CHEM400/740: Quantum Mechanics in Chemistry
Chapter#04: Slater Rules and Examples

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Contents

1. Evaluating Matrix Elements Over Slater Determinants

Formulation of the problem:

Given a set of orthonormal spin-orbitals, $\psi_a, \psi_b, ..., \psi_m$, we can construct determinants.

e.g: $|\psi_a \psi_b \psi_c \psi_d| = -|\psi_a \psi_b \psi_d \psi_c| = +|\psi_a \psi_d \psi_b \psi_c| = |K\rangle$

We want to evaluate $\langle K|L\rangle$ and $\langle K|\hat{H}|L\rangle = \langle K|\hat{h}|L\rangle + \langle K|\hat{V}|L\rangle$.

Note that $\hat{H} = \sum_i \hat{h}(i) + \sum_{i<j} \frac{1}{r_{ij}}$ and $\hat{h}(i) = \hat{T}_{(i)} + \hat{V}_{(i)}^{Ne}$.

We will use antisymmetrizer $\hat{A}$ to define the determinant.

$$\hat{A} = \frac{1}{N!} \sum_{k=1}^{N!} (-)^{P_k} \hat{P}_k \tag{1}$$

$$\hat{A}^\dagger = \hat{A} \tag{2}$$

$$\hat{A}\hat{A} = N!\hat{A} = \hat{A}^\dagger \hat{A} = N!\hat{A}^\dagger \tag{3}$$

Normalized basis states:

$$|K\rangle = \frac{1}{\sqrt{N!}} \hat{A}(\psi_a(1)\psi_b(2)\cdots\psi_z(N)) \tag{4}$$

Let us prove this, $\langle K|K\rangle = 1$:

$$
\begin{aligned}
\langle K|K\rangle &= \frac{1}{\sqrt{N!}} \frac{1}{\sqrt{N!}} \langle \hat{A}\psi_a(1)\cdots\psi_z(N)|\hat{A}(\psi_a(1)\cdots\psi_z(N)\rangle \\
&= \frac{1}{N!} \langle \psi_a(1)\cdots\psi_z(N)|\hat{A}^\dagger \hat{A}(\psi_a(1)\cdots\psi_z(N))\rangle \\
&= \frac{1}{N!} N! \langle \psi_a(1)\cdots\psi_z(N)|\hat{A}^\dagger(\psi_a(1)\cdots\psi_z(N))\rangle \\
&= 1 \cdot \langle \hat{A}(\psi_a(1)\cdots\psi_z(N))|\psi_a(1)\cdots\psi_z(N)\rangle \\
&= \int \sum_i (-)^{P_i} \hat{P}_i(\psi_a^*(1)\cdots\psi_z^*(N)) \cdot (\psi_a(1)\cdots\psi_z(N))d1d2\cdots dN \\
&= \int \psi_a^*(1)\psi_b^*(2)\cdots\psi_z^*(N) \cdot \psi_a(1)\psi_b(2)\cdots\psi_z(N)d\tau \\
&\quad - \int \psi_b^*(1)\psi_a^*(2)\cdots\psi_z^*(N) \cdot \psi_a(1)\psi_b(2)\cdots\psi_z(N)d\tau + \cdots + \\
&\quad (-) \int \psi_c^*(1)\psi_b^*(2)\cdots\psi_a^*(N)\cdots\psi_a(1)\psi_b(2)\cdots\psi_z(N)d\tau \\
&= 1
\end{aligned}
\tag{5}
$$

NOTE:

- $(|\text{ket}\rangle)^\dagger \implies \langle\text{bra}|$. e.g. $(\hat{A}|\psi_a\cdots\psi_b\rangle)^\dagger = \langle\psi_a\cdots\psi_b|\hat{A}^\dagger$

- Only the identity peremutation contributes; otherwise mismatch.

  $\int \psi_a^*(1)\psi_b^*(2)\cdots\psi_z^*(N) \cdot \psi_a(1)\psi_b(2)\cdots\psi_z(N)d\tau = \langle a|a\rangle_1 \langle b|b\rangle_2 \cdots \langle z|z\rangle_N = 1$.

  $\int \psi_b^*(1)\psi_a^*(2)\cdots\psi_z^*(N) \cdot \psi_a(1)\psi_b(2)\cdots\psi_z(N)d\tau = \langle b|a\rangle_1 \langle a|b\rangle_2 \cdots \langle z|z\rangle_N = 0$

- $\langle K|K'\rangle = 0$. Note that K' differs by one orbital.
  SAME:$|K\rangle = |\psi_a\psi_b\cdots\psi_z|$ DIFFERENT:$|K'\rangle = |\psi_p\psi_b\cdots\psi_z|$
  Everything works as before: Mismatch in $b, c, d, \ldots$ unless identity permutation, like $K = K'$.
  $\langle K|K'\rangle = \langle a|p\rangle_1\langle b|b\rangle_2\cdots\langle z|z\rangle_N = \langle a|p\rangle_1 \cdot 1 \cdot 1 \cdot 1 = \delta_{ap} = 0$

Important: Define determinants K and K' to have maximum coincidence: line up the orbitals they have in common. Put their differences in same. e.g, first spot.

