Experimental observables / Unpaired electrons

C.-K. Skylaris

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

\[ \hat{O} = \sum_{i=1}^{N_{\text{elec}}} \hat{\varrho}(\mathbf{r}_i) \]

• 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

\[
\langle O \rangle = \frac{\langle \Psi_{SD} | \hat{O} | \Psi_{SD} \rangle}{\langle \Psi_{SD} | \Psi_{SD} \rangle} = \langle \Psi_{SD} | \hat{O} | \Psi_{SD} \rangle = \langle \Psi_{SD} | \sum_{i=1}^{N_{\text{elec}}} \hat{\varrho}(\mathbf{r}_i) | \Psi_{SD} \rangle \\
= 2 \sum_{i=1}^{N_{\text{elec}}/2} \langle \psi_i | \hat{\varrho} | \psi_i \rangle
\]
Example: Dipole moment

\[ \hat{\mu}_{\text{elec}} = \sum_{i=1}^{N_{\text{elec}}} -r_i \]

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

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

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

\[ \langle \hat{\mu}_{\text{total}} \rangle = \langle \hat{\mu}_{\text{elec}} \rangle + \langle \hat{\mu}_{\text{nuc}} \rangle = \sum_{\alpha=1}^{N_{BF}} \sum_{\beta=1}^{N_{BF}} P_{\beta \alpha} \langle G_\alpha | -r | G_\beta \rangle + \sum_{I=1}^{N_{nuc}} Z_I R_I \]
### Dipole moment of HCl

<table>
<thead>
<tr>
<th>Basis</th>
<th>$N_{BF}$</th>
<th>Dipole moment (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO-3G</td>
<td>10</td>
<td>1.73</td>
</tr>
<tr>
<td>6-31+G*</td>
<td>25</td>
<td>1.53</td>
</tr>
<tr>
<td>aug-cc_pVTZ</td>
<td>84</td>
<td>1.20</td>
</tr>
<tr>
<td>aug-cc_pVQZ</td>
<td>164</td>
<td>1.19</td>
</tr>
<tr>
<td>aug-cc_pV5Z</td>
<td>291</td>
<td>1.18</td>
</tr>
</tbody>
</table>

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 H₂ 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 $\psi(r)$.

$$\chi^\uparrow(x) = \psi(r) \alpha(\omega)$$

$$\chi^\downarrow(x) = \psi(r) \beta(\omega)$$

• In the unrestricted formalism the up and down spins are free to have different spatial orbitals $\psi^\uparrow(r)$ and $\psi^\downarrow(r)$.

$$\chi^\uparrow(x) = \psi^\uparrow(r) \alpha(\omega)$$

$$\chi^\downarrow(x) = \psi^\downarrow(r) \beta(\omega)$$

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 $\text{H}_2$ molecule

RHF

$\sigma^*$

$\sigma$

UHF

$\sigma^*_{\uparrow}$  $\sigma^*_{\downarrow}$

$\sigma_{\uparrow}$  $\sigma_{\downarrow}$

Can only obtain $\text{H}^-$ and $\text{H}^+$

Can obtain two neutral H atoms
Spin density – E.g. the methyl radical

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

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

ROHF spin density

UHF spin density
Unrestricted Hartree-Fock (UHF) equations

- Two Hartree-Fock eigenvalue equations, one for each spin
- They are coupled and need to be solved simultaneously

\[ \hat{f}^\uparrow = \hat{h} + \sum_{i=1}^{N_{\text{elec}}} \hat{J}_i^\uparrow + \sum_{j=1}^{N_{\text{elec}}} \hat{J}_j^\downarrow - \sum_{l=1}^{N_{\text{elec}}} \hat{K}_l^\uparrow \]

Coulomb operator (same for both spins)

\[ \hat{f}^\downarrow = \hat{h} + \sum_{i=1}^{N_{\text{elec}}} \hat{J}_i^\downarrow + \sum_{j=1}^{N_{\text{elec}}} \hat{J}_j^\uparrow - \sum_{l=1}^{N_{\text{elec}}} \hat{K}_l^\downarrow \]

Exchange operator (spin-specific)

\[ \hat{f}^\uparrow \psi_i^\uparrow(\mathbf{r}) = \varepsilon_i^\uparrow \psi_i^\uparrow(\mathbf{r}) \]

\[ \hat{f}^\downarrow \psi_i^\downarrow(\mathbf{r}) = \varepsilon_i^\downarrow \psi_i^\downarrow(\mathbf{r}) \]
UHF electronic energy

