

# CHEM6085: Density Functional Theory

## Lecture 10

- 1) Spin-polarised calculations
- 2) Geometry optimisation

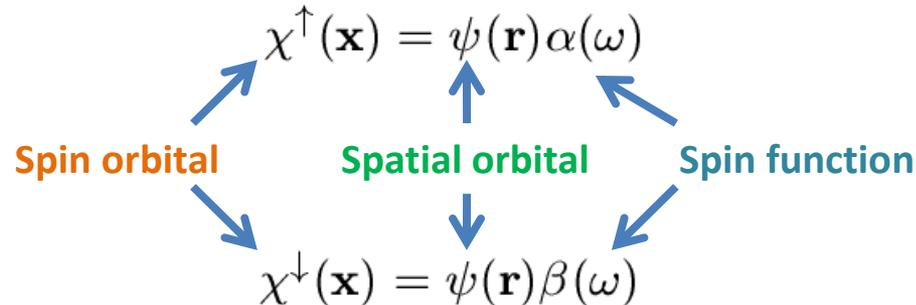
C.-K. Skylaris

# Unpaired electrons

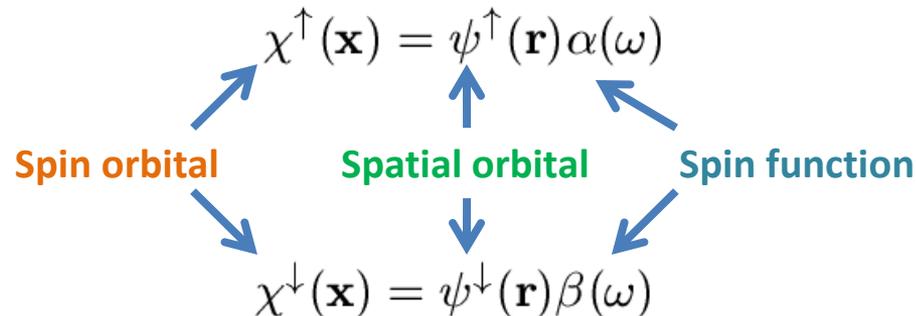
- So far we have developed Kohn-Sham DFT for the case of paired electrons in doubly-occupied molecular orbitals
- Such calculations are called “restricted closed-shell” or “spin unpolarised”
  - Restricted because pairs of alpha and beta spin orbitals are restricted to have the same spatial part
  - Closed shell because each spatial orbital (a “shell”) is closed, i.e. doubly occupied
- Can not describe molecules with unpaired electrons, such as free radicals
- Another failure is in the description of homolytic bond breaking. For example with spin unpolarised calculations a  $\text{H}_2$  molecule can only be dissociated to  $\text{H}^-$  and  $\text{H}^+$  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  $\psi^\downarrow(\mathbf{r})$  ,

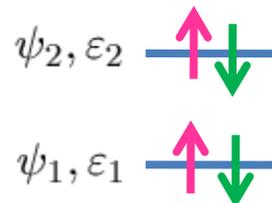


and hence different energies

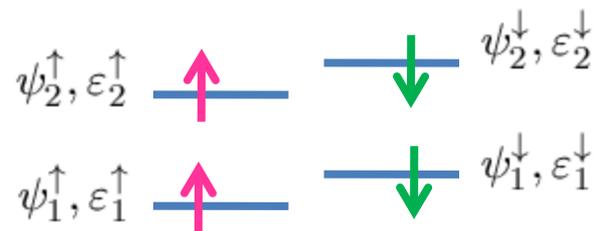
# Spin polarised Kohn-Sham DFT

To deal with unpaired electrons

- **Restricted (spin unpolarised)**  
Spatial orbitals are restricted to be the same for opposite spins



- **Unrestricted (spin polarised)**  
Up and down spins in each electron pair are no longer restricted to share the same spatial orbital