Let us use similar procedures to obtain other matrix elements of $\hat{H}$.
Preliminaries:

$$\frac{1}{N!}\langle \hat{A}(\psi_a(1)\cdots\psi_z(N))|\hat{H}|\hat{A}(\psi_a(1)\cdots\psi_z(N))\rangle$$
$$= \frac{1}{N!}\langle \psi_a(1)\cdots\psi_z(N)|\hat{A}^\dagger\hat{H}\hat{A}|\psi_a(1)\cdots\psi_z(N)\rangle$$
$$= \frac{1}{N!}\langle \psi_a(1)\cdots\psi_z(N)|\hat{A}^\dagger\hat{A}\hat{H}|\psi_a(1)\cdots\psi_z(N)\rangle$$
$$= \frac{1}{N!}\langle \psi_a(1)\cdots\psi_z(N)|\hat{A}^\dagger\hat{A}\hat{H}|\psi_a(1)\cdots\psi_z(N)\rangle$$
$$= \langle \psi_a(1)\cdots\psi_z(N)|\hat{A}^\dagger\hat{H}|\psi_a(1)\cdots\psi_z(N)\rangle$$
$$= \langle \hat{A}(\psi_a(1)\cdots\psi_z(N))|\hat{H}(\psi_a(1)\cdots\psi_z(N))\rangle \tag{6}$$

This is true for any operator $\hat{O}$, like Hamiltonian $\hat{H}$, which is symmetric in electron labels. i.e. Any operator in electronic structure theory follows:

$$\left[\hat{A}, \hat{O}\right] = 0 \tag{7}$$

1.1   Evaluate One-electron Matrix Elements

- Diagonal: $\langle K|\hat{h}|K\rangle$

$$\langle K|\hat{h}|K\rangle = \langle \hat{A}(\psi_a(1)\cdots\psi_z(N))|\hat{h}(1) + \hat{h}(2) + \cdots + \hat{h}(N)|\psi_a(1)\cdots\psi_z(N)\rangle$$
$$= \langle a|\hat{h}|a\rangle_1\langle b|b\rangle_2\cdots\langle z|z\rangle_N$$
$$+ \langle a|a\rangle_1\langle b|\hat{h}|b\rangle_2\cdots\langle z|z\rangle_N + \cdots$$
$$+ \langle a|a\rangle_1\langle b|b\rangle_2\cdots\langle z|\hat{h}|z\rangle_N$$
$$= \sum_{i\in K}\langle i|\hat{h}|i\rangle \tag{8}$$

NOTE:
  Only identity permutation contributes, otherwise mismatch in overlap.
  All other permutations mismatch. e.g. $\langle b|\hat{h}|a\rangle_1$, $\langle b|a\rangle_2$
Example of 2 electrons:

$$= \int (a(1)b(2) - b(1)a(2))\left[\hat{h}(1) + \hat{h}(2)\right]a(1)b(2)$$

$$= \langle a|\hat{h}|a\rangle_1 \langle b|b\rangle_2 + \langle a|a\rangle_1 \langle b|\hat{h}|b\rangle_2$$
$$- \langle b|\hat{h}|a\rangle_1 \langle a|b\rangle_2 - \langle b|a\rangle_1 \langle a|\hat{h}|b\rangle_2$$
$$= \langle a|\hat{h}|a\rangle + \langle b|\hat{h}|b\rangle \tag{9}$$

- Single mismatch: $\langle K'|\hat{h}|K\rangle$

$$\langle K'|\hat{h}|K\rangle = \langle \hat{A}(\psi_p(1)\psi_b(2)\cdots\psi_z(N))|\hat{h}(1) + \hat{h}(2) + \cdots + \hat{h}(N)|\psi_a(1)\psi_b(2)\cdots\psi_z(N)\rangle$$
$$= \langle p|\hat{h}|a\rangle_1 \langle b|b\rangle_2 \cdots \langle z|z\rangle_N + \langle p|a\rangle_1 \langle b|\hat{h}|b\rangle_2 \cdot 1 + \langle p|a\rangle_1 \langle c|\hat{h}|c\rangle_N \cdot 1 + \cdots$$
$$= \langle pbc\cdots|\hat{h}|abc\cdots\rangle$$
$$= \langle p|\hat{h}|a\rangle \tag{10}$$

- Double mismatch: $\langle K''|\hat{h}|K\rangle$

$$\langle K''|\hat{h}|K\rangle = \langle \hat{A}(\psi_p(1)\psi_q(2)\cdots\psi_z(N))|\hat{h}(1) + \hat{h}(2) + \cdots + \hat{h}(N)|\psi_a(1)\psi_b(2)\cdots\psi_z(N)\rangle$$
$$= \langle p|\hat{h}|a\rangle\langle q|b\rangle + \langle p|a\rangle\langle q|\hat{h}|b\rangle - \langle q|\hat{h}|a\rangle\langle p|b\rangle - \langle q|a\rangle\langle p|\hat{h}|b\rangle$$
$$= 0 \tag{11}$$

Second terms from permutation: $p \longleftrightarrow q$. Also, $p \neq q$

There is at least one mismatch in orbital overlaps: $\langle K''|\hat{h}|K\rangle = 0$

Summary 1.1

- Identity Permutation:

$$\langle K|\hat{h}|K\rangle = \sum_{i\in K}\langle i|\hat{h}|i\rangle$$

- Single Mismatch with $p \neq a, p \in K', a \in K$:

$$\langle K'|\hat{h}|K\rangle = \langle p|\hat{h}|a\rangle$$

- Double Mismatch with $p \neq q, p, q \in K'', a, b \in K$:

$$\langle K''|\hat{h}|K\rangle = 0$$

- Additional sign to bring orbitals to maximal coincidence.

