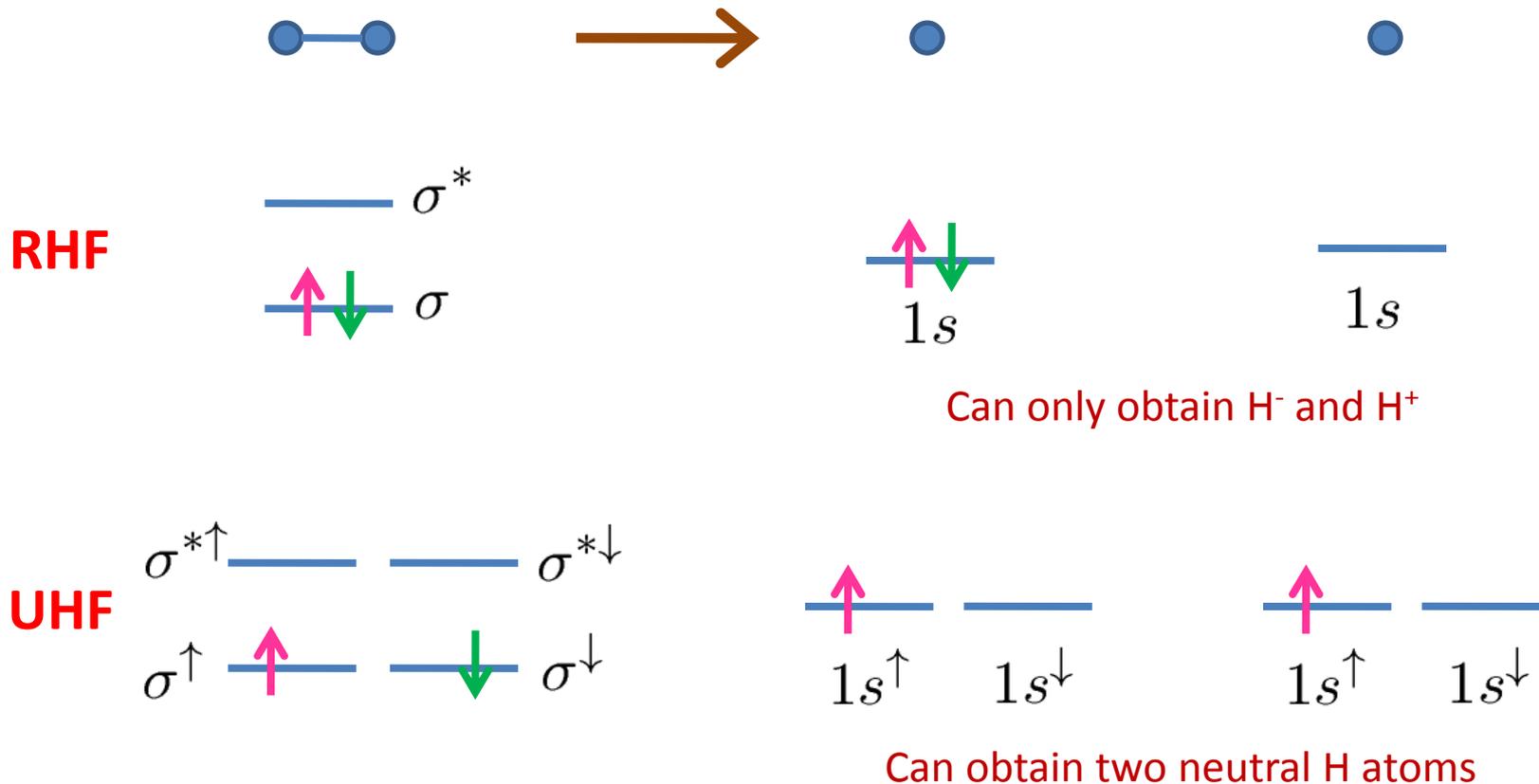


- **Unrestricted Hartree-Fock (UHF)**  
Up and Down spins in each electron pair are no longer restricted to share the same spatial orbital

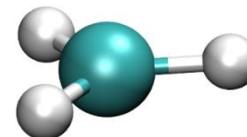


# Homolytic bond breaking

Example: dissociation of a H<sub>2</sub> molecule



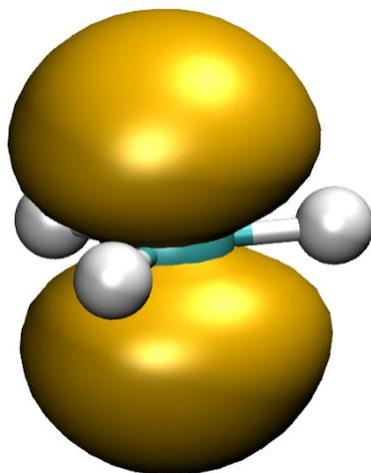
## Spin density – E.g. the methyl radical