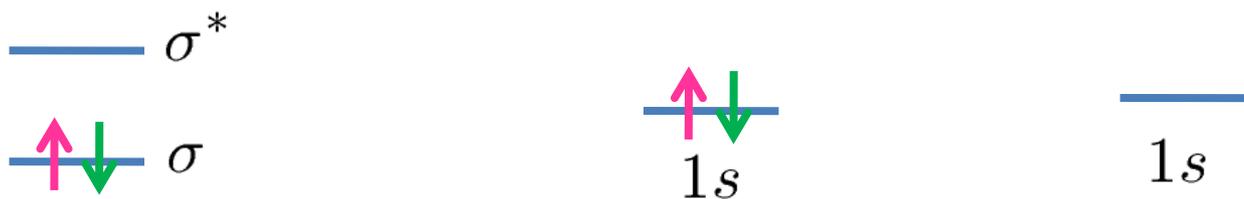


# Homolytic bond breaking

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

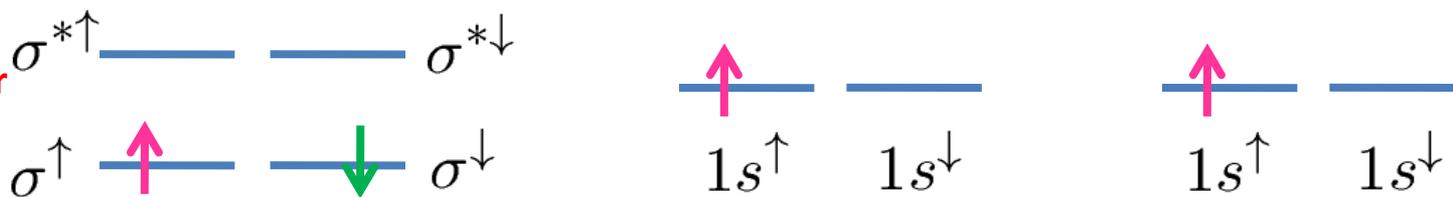


Restricted  
closed shell



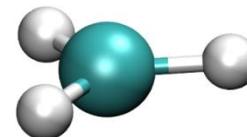
Can only obtain H<sup>-</sup> and H<sup>+</sup>

Restricted or  
Unrestricted  
open shell



Can obtain two neutral H atoms

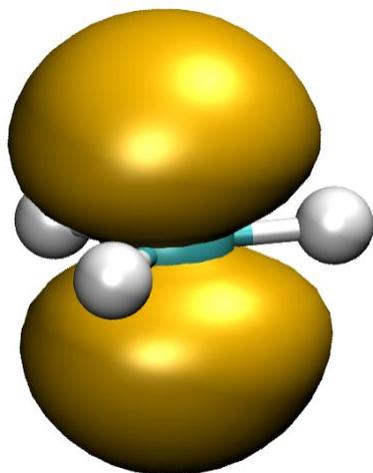
## Spin density – E.g. the methyl radical



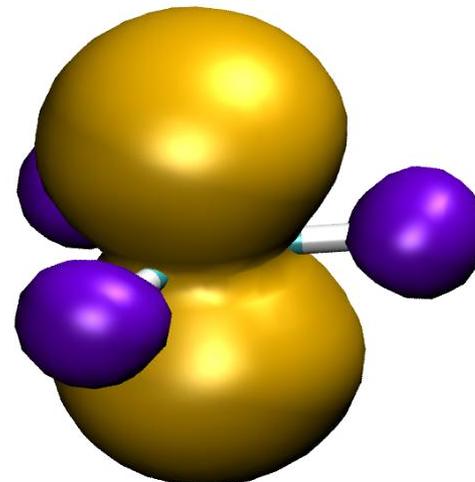
Total density  $n(\mathbf{r}) = n^\uparrow(\mathbf{r}) + n^\downarrow(\mathbf{r}) = \sum_{i=1}^{N_{\text{el}}^\uparrow} |\psi_i^\uparrow(\mathbf{r})|^2 + \sum_{i=1}^{N_{\text{el}}^\downarrow} |\psi_i^\downarrow(\mathbf{r})|^2$