1.2   Evaluate Two-electron Matrix Elements

Let us first consider 2-electron system:

$$\langle K|\hat{h}|L\rangle = \langle \hat{A}(\psi_p^*(1)\psi_q^*(2))|\hat{V}|\psi_a(1)\psi_b(2)\rangle$$
$$= \int (\psi_p^*(1)\psi_q^*(2) - \psi_q^*(1)\psi_p^*(2))\frac{1}{r_{12}}\psi_a(1)\psi_b(2)d1d2$$

$$= \langle pq|\frac{1}{r_{12}}|ab\rangle - \langle qp|\frac{1}{r_{12}}|ab\rangle \qquad \text{in quantum chemistry notation}$$

$$\equiv \langle pq|ab\rangle - \langle qp|ab\rangle \qquad \frac{1}{r_{12}} \text{is implied}$$

$$\equiv \langle pq||ab\rangle \tag{12}$$

NOTE:

1. The expressions, $\langle pq|\frac{1}{r_{12}}|ab\rangle$ and $\langle qp|\frac{1}{r_{12}}|ab\rangle$, are in quantum chemistry notation.
2. If 2 orbitals are in ket, $\frac{1}{r_{12}}$ can be implied, such as: $\langle pq|ab\rangle$, $\langle qp|ab\rangle$.

Double bar indicates anti-symmetrized 2-electron integral. q, p, r, s are spin orbitals.

$$\langle pq||ab\rangle = \langle pq|ab\rangle - \langle qp|ab\rangle \tag{13}$$

Permutational symmetry:

$$\langle pq||ab\rangle = -\langle qp||ab\rangle = +\langle qp||ba\rangle = -\langle pq||ba\rangle \tag{14}$$

If orbitals are real:

$$\langle pq||ab\rangle = \langle ab||pq\rangle = -\langle ba||pq\rangle = -\langle ab||qp\rangle = \langle ba||qp\rangle \tag{15}$$

$$\langle pq||ab\rangle = \langle pq|ab\rangle - \langle pq|ba\rangle \tag{16}$$

The purpose of using these relations:

1. Calculate and store only unique integrals.
2. Simplify results.

General treatment of $\hat{V}$:

$$\hat{V} = \sum_{i<j} \frac{1}{r_{ij}} = \hat{V}_{12} + \hat{V}_{13} + \hat{V}_{23} + \cdots \tag{17}$$

Sum over all pairs.

• The diagonal term: $\langle K|\hat{V}|K\rangle$.

$$\langle K|\hat{V}|K\rangle = \langle \hat{A}(\psi_a\psi_b\cdots\psi_z) \left[\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} + \cdots\right] |\psi_a\psi_b\cdots\psi_z\rangle$$

$$= \langle ab||ab\rangle_{12}\langle c|c\rangle \cdots \langle z|z\rangle$$

$$+ \langle ac||ac\rangle_{13}\langle b|b\rangle \cdots \langle z|z\rangle$$

$$+ \cdots$$

$$+ \langle bc||bc\rangle_{23}\langle a|a\rangle \cdots \langle z|z\rangle$$

$$+ \cdots$$

$$= \sum_{i<j\in K} \langle ij||ij\rangle \tag{18}$$

NOTE:

Only identity permutation contributes, otherwise mismatch in overlap.

Example: for the term $\frac{1}{r_{12}}$, it's only the identity permutation and 1 and 2 interchange.

- Single mismatch: $\langle K'|\hat{V}|K\rangle$.

$$\langle K'|\hat{h}|K\rangle = \langle \hat{A}(\psi_p\psi_b\cdots\psi_z)|\hat{V}|\psi_a\psi_b\cdots\psi_z\rangle \tag{19}$$

p and a must be in $\hat{V}$, otherwise overlap mismatch.

$\Rightarrow$ Only $\hat{V}_{12}, \hat{V}_{13}, \hat{V}_{1N}$, etc contribute, not $\hat{V}_{23}, \cdots$

$$\langle K'|\hat{V}|K\rangle = \langle pb||ab\rangle_{12} + \langle pc||ab\rangle_{13} + \cdots + \langle pz||az\rangle_{1N}$$
$$= \sum_{i\in K,K'} \langle pi||ai\rangle \tag{20}$$

NOTE:

$\quad p \in i \qquad \langle pp||ap\rangle = 0$

$\quad a \in i \qquad \langle pa||aa\rangle = 0$

This is due to antisymmetry.

- Double mismatch: $\langle K''|\hat{V}|K\rangle$.

$$\langle K''|\hat{V}|K\rangle = \langle \hat{A}(\psi_p\psi_q\psi_c\cdots\psi_z)|\hat{V}|\psi_a\psi_b\psi_c\cdots\psi_z\rangle \tag{21}$$

Only the $\frac{1}{r_{12}}$ contributes.

$$\langle pq||ab\rangle\langle c|c\rangle\cdots\langle z|z\rangle = \langle pq||ab\rangle \tag{22}$$

> **Summary 1.2**
>
> - Summary all matrix-elements:
>
> | Integrals | $\hat{h}$ | $\hat{V}$ |
> |---|---|---|
> | $\langle K|\hat{H}|K\rangle$ | $\sum_{a\in K}\langle a|\hat{h}|a\rangle$ | $\sum_{a<b\in K}\langle ab||ab\rangle$ |
> | $\langle K'|\hat{H}|K\rangle$ | $\langle p|\hat{h}|a\rangle$ | $\sum_{b\in K,K'}\langle pb||ab\rangle$ |
> | $\langle K''|\hat{H}|K\rangle$ | 0 | $\langle pq||ab\rangle$ |
> | $\langle K'''|\hat{H}|K\rangle$ | 0 | 0 |
>
> NOTE:
>
> 1) Sum over all contributions that include the special (different) orbitals in the two determinants.
> 2) Signs: Bring determinants into maximum coincidence first. Note that permutation can introduce a sign change.