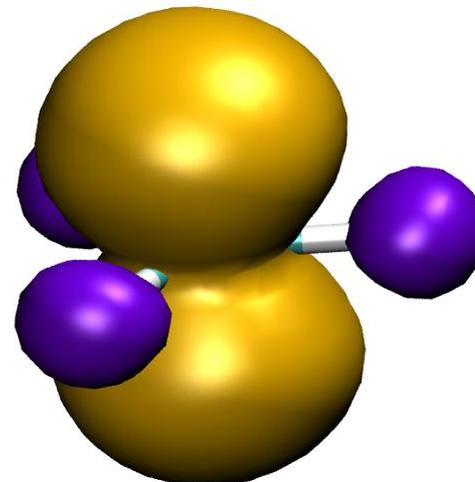
Total density  $\rho(\mathbf{r}) = \rho^\uparrow(\mathbf{r}) + \rho^\downarrow(\mathbf{r}) = \sum_{i=1}^{N_{elec}^\uparrow} |\psi_i^\uparrow(\mathbf{r})|^2 + \sum_{i=1}^{N_{elec}^\downarrow} |\psi_i^\downarrow(\mathbf{r})|^2$

Spin density  $\rho^{spin}(\mathbf{r}) = \rho^\uparrow(\mathbf{r}) - \rho^\downarrow(\mathbf{r}) = \sum_{i=1}^{N_{elec}^\uparrow} |\psi_i^\uparrow(\mathbf{r})|^2 - \sum_{i=1}^{N_{elec}^\downarrow} |\psi_i^\downarrow(\mathbf{r})|^2$

ROHF spin density



UHF spin density



## Unrestricted Hartree-Fock (UHF) equations

- Two Hartree-Fock eigenvalue equations, one for each spin  $\hat{f}^\uparrow \psi_i^\uparrow(\mathbf{r}) = \varepsilon_i^\uparrow \psi_i^\uparrow(\mathbf{r})$
- They are coupled and need to be solved simultaneously  $\hat{f}^\downarrow \psi_i^\downarrow(\mathbf{r}) = \varepsilon_i^\downarrow \psi_i^\downarrow(\mathbf{r})$

$$\hat{f}^\uparrow = \hat{h} + \left( \sum_{i=1}^{N_{elec}^\uparrow} \hat{J}_i^\uparrow + \sum_{j=1}^{N_{elec}^\downarrow} \hat{J}_j^\downarrow \right) - \sum_{l=1}^{N_{elec}^\uparrow} \hat{K}_l^\uparrow$$

↑ ↑

Coulomb operator  
(same for both spins)
Exchange operator  
(spin-specific)

$$\hat{f}^\downarrow = \hat{h} + \left( \sum_{i=1}^{N_{elec}^\uparrow} \hat{J}_i^\uparrow + \sum_{j=1}^{N_{elec}^\downarrow} \hat{J}_j^\downarrow \right) - \sum_{l=1}^{N_{elec}^\downarrow} \hat{K}_l^\downarrow$$

↓ ↓

## UHF electronic energy

- Contains the same terms we have encountered already in RHF calculations, arranged between the different spatial orbitals of each spin

$$E_0^{UHF} = \sum_{i=1}^{N_{elec}^{\uparrow}} h_i^{\uparrow} + \sum_{i=1}^{N_{elec}^{\downarrow}} h_i^{\downarrow} + \frac{1}{2} \sum_{i=1}^{N_{elec}^{\uparrow}} \sum_{j=1}^{N_{elec}^{\uparrow}} (J_{ij}^{\uparrow\uparrow} - K_{ij}^{\uparrow\uparrow}) + \frac{1}{2} \sum_{i=1}^{N_{elec}^{\downarrow}} \sum_{j=1}^{N_{elec}^{\downarrow}} (J_{ij}^{\downarrow\downarrow} - K_{ij}^{\downarrow\downarrow}) + \sum_{i=1}^{N_{elec}^{\uparrow}} \sum_{j=1}^{N_{elec}^{\downarrow}} J_{ij}^{\uparrow\downarrow}$$

Core Hamiltonian integral  $h_i^{\uparrow} = \langle \psi_i^{\uparrow} | \hat{h} | \psi_i^{\uparrow} \rangle$

Coulomb integral  $J_{ij}^{\uparrow\downarrow} = \int \int \psi_i^{\uparrow*}(\mathbf{r}_1) \psi_i^{\uparrow}(\mathbf{r}_1) \frac{1}{r_{12}} \psi_j^{\downarrow*}(\mathbf{r}_2) \psi_j^{\downarrow}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$

Exchange integral  $K_{ij}^{\uparrow\uparrow} = \int \int \psi_i^{\uparrow*}(\mathbf{r}_1) \psi_j^{\uparrow}(\mathbf{r}_1) \frac{1}{r_{12}} \psi_j^{\uparrow*}(\mathbf{r}_2) \psi_i^{\uparrow}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$