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

Restricted open shell spin density



Unrestricted open shell spin density



# Kohn-Sham Energy

- Separate kinetic and exchange-correlation energies for each spin
- Coulomb and external potential energies are calculated for the total density

$$\sum_{i=1}^{N_{\text{el}}^{\uparrow}} \int \psi_i^{\uparrow*}(\mathbf{r}) \left( -\frac{1}{2} \nabla^2 \right) \psi_i^{\uparrow}(\mathbf{r}) d\mathbf{r} \qquad \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r}$$
$$E[n] = E_{\text{kin,KS}}[n^{\uparrow}] + E_{\text{kin,KS}}[n^{\downarrow}] + E_{\text{Coul}}[n] + E_{\text{ext}}[n] + E_{\text{xc}}[n^{\uparrow}] + E_{\text{xc}}[n^{\downarrow}]$$
$$\sum_{i=1}^{N_{\text{el}}^{\downarrow}} \int \psi_i^{\downarrow*}(\mathbf{r}) \left( -\frac{1}{2} \nabla^2 \right) \psi_i^{\downarrow}(\mathbf{r}) d\mathbf{r} \qquad \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$

## Kohn-Sham Hamiltonian

- A separate exchange-correlation operator for each spin results in different Kohn-Sham Hamiltonians for each spin

$$\hat{h}_{\text{KS}}^{\uparrow} = -\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{Coul}}[n](\mathbf{r}) + V_{\text{xc}}[n^{\uparrow}](\mathbf{r})$$

$$\hat{h}_{\text{KS}}^{\downarrow} = -\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{Coul}}[n](\mathbf{r}) + V_{\text{xc}}[n^{\downarrow}](\mathbf{r})$$

- The iterative solution of each Hamiltonian will provide the Kohn-Sham orbitals for each spin
- However the Hamiltonians depend also on the total density (up plus down spins) through the Coulomb operator so these Hamiltonians are coupled and they have to be solved simultaneously via the SCF procedure

# Moving the atoms: Potential Energy Surface (PES)

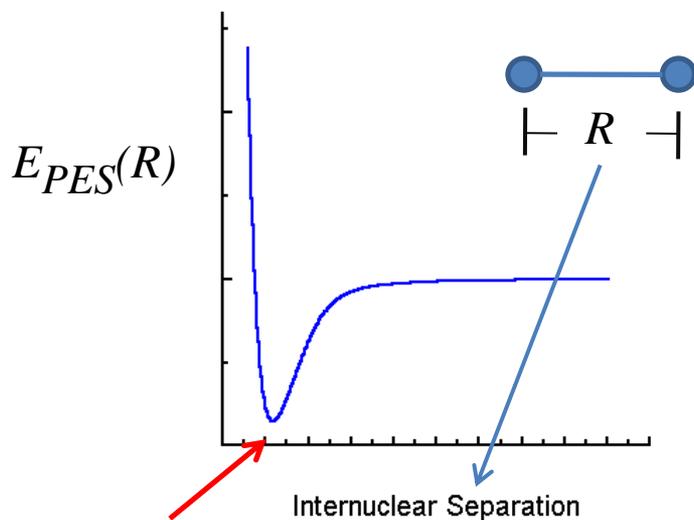
- The electronic energy is a function of the nuclear positions. So is the internuclear repulsion energy
- Their sum is called the Potential Energy Surface (PES). It is a function of  $3 \times N_{\text{atoms}}$  variables that represents a “surface” in  $(3 \times N_{\text{atoms}} + 1)$  dimensions

$$E_{PES}(\{\mathbf{R}_I\}) = E_{elec}(\{\mathbf{R}_I\}) + \sum_I \sum_{J>I} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