Basic building blocks that construct matrix-elements:

To evaluate matrix elements $\langle K|\hat{H}|L\rangle$ we only require one- and two-electron integrals, how many integrals we have: (M is the number of spin/spatial orbitals)

$$\langle p|\hat{h}|q\rangle \qquad \frac{1}{2}M^2$$
$$\langle pq||rs\rangle \qquad \frac{1}{8}M^4$$

For large systems, even the number of 2-electron integrals is large to store.

1) Many integrals are almost zero.
   $\Rightarrow$ screen (need clear algorithms)
2) Storage on disk is bottleneck:
   $\Rightarrow$ recompute integrals when needed.
   $\boxed{\text{Integrals direct techniques}}$
   Widely used in practical Quantum Chemistry. We will regard this as technical detail, likewise for calculating integrals themselves.

We typically cannot store Hamiltonian $\langle K|\hat{H}|L\rangle$, and all determinants $\frac{1}{2}\binom{M}{N}^2$

1.3   Example: H_2 Molecule

Let us look at a prototypical example first.
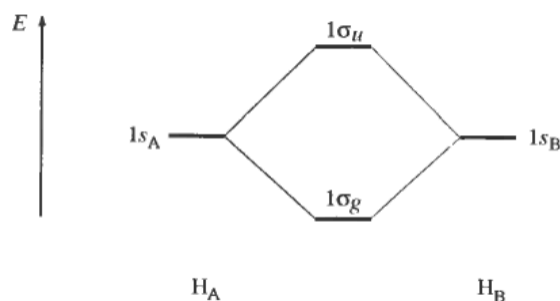H_2 in a minimal basis set.

Figure 1   Molecular Orbital Energy Level Diagram for H_2
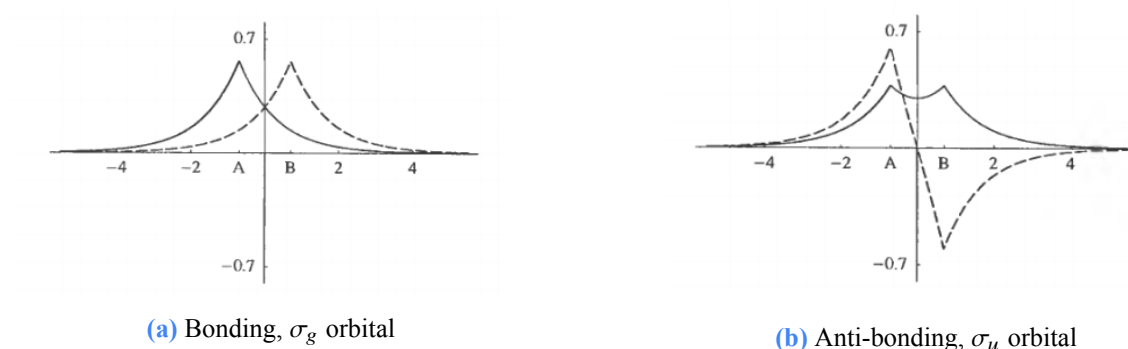
The overlap integral of the H_2 molecule:

$$S = \int 1S_A(\vec{r}) \cdot 1S_B(\vec{r})dr^3 \tag{23}$$

Symmetry-adapted atomic orbitals: (g is gerade, u is ungerade)

$$\sigma_g = (1S_A + 1S_B) \cdot \frac{1}{\sqrt{2(1+S)}} \tag{24}$$

$$\sigma_u = (1S_A - 1S_B) \cdot \frac{1}{\sqrt{2(1-S)}} \tag{25}$$

(a) Bonding, σ_g orbital

(b) Anti-bonding, σ_u orbital

Figure 2 H_2 Electronic Wavefunction

1.3.1   Molecular Orbital Theory

Here are some basic orbital diagram (after Hartree-Fock calculation usually). It introduces the the spin-up (α) and spin-down (β) in molecular orbital diagram.

$$1(\sigma_g) \qquad \bar{1}(\bar{\sigma}_g) \qquad 2(\sigma_u) \qquad \bar{2}(\bar{\sigma}_u)$$
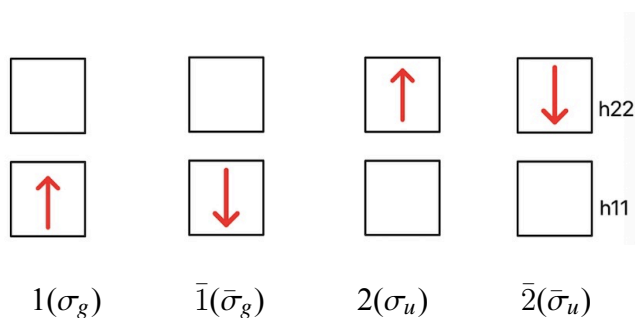
Figure 3   Molecular Orbital Diagram

In molecular orbital theory, put both electrons in bonding orbital. The state is $|1\bar{1}\rangle$.

