Advanced Materials Modeling

Lecture on
Second quantization in quantum chemistry

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April 26, 2020

Outline

- Concepts of many-body quantum mechanics
- Slater determinant
- Fock space
- Creation and annihilation operators
- Spin-orbitals
- Examples

What are we going to achieve?

- There are multiple ways to introduce second quantization relevant to specific research field:
  - Quantum field theory
  - Condensed matter theory
  - Quantum chemistry

- Here we consider second quantization from the perspective of Computational Quantum Chemistry – as a basis for many-body wave-function expansion

- We will focus on nonrelativistic electronic structure problem which consists of two problems:
  1. One-electron problem – usually we use basis set of AO or PW
  2. Many-body problem – usually we need many-body basis set to go beyond mean field (HF, DFT)

Goal is to introduce a formalism for solving many-body problem

Notations

- N electrons
- Wave-function $\Psi(\xi_1, \xi_2, \xi_3, \dots, \xi_N)$
- Antisymmetric with respect to exchange of any $\xi_k \leftrightarrow \xi_l$
- ξ includes both spatial and spin coordinates, x and σ
- Hamiltonian

$$H(\xi_1, \dots, \xi_N) = \sum_{k=1}^{N} H^{1\text{e}}(\xi_k) + \sum_{k<l} W(\xi_k, \xi_l)$$

- One-electron Hamiltonian is usually $H^{1\text{e}}(\xi) = -\frac{\hbar^2}{2m}\Delta + V(\xi)$
- Electron-electron interaction $W(\xi_1, \xi_2)$ is usually the Coulomb repulsion

Density matrices

Ψ is rarely needed – all practically relevant observables (including Hamiltonian!) can be obtained from 1e and 2e density matrices.

- 1e transition density matrix

$$\rho^{1e}_{\Psi\Phi}(\xi_1;\eta_1) = N\int \Psi(\xi_1,\zeta_2,\zeta_3,\ldots,\zeta_N)\overline{\Phi}(\eta_1,\zeta_2,\zeta_3,\ldots,\zeta_N)\,\mathrm{d}\zeta_2\,\mathrm{d}\zeta_3\ldots\,\mathrm{d}\zeta_N$$

- 2e transition density matrix

$$\rho^{2e}_{\Psi\Phi}(\xi_1,\xi_2;\eta_1,\eta_2) = N(N-1)\int \Psi(\xi_1,\xi_2,\zeta_3,\ldots,\zeta_N)\overline{\Phi}(\eta_1,\eta_2,\zeta_3,\ldots,\zeta_N)\,\mathrm{d}\zeta_3\ldots\,\mathrm{d}\zeta_N$$

Examples:

- electron density $\rho^{1e}_{\Psi\Psi}(\xi)$
- transition dipole moment $\langle\Phi|\; e\sum_{k=1}^{N}\hat{\xi}_k\;|\Psi\rangle = e\int \xi\;\rho^{1e}_{\Psi\Phi}(\xi)\,\mathrm{d}\xi$
- Hamiltonian

$$\langle\Phi|\mathrm{H}|\Psi\rangle = \int h^{1e}(\xi,\eta)\rho^{1e}_{\Psi\Phi}(\eta,\xi)\,\mathrm{d}\eta\,\mathrm{d}\xi + \frac{1}{2}\int W(\xi_1,\xi_2)\rho^{2e}_{\Psi\Phi}(\xi_1,\xi_2)\,\mathrm{d}\xi_1\,\mathrm{d}\xi_2$$

$\rho^{1e}(\xi)\equiv\rho^{1e}(\xi,\xi)$, $\rho^{2e}(\xi_1,\xi_2)\equiv\rho^{2e}(\xi_1,\xi_2;\xi_1,\xi_2)$, $\left(H^{1e}\varphi\right)(\xi)=\int h^{1e}(\xi,\eta)\varphi(\eta)\,\mathrm{d}\eta$

Questions

1. What is $H^{1\mathrm{e}}(\xi)$ for a molecule or a solid?
2. $H^{1\mathrm{e}}(\xi)$ is not a many-body operator. How to construct its many-body version?
3. In analogy with DFT we can use variational method over $\rho^{2\mathrm{e}}(\xi_1, \xi_2)$. What is the main challenge in this approach?