Electronic energy

Repulsion energy between nuclei I and J

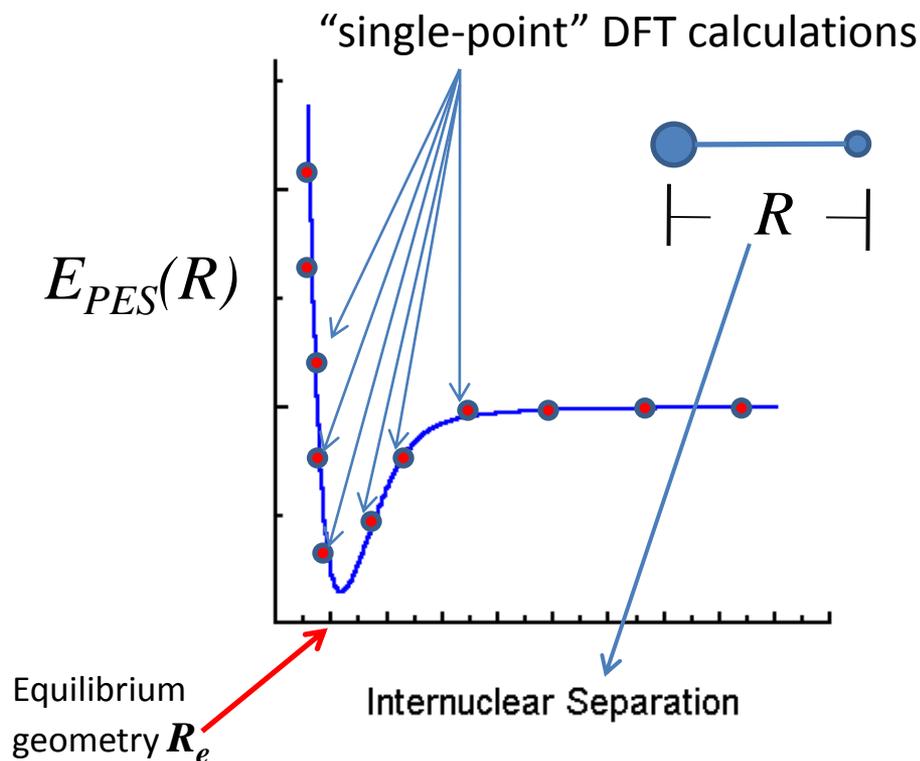
Example: PES of a diatomic



Equilibrium geometry  $R_e$

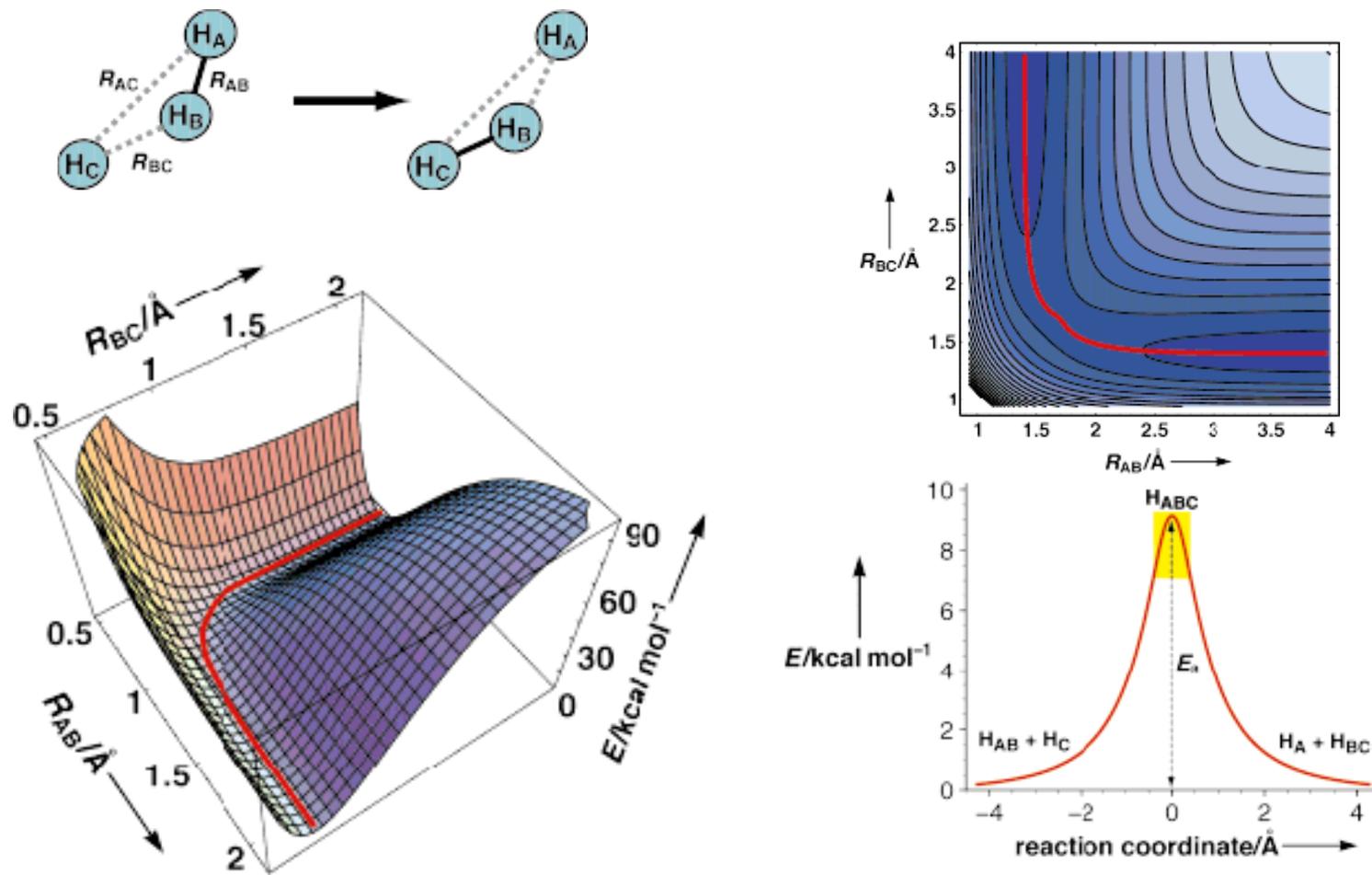
## Example: PES of HCl

- The PES is a function of 6 coordinates