1.3.2   Configuration Interaction

True wavefunction for ground state in the minimal basis set is a linear combination.

$$\begin{aligned}
|\psi_g\rangle &= c_1|\sigma_g\bar{\sigma}_g\rangle + c_2|\sigma_u\bar{\sigma}_u\rangle \\
&= c_1|1\bar{1}\rangle + c_2|2\bar{2}\rangle
\end{aligned} \tag{26}$$

Note that the other determinants $\sigma_g\bar{\sigma}_u$ and $\sigma_u\bar{\sigma}_g$ have wrong symmetry: $g \times u = u$.
In CI : create Hamiltonian matrix $\langle\lambda|\hat{H}|\mu\rangle$

$\hat{H}$	$|1\bar{1}\rangle$	$|2\bar{2}\rangle$
$\langle 1\bar{1}|$	$\langle 1|\hat{h}|1\rangle + \langle\bar{1}|\hat{h}|\bar{1}\rangle + \langle 1\bar{1}||1\bar{1}\rangle$	$\langle 1\bar{1}||2\bar{2}\rangle$
$\langle 2\bar{2}|$	$\langle 2\bar{2}||1\bar{1}\rangle$	$\langle 2|\hat{h}|2\rangle + \langle\bar{2}|\hat{h}|\bar{2}\rangle + \langle 2\bar{2}||2\bar{2}\rangle$

Simplify the matrix, we can get: $\begin{bmatrix} \varepsilon_1 & v \\ v & \varepsilon_2 \end{bmatrix}$

Next, diagonal the matrix in order to get the energy from the Hamiltonian matrix.

$$\begin{bmatrix} \varepsilon_1 - \lambda & v \\ v & \varepsilon_2 - \lambda \end{bmatrix} \tag{27}$$

$$(\varepsilon_1 - \lambda)(\varepsilon_2 - \lambda) - v^2 = 0 \tag{28}$$

$$\varepsilon_1 \varepsilon_2 - \lambda(\varepsilon_1 + \varepsilon_2) + \lambda^2 - v^2 = 0 \tag{29}$$

We can get two solutions from this problem.

- Full CI solutions:

$$\begin{aligned} \lambda &= \frac{1}{2}(\varepsilon_1 + \varepsilon_2) \pm \sqrt{(\varepsilon_1 + \varepsilon_2)^2 - 4\left[(\varepsilon_1 - \varepsilon_2) - v^2\right]}) \\ &= \frac{1}{2}(\varepsilon_1 + \varepsilon_2) \pm \frac{1}{2}\sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4v^2} \end{aligned} \tag{30}$$

- Second order perturbation(MP2) solutions:
  Approximation:

$$\sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4v^2} = (\varepsilon_2 - \varepsilon_1)\sqrt{1 + \frac{4v^2}{(\varepsilon_2 - \varepsilon_1)^2}} \qquad \text{use Taylor:} \sqrt{1+x} \approx 1 + \frac{1}{2}x \tag{31}$$

$$\approx (\varepsilon_1 - \varepsilon_2) + \frac{1}{2}\frac{4v^2}{(\varepsilon_2 - \varepsilon_1)} \qquad \varepsilon_2 - \varepsilon_1 > 0 \tag{32}$$

Energy with MP2 approximation:

$$E_\pm \cong \frac{1}{2}(\varepsilon_1 + \varepsilon_2) \pm \left[\frac{1}{2}(\varepsilon_1 - \varepsilon_2) + \frac{v^2}{\varepsilon_2 - \varepsilon_1}\right] \tag{33}$$

Note that the lower energy, E_-, should be the energy of ground state; the higher energy, E_+, should be the energy of excited state.

Sketch the potential energy curve (PES) for the H_2 molecule for variety of methods.
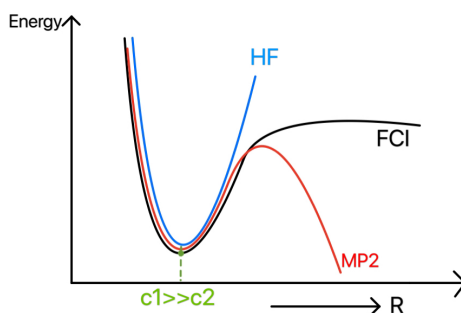

Figure 4   Potential Energy Curve at HF+ MP2 +FCI

Due to the FCI, the energy levels shift from ε_1 and ε_2. The shift depends on the $\hat{V}$: $\langle 1\bar{1}||2\bar{2}\rangle$, and $\varepsilon_1 - \varepsilon_2$. The FCI (diagonalize the matrix) is the correct result at long distance. When $\varepsilon_1 \approx \varepsilon_2$, second order correction(MP2) is not accurate, because the existence of the term $\frac{v^2}{\varepsilon_1 - \varepsilon_2} \to -\infty$! This is the behaviour of MP2 in Gaussian.

1.4 Example: Excited States of H_2 Molecule

Let us analyze the excited states of H_2 molecule in a minimal basis, singlet $^1\Sigma_u$ and triplet $^3\Sigma_u$.