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

\[
E_{0}^{UHF} = \sum_{i=1}^{N_{\text{elec}}} h_{i}^{\uparrow} + \sum_{i=1}^{N_{\text{elec}}} h_{i}^{\downarrow} + \frac{1}{2} \sum_{i=1}^{N_{\text{elec}}} \sum_{j=1}^{N_{\text{elec}}} (J_{ij}^{\uparrow\downarrow} - K_{ij}^{\uparrow\uparrow}) + \frac{1}{2} \sum_{i=1}^{N_{\text{elec}}} \sum_{j=1}^{N_{\text{elec}}} (J_{ij}^{\downarrow\uparrow} - K_{ij}^{\downarrow\downarrow}) + \sum_{i=1}^{N_{\text{elec}}} \sum_{j=1}^{N_{\text{elec}}} J_{ij}^{\uparrow\downarrow}
\]

Core Hamiltonian integral

\[ h_{i}^{\uparrow} = \langle \psi_{i}^{\uparrow} \mid \hat{h} \mid \psi_{i}^{\uparrow} \rangle \]

Coulomb integral

\[ J_{ij}^{\uparrow\downarrow} = \int \int \psi_{i}^{\uparrow\ast} (\mathbf{r}_{1}) \psi_{j}^{\downarrow} (\mathbf{r}_{1}) \frac{1}{r_{12}} \psi_{j}^{\downarrow\ast} (\mathbf{r}_{2}) \psi_{i}^{\uparrow} (\mathbf{r}_{2}) d\mathbf{r}_{1} d\mathbf{r}_{2} \]

Exchange integral

\[ K_{ij}^{\uparrow\downarrow} = \int \int \psi_{i}^{\uparrow\ast} (\mathbf{r}_{1}) \psi_{j}^{\downarrow\ast} (\mathbf{r}_{1}) \frac{1}{r_{12}} \psi_{j}^{\downarrow\ast} (\mathbf{r}_{2}) \psi_{i}^{\uparrow} (\mathbf{r}_{2}) d\mathbf{r}_{1} d\mathbf{r}_{2} \]
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

\[
\rho^{\uparrow}(r) = \sum_{\zeta=1}^{N_{BF}} \sum_{\eta=1}^{N_{BF}} P_{\zeta\eta}^{\uparrow} G_{\eta}(r) G_{\zeta}^{\ast}(r) \quad \rho^{\downarrow}(r) = \sum_{\zeta=1}^{N_{BF}} \sum_{\eta=1}^{N_{BF}} P_{\zeta\eta}^{\downarrow} G_{\eta}(r) G_{\zeta}^{\ast}(r)
\]

\[
P = P^{\uparrow} + P^{\downarrow}
\]

\[
P^{spin} = P^{\uparrow} - P^{\downarrow}
\]

- 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:

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

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

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

\[ \psi_i(\vec{r}) = \sum_{\alpha=1}^{N_{\text{BF}}} G_\alpha(\vec{r}) c_{\alpha i} \]

2) Use the expression for the density matrix

\[ P_{\alpha\beta} = 2 \sum_{i=1}^{N_{\text{elec}}} c_{\alpha i} c_{\beta i}^* \]
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:

\[
(\alpha\beta|\gamma\delta) = \int \int G^*_\alpha(r_1) G_\beta(r_1) \frac{1}{r_{12}} G^*_\gamma(r_2) G_\delta(r_2) dr_1 dr_2
\]

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

\[
E_0 = 2 \sum_{i=1}^{N_{\text{elec}}/2} h_{ii} + \sum_{i=1}^{N_{\text{elec}}/2} \sum_{j=1}^{N_{\text{elec}}/2} (2J_{ij} - K_{ij})
\]

\[
= \sum_{i=1}^{N_{\text{elec}}/2} 2 \left[ h_{ii} + \sum_{j=1}^{N_{\text{elec}}/2} (2J_{ij} - K_{ij}) \right] - \sum_{k=1}^{N_{\text{elec}}/2} \sum_{l=1}^{N_{\text{elec}}/2} (2J_{kl} - K_{kl})
\]

\[
= \sum_{i=1}^{N_{\text{elec}}/2} 2F_{ii} - \sum_{k=1}^{N_{\text{elec}}/2} \sum_{l=1}^{N_{\text{elec}}/2} (2J_{kl} - K_{kl})
\]

Re-write this in terms of the basis set

\[
= \sum_{i=1}^{N_{\text{elec}}/2} 2\varepsilon_i - \sum_{k=1}^{N_{\text{elec}}/2} \sum_{l=1}^{N_{\text{elec}}/2} (2J_{kl} - K_{kl})
\]

- 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