- 5 of these can be removed as they correspond to entire-molecule translation (3 coordinates) and rotation (2 coordinates)
- So in practice the PES depends only on 1 coordinate (the H-Cl distance)



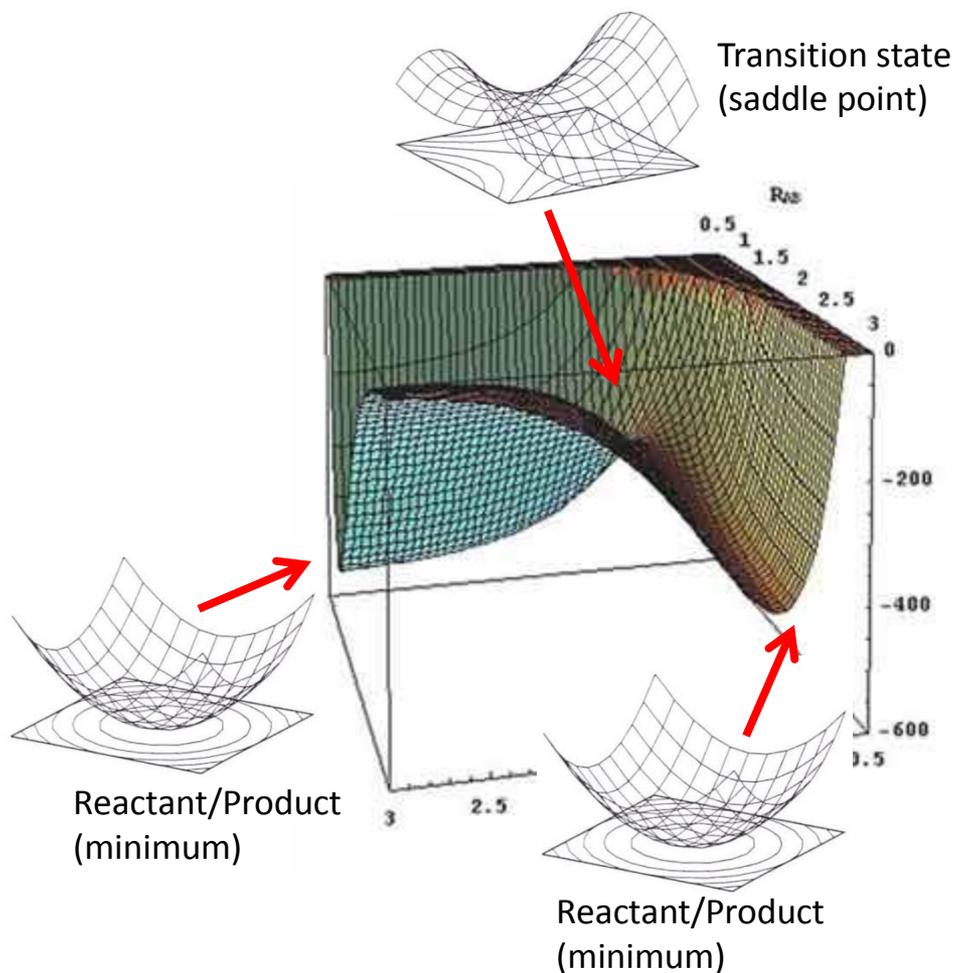
Method	$R_e$ (Å)
HF/STO-3G	1.31328
HF/6-31+G*	1.26712
HF/aug-cc_pVTZ	1.26752
Experiment	1.27455