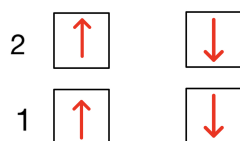- Triplet state: (both electrons are spin-up or spin-down in different orbitals)

Figure 5   MO Diagram of Triplet States

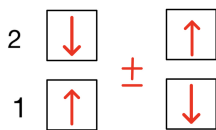- Singlet or Triplet state: (linear combinations of spin-up electron and spin-down electron)

Figure 6   MO Diagram of Triplet States or Single States

$$E_T = \langle 1|\hat{h}|1\rangle + \langle 2|\hat{h}|2\rangle + \langle 12||12\rangle \tag{34}$$

To calculate singlet energy, set up the 2×2 matrix:

$\hat{H}$	$|1\bar{2}\rangle$	$|\bar{1}2\rangle$
$\langle 1\bar{2}|$	$\langle 1|\hat{h}|1\rangle + \langle \bar{2}|\hat{h}|\bar{2}\rangle + \langle 1\bar{2}||1\bar{2}\rangle$	$\langle 1\bar{2}||\bar{1}2\rangle$
$\langle \bar{1}2|$	$\langle \bar{1}2||1\bar{2}\rangle$	$\langle 2|\hat{h}|2\rangle + \langle \bar{1}|\hat{h}|\bar{1}\rangle + \langle \bar{1}2||\bar{1}2\rangle$

What can we say about the integrals in terms of the spin-orbitals?

Let us assume that the spatial parts of the orbitals are the same. $|1\rangle = \psi_1(\vec{r})|\alpha\rangle, |1\rangle = \psi_1(\vec{r})|\beta\rangle$.

$$
\begin{aligned}
\langle 1\bar{2}||1\bar{2}\rangle &= \langle 1\bar{2}|1\bar{2}\rangle - \langle 1\bar{2}|\bar{2}1\rangle \\
&= \int \psi_1(1)\bar{\psi}_2(2)\frac{1}{r_{12}}\psi_1(1)\bar{\psi}_2(2) - \int \psi_1(1)\bar{\psi}_2(2)\frac{1}{r_{12}}\bar{\psi}_2(1)\psi_1(2)d1d2 \\
&= \langle \alpha|\alpha\rangle_1 \langle \beta|\beta\rangle_2 - \langle \alpha|\beta\rangle_1 \langle \beta|\alpha\rangle_2
\end{aligned} \tag{35}
$$

NOTE:

The second integral is zero because the spin does note match. eg, $\langle \alpha(1)|\beta(1)\rangle = 0$

On the other hand:

$$\langle 1\bar{2}||\bar{1}2\rangle = \langle 1\bar{2}|\bar{1}2\rangle - \langle 1\bar{2}|2\bar{1}\rangle$$

$$= 0 - \langle 12|21\rangle \tag{36}$$

NOTE:

1. The integral $\langle 12|21\rangle$ is spatial integral.
2. Because these integrals occur often, they get a special symbol for convenience.

$$\langle ab|ab\rangle = J_{12} \quad ; \quad \langle 12|12\rangle = J_{12} \tag{37}$$

$$\langle ab|ba\rangle = K_{12} \quad ; \quad \langle 12|21\rangle = K_{12} \tag{38}$$

$$\langle a|\hat{h}|a\rangle = \langle \bar{a}|\hat{h}|\bar{a}\rangle = h_{aa} \tag{39}$$

J is Coulomb integral; K is Exchange integral.

Then, CI matrix can be reduced to:

$\hat{H}$	$|1\bar{2}\rangle$	$|\bar{1}2\rangle$
$\langle 1\bar{2}|$	$h_{11} + h_{22} + J_{12}$	$-K_{12}$
$\langle \bar{1}2|$	$-K_{12}$	$h_{11} + h_{22} + J_{12}$

$$\begin{bmatrix} \varepsilon & -K_{12} \\ -K_{12} & \varepsilon \end{bmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = (\varepsilon - K_{12}) \begin{pmatrix} 1 \\ 1 \end{pmatrix} \tag{40}$$

$$\begin{bmatrix} \varepsilon & -K_{12} \\ -K_{12} & \varepsilon \end{bmatrix} \begin{pmatrix} 1 \\ -1 \end{pmatrix} = (\varepsilon + K_{12}) \begin{pmatrix} 1 \\ -1 \end{pmatrix} \tag{41}$$

$$E_- = \varepsilon - K_{12} \tag{42}$$

$$E_+ = \varepsilon + K_{12} \tag{43}$$

We can a higher energy, E_+, and a lower energy, E_-.
Compare to triplet energy:

$$h_{11} + h_{12} + \langle 12||12\rangle = h_{11} + h_{12} + J_{12} - K_{12}$$

$$= \varepsilon - K_{12}$$

$$= E_- = E_{\text{triplet}} \tag{44}$$

Similarly, the singlet energy:

$$E_+ = E_{\text{singlet}} \tag{45}$$

Like spin in Figure 5 is lower in energy than singlet coupled opposite spin (Figure 6).

- The singlet spin(1 state): $\hat{S}_+|12\rangle = |1\bar{2}\rangle - |\bar{1}2\rangle = |1\bar{2}\rangle + |\bar{1}2\rangle$

- The triplet spin(3 states): $\hat{S}_-|12\rangle = |12\rangle, |\bar{1}\bar{2}\rangle, |1\bar{2}\rangle + |\bar{1}2\rangle$

The integral $K_{12} = \int \psi_1(1)\psi_2(2)\frac{1}{r_{12}}\psi_2(1)\psi_1(2) > 0$, hence in this 2×2 model: $E_{\text{singlet}} > E_{\text{triplet}}$

This is the origin of Hund's rule in atomic spectra. Hund's rule: put the electrons(spin configuration) in the lowest energy. Because exchange interaction due to antisymmetry of wave function.