## UHF density and density matrix in terms of the basis set

- Using the expression the basis set expansion of the spatial orbitals for each spin, we can derive expressions for the density matrix

$$\rho^\uparrow(\mathbf{r}) = \sum_{\zeta=1}^{N_{BF}} \sum_{\eta=1}^{N_{BF}} P_{\zeta\eta}^\uparrow G_\eta(\mathbf{r}) G_\zeta^*(\mathbf{r}) \quad \rho^\downarrow(\mathbf{r}) = \sum_{\zeta=1}^{N_{BF}} \sum_{\eta=1}^{N_{BF}} P_{\zeta\eta}^\downarrow G_\eta(\mathbf{r}) G_\zeta^*(\mathbf{r})$$

$$\mathbf{P} = \mathbf{P}^\uparrow + \mathbf{P}^\downarrow$$

$$\mathbf{P}^{spin} = \mathbf{P}^\uparrow - \mathbf{P}^\downarrow$$

- UHF calculations are also called “spin-polarised” calculations, especially in simulations of materials

## Summary / Reading assignment

- Properties related to the charge distribution (Cramer, pages 305-306)
- Open-shell molecules, Unrestricted Hartree-Fock calculations (Cramer, pages 188-190)

## Optional: RHF electronic energy in terms of the basis set

The total electronic energy of the Hartree-Fock wavefunction, is given by the expression for the energy of a Slater determinant:

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = 2 \sum_{i=1}^{N_{elec}/2} h_{ii} + \sum_{i=1}^{N_{elec}/2} \sum_{j=1}^{N_{elec}/2} (2J_{ij} - K_{ij})$$

$$= 2 \sum_{i=1}^{N_{elec}} \int \psi_i^*(\mathbf{r}) \hat{h} \psi_i(\mathbf{r}) d\mathbf{r} + \sum_{i=1}^{N_{elec}/2} \sum_{j=1}^{N_{elec}/2} \left[ 2 \int \int \psi_i^*(\mathbf{r}_1) \psi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_i(\mathbf{r}_1) \psi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 - \int \int \psi_i^*(\mathbf{r}_1) \psi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_j(\mathbf{r}_1) \psi_i(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \right]$$

To convert it to an expression in terms of the basis set, we need to:

1) Write the molecular orbitals as a linear-combinations of the basis functions

$$\psi_i(\mathbf{r}) = \sum_{\alpha=1}^{N_{BF}} G_{\alpha}(\mathbf{r}) c_{\alpha i}$$

2) Use the expression for the density matrix  $P_{\alpha\beta} = 2 \sum_{i=1}^{N_{elec}} c_{\alpha i} c_{\beta i}^*$

After substituting these two expressions in the formula for the Hartree-Fock total electronic energy, we obtain (show this!):

$$E_0 = \sum_{\alpha=1}^{N_{BF}} \sum_{\beta=1}^{N_{BF}} P_{\alpha\beta} \langle G_{\beta} | \hat{h} | G_{\alpha} \rangle + \sum_{\alpha=1}^{N_{BF}} \sum_{\beta=1}^{N_{BF}} \sum_{\gamma=1}^{N_{BF}} \sum_{\delta=1}^{N_{BF}} P_{\beta\alpha} \left[ (\alpha\beta|\gamma\delta) - \frac{1}{2}(\alpha\delta|\gamma\beta) \right] P_{\delta\gamma}$$

which includes **two-electron repulsion integrals**:

$$(\alpha\beta|\gamma\delta) = \int \int G_{\alpha}^*(\mathbf{r}_1) G_{\beta}(\mathbf{r}_1) \frac{1}{r_{12}} G_{\gamma}^*(\mathbf{r}_2) G_{\delta}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

**Notice that the computational effort (memory and CPU time) will be proportional to  $N_{BF}^4$**

**Exercise : Derive an expression for the UHF energy in terms of the basis set**

## Relation between total electronic energy and molecular orbital energies

$$\begin{aligned} E_0 &= 2 \sum_{i=1}^{N_{elec}/2} h_{ii} + \sum_{i=1}^{N_{elec}/2} \sum_{j=1}^{N_{elec}/2} (2J_{ij} - K_{ij}) \\ &= \sum_{i=1}^{N_{elec}/2} 2 \left[ h_{ii} + \sum_{j=1}^{N_{elec}/2} (2J_{ij} - K_{ij}) \right] - \sum_{k=1}^{N_{elec}/2} \sum_{l=1}^{N_{elec}/2} (2J_{kl} - K_{kl}) \\ &= \sum_{i=1}^{N_{elec}/2} 2F_{ii} - \sum_{k=1}^{N_{elec}/2} \sum_{l=1}^{N_{elec}/2} (2J_{kl} - K_{kl}) \\ &= \sum_{i=1}^{N_{elec}/2} 2\varepsilon_i - \sum_{k=1}^{N_{elec}/2} \sum_{l=1}^{N_{elec}/2} (2J_{kl} - K_{kl}) \end{aligned}$$

Re-write this in terms  
of the basis set

- The electronic energy is not equal to the sum of the molecular orbital energies
- The sum of orbital energies results in “double counting” of the Coulomb and exchange energies which needs to be subtracted to obtain the electronic energy