## PES for $\text{H}_2 + \text{H} \rightarrow \text{H} + \text{H}_2$



This PES represents chemical interactions that can take place between 3 H atoms

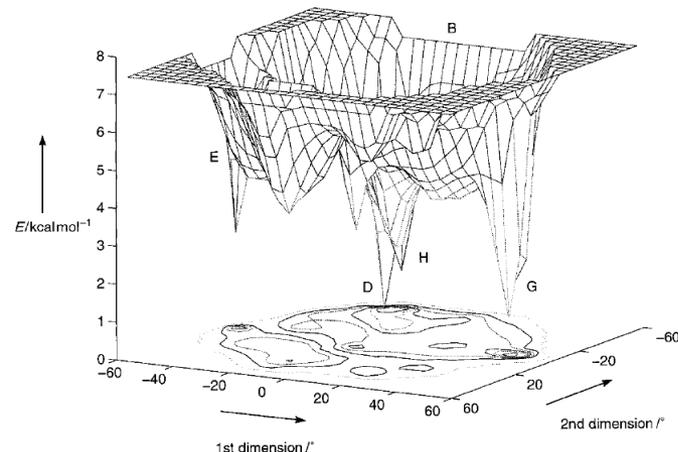
# Minima and saddle points



Products, reactants and transition states are **stationary points**, i.e. they are points on the PES where the derivative of  $E_{PES}$  with respect to all nuclear coordinates is zero

$$\frac{\partial E_{PES}}{\partial R_{I\gamma}} = 0, \quad \gamma = x, y, z$$

A more complicated PES...



# Homework

1) Examine the form of the Kohn-Sham Hamiltonians for each spin and decide in which cases the up-spin electrons will experience different interactions from the down-spin ones, and hence the orbital energies for the same orbital will be different for each spin.

2) Each spin function is an eigenfunction of the operator for the z-component of the spin of an electron. In atomic units the eigenvalue equation is as follows:

$$\hat{s}_z \alpha(\omega) = \frac{1}{2} \alpha(\omega) \quad \hat{s}_z \beta(\omega) = -\frac{1}{2} \beta(\omega)$$

Show that any Slater determinant wavefunction is an eigenfunction of the total z-component spin operator

$$\hat{S}_z = \sum_{i=1}^{N_{\text{el}}} \hat{s}_z(i)$$

with eigenvalue  $\frac{1}{2}(N_{\text{el}}^{\uparrow} - N_{\text{el}}^{\downarrow})$  regardless of whether the Slater determinant is made of restricted or unrestricted spin orbitals.

3) Assume that a simple potential energy surface (PES) is defined by only two coordinates x and y and has the expression  $E(x,y) = 2xy + 3x^2 + 2y + 5$ . Find the stationary points of this PES and determine whether they are equilibrium geometries or transition states.

## 5-minute quiz

Name :  
Surname:

Date :

- 1) How do the Kohn-Sham molecular orbitals differ between a conventional and a spin-polarised DFT calculation?
- 2) Write down the expression for the LDA exchange energy in a spin-polarised calculation (so use the up-spin and down-spin densities)
- 3) Considering the general shape (saddle) of the energy surface on a transition state point on the PES, what do you expect a molecule whose geometry is a transition state to do?