1.5   Some Useful Notations for Evaluating Matrix Elements

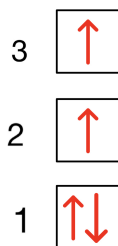Using the Slater rules we can easily write down the energy expression for any determinant. Example:

Figure 7   MO Diagram of Example

The element of Slater rules are the diagonal elements, $\langle K|\hat{H}|K\rangle$. The energy of this determinant:

$$E = \langle 1|\hat{h}|1\rangle + \langle \bar{1}|\hat{h}|\bar{1}\rangle + \langle 2|\hat{h}|2\rangle + \langle 3|\hat{h}|3\rangle$$
$$+ \langle 1\bar{1}||1\bar{1}\rangle + \langle 12||12\rangle + \langle 13||13\rangle + \langle \bar{1}2||\bar{1}2\rangle + \langle \bar{1}2||\bar{1}3\rangle + \langle 23||23\rangle \tag{46}$$

Here is the general formula of energy:

$$E = \sum_{a\in K}\langle a|\hat{h}|a\rangle + \sum_{a<b\in K}\langle ab||ab\rangle \tag{47}$$

Let us condense a little bit and consider spin explicitly. Assume same spatial orbitals for α and β spin. Consider real orbitals only.

$$\langle a|\hat{h}|a\rangle = \langle \bar{a}|\hat{h}|\bar{a}\rangle = h_{aa} \tag{48}$$
$$\langle a|\hat{h}|\bar{b}\rangle = 0 \tag{49}$$
$$\langle ab|ab\rangle = J_{ab} \tag{50}$$
$$\langle ab|ba\rangle = K_{ab} \tag{51}$$

NOTE:

- J_{ab} is spatial Colomb integral. Coulomb interaction between $|\psi_a(1)|^2$ and $|\psi_b(2)|^2$

$$J_{ab} = \int \psi_a^*(1)\psi_a(1)\frac{1}{r_{12}}\psi_b^*(2)\psi_b(2)d1d2 \tag{52}$$

- K_{ab} is spatial exchange integral. Exchange interaction between $\psi_a(1)\psi_b(1)$ and $\psi_a(2)\psi_b(2)$. $\psi_a\psi_b$ may not be positive everywhere, but $K_{ab} > 0$ is always true.

$$K_{ab} = \int \psi_a^*(1)\psi_b(1)\frac{1}{r_{12}}\psi_a^*(2)\psi_b(2)d1d2 \tag{53}$$

We would have more integrals $\langle pq|rs\rangle$, but in the example we can use the 'diagonal' integrals exclusively.

$$\langle ab||ab\rangle = \langle ab|ab\rangle - \langle ab|ba\rangle = J_{ab} - K_{ab} \tag{54}$$

$$\langle a\bar{b}||a\bar{b}\rangle = \langle a\bar{b}|a\bar{b}\rangle - \langle a\bar{b}|\bar{b}a\rangle = J_{ab} \tag{55}$$

$$\langle a\bar{b}||\bar{a}b\rangle = -\langle a\bar{b}|b\bar{a}\rangle = -K_{ab} \tag{56}$$

Moreover the integrals/ orbitals are real. Then, we can flip(interchange) the a and b labels due to symmetry.

$$\langle aa|bb\rangle = \langle ab|ba\rangle = K_{ab} \tag{57}$$

$$\langle a\bar{a}||b\bar{b}\rangle = \langle a\bar{a}|b\bar{b}\rangle - \underbrace{\langle a\bar{a}|\bar{b}b\rangle}_{0} = K_{ab} \tag{58}$$

Using these integrals we can set up some interesting problems.

1.6   Example: Carbon Atom

Example: Carbon.

Firstly, we need some background about angular momentum. See Link: Atomic Term Symbol.

- Angular momentum theory:

  For states, we use upper case.

  The orbital angular momentum: $L, M_L = -L, \ldots, +L$. $(2L + 1)$ states associated with orbital.

  The spin angular momentum: $S, M_S = -S, \ldots, +S$. $(2S + 1)$ states associated with spin.

- The easiest way to construct:

  1) highest M_S: $M_S = \sum m_s$

      $m_s = \frac{1}{2}$ for α $m_s = -\frac{1}{2}$ for β

  2) highest M_L: $M_L = \sum m_l$

- Term symbol: $^{(2S+1)}L$

  $L = 0, 1, 2, 3, 4 \Rightarrow S, P, D, F, G$

Return to atom: Carbon.

The ground state configuration of Carbon atom: $1s^2 2s^2(2p)^2$. There are $C_6^2 = 15$ different quantum states.

Regardless of the close shell $(1s^2 2s^2)$, we have six spin-orbitals, $p_1, p_0, p_{-1}, \bar{p}_1, \bar{p}_0, \bar{p}_{-1}$.

1) Highest M_S, of theses highest M_L: $|p_1 p_0|$ state

$M_S = \frac{1}{2} + \frac{1}{2} = 1$ $\qquad$ $S = M_S = 1$ $\qquad$ $(2S + 1) = 3$

$M_L = 1 + 0 = 1$ $\qquad$ $L = M_L = 1$ $\qquad$ $(2L + 1) = 3$

There are 9 degeneracies in total. $(2S + 1)(2L + 1) = 9$.

Term symbol ^3P has 9 states. (Neglect $J-$coupling spin-orbital.)

These 9 states are all degenerate.

2) Highest M_L, of theses highest M_S: $|p_1 \bar{p}_1|$ state

$M_S = \frac{1}{2} - \frac{1}{2} = 0$ $\qquad$ $S = M_S = 0$ $\qquad$ $(2S + 1) = 1$

$M_L = 1 + 1 = 2$ $\qquad$ $L = M_L = 2$ $\qquad$ $(2L + 1) = 5$

There are 9 degeneracies in total. $(2S + 1)(2L + 1) = 5$.

Term symbol ^1D has 5 states. (Neglect $J-$coupling spin-orbital.)

These 5 states are all degenerate.

3) One state left: ^1S

We get degeneracy pattern from angular momentum theory.

Next, we will do Carbon atom by diagonalizing Hamiltonian 15×15 matrix. Use symmetry to do small blocks. We will use abbreviate symbols, $x, y, z, \bar{x}, \bar{y}, \bar{z}$, represent real orbitals $p_x, p_y, p_z, \bar{p}_x, \bar{p}_y, \bar{p}_z$. There are three types of M_S function:

- $M_S = 0$: $|x\bar{x}|, |y\bar{y}|, |z\bar{z}|,$

  $\qquad\quad |x\bar{y}|, |x\bar{z}|, |y\bar{x}|, |y\bar{z}|, |z\bar{x}|, |z\bar{y}|$

- $M_S = 1$: $|xy|, |xz|, |yz|$

- $M_S = -1$: $|\bar{x}\bar{y}|, |\bar{x}\bar{z}|, |\bar{y}\bar{z}|$

Types of 2-electron integrals:

1) $h_{xx} = h_{yy} = h_{zz} \equiv h$

2) $\langle xx|xx \rangle = \langle yy|yy \rangle = \langle zz|zz \rangle = D$

3) $\langle xy|xy \rangle = \langle xz|xz \rangle = \langle yz|yz \rangle = J$

4) $\langle xy|yx \rangle = \langle xz|zx \rangle = \langle yz|zy \rangle = \langle xx|yy \rangle = \langle xx|zz \rangle = \langle yy|zz \rangle = K$

5) Integrals in which x, y, z occur an odd number of times are zero.

6) There is one more important about relation between the integrals: $D = J + 2K$

Now we can partition Hamiltonian in small sub-blocks:

- $M_S = 1$:

	xy	xz	yz
xy	$2h + J - K$	0	0
xz	0	$2h + J - K$	0
yz	0	0	$2h + J - K$

$E(^3P) = 2h + J - K$, same for $M_S = -1$, likewise $\bar{x}\bar{y}, \bar{x}\bar{z}, \bar{y}\bar{z}$

- $M_S = 0$:

	$x\bar{y}$	$y\bar{x}$
$x\bar{y}$	$2h + J$	$+K$
$y\bar{x}$	$+K$	$2h + J$

NOTE: $\langle x\bar{y}||y\bar{x}\rangle = \langle x\bar{y}|y\bar{x}\rangle - \langle x\bar{y}|\bar{x}y\rangle = \langle xy|yx\rangle - 0 = K$

$E = 2h + J \pm K$, for $x\bar{y} + \bar{x}y$

$E(^3P) = 2h + J - K$, for $|x\bar{y}\rangle - |y\bar{x}\rangle$

$E(^1D) = 2h + J + K$, for $|x\bar{y}\rangle + |y\bar{x}\rangle$

Same for $x\bar{z} \pm z\bar{x}$ and $y\bar{z} \pm z\bar{y}$

$\Rightarrow$ 9 states found for triplet ^3P ; 3 states for singlet ^1D.

Finally:

	$x\bar{x}$	$y\bar{y}$	$z\bar{z}$
$x\bar{x}$	$2h + D$	K	K
$y\bar{y}$	K	$2h + D$	K
$z\bar{z}$	K	K	$2h + D$

NOTE: $\langle x\bar{x}||y\bar{y}\rangle = \langle x\bar{y}|y\bar{x}\rangle = K$

Familiar with Hamiltonian, diagonalize the matrix and get eigenvectors and eigenvalues.

The eigenvector $\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$ with the eigenvalue $E = 1h + D + 2K = 2h + J + 4K \Rightarrow {}^1S$.

The eigenvectors $\begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}$ and $\begin{pmatrix} 2 \\ -1 \\ -1 \end{pmatrix}$ with the same eigenvalue $E = 2h + D - K = 2h + J + K \Rightarrow$

^1D .

Hence, $^1S = |x\bar{x}\rangle + |y\bar{y}\rangle + |z\bar{z}\rangle$

$$^1D = \begin{cases} |y\bar{y}\rangle - |z\bar{z}\rangle \\ 2|x\bar{x}\rangle - |y\bar{y}\rangle - |z\bar{z}\rangle \end{cases}$$

$$^1D = \begin{cases} |x\bar{x}\rangle - |y\bar{y}\rangle \\ 2|z\bar{z}\rangle - |x\bar{x}\rangle - |y\bar{y}\rangle \end{cases}$$

Atom: small but complicated due to degeneracies and small excitation energies. Many states are linear combinations of determinants.

Hartree-Fock is useless, because HF method depends on single determinants.

DFT is also useless.

Electronic structure (multireference method): Qualitative wave functions, required more than one determinants.