Slater determinant

The simplest representation of $\Psi(\xi_1, \xi_2, \xi_3, \dots, \xi_N)$ is via sum of products of one-electron functions. Because of permutational antisymmetry, the elementary many-electron basis function is given by Slater determinant:

$$|\psi_1, \psi_2, \dots, \psi_N\rangle(\xi_1, \dots, \xi_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\xi_1) & \psi_1(\xi_2) & \dots & \psi_1(\xi_N) \\ \psi_2(\xi_1) & \psi_2(\xi_2) & \dots & \psi_2(\xi_N) \\ \dots & \dots & \dots & \dots \\ \psi_N(\xi_1) & \psi_N(\xi_2) & \dots & \psi_N(\xi_N) \end{vmatrix}$$

Basic properties

- Nonzero only if $\{\psi_i, i = \overline{1, N}\}$ are linearly independent
- If $\psi'_i = \sum_j T_{ij}\psi_j$ then $|\psi'_1, \dots, \psi'_N >= \det T |\psi_1, \dots, \psi_N >$ $\Longrightarrow$
  - invariant under unitary transformations
  - can always be considered orthonormalized

Slater determinant: many-body matrix elements

- Overlap matrix

$$\langle \varphi_1, \ldots, \varphi_N | \psi_1, \ldots, \psi_N \rangle = \begin{vmatrix} \langle \varphi_1 | \psi_1 \rangle & \langle \varphi_1 | \psi_2 \rangle & \ldots & \langle \varphi_1 | \psi_N \rangle \\ \langle \varphi_2 | \psi_1 \rangle & \langle \varphi_2 | \psi_2 \rangle & \ldots & \langle \varphi_2 | \psi_N \rangle \\ \ldots & \ldots & \ldots & \ldots \\ \langle \varphi_N | \psi_1 \rangle & \langle \varphi_N | \psi_2 \rangle & \ldots & \langle \varphi_N | \psi_N \rangle \end{vmatrix} \equiv \det O$$

- One-electron operators*

$$\langle \Phi | A(\xi_1) | \Psi \rangle = \frac{\det O}{N} \operatorname{tr} A O^{-1}$$

where $A_{ik} = \int \overline{\psi}_i(\xi)(A\varphi_k)(\xi)\,\mathrm{d}\xi$

- One-electron transition density matrix

$$\rho^{1e}_{\Psi\Phi}(\xi;\eta) = \det O \sum_i^{\Psi} \sum_k^{\Phi} \psi_i(\xi) \left(O^{-1}\right)_{ik} \overline{\varphi}_k(\eta)$$

here and below $\sum_i^{\Psi}$ means sum over all ψ_i in $\Psi = |\psi_1, \ldots, \psi_N\rangle$

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*If O is degenerate use its minors or take limit to find $O^{-1} \det O$

Slater determinant: 2e matrix elements

- Electron-electron interaction

$$\langle\Phi|W(\xi_1,\xi_2)|\Psi\rangle = \frac{\det O}{N(N-1)} \sum_{i,j}^{\Phi} \sum_{k,l}^{\Psi} \left(W_{ikjl} - W_{iljk}\right) \left(O^{-1}\right)_{ki} \left(O^{-1}\right)_{lj}$$

where* $W_{ikjl} = \iint \overline{\psi}_i(\xi)\overline{\psi}_j(\eta) W(\xi,\eta) \varphi_k(\xi)\varphi_l(\eta)\,\mathrm{d}\xi\,\mathrm{d}\eta \equiv W_{jlik}$

- 2e transition density matrix

$$\rho^{2e}_{\Psi\Phi}(\xi_1,\xi_2;\eta_1,\eta_2) = \frac{1}{\det O} \begin{vmatrix} \rho^{1e}(\xi_1;\eta_1) & \rho^{1e}(\xi_2;\eta_1) \\ \rho^{1e}(\xi_1;\eta_2) & \rho^{1e}(\xi_2;\eta_2) \end{vmatrix}$$

Be very careful with indices in W – different conventions might be used

Questions

1. What other representations of many-electron wave-functions do you know, e.g. explicitly correlated?
2. Any examples of practical use of unitary invariance of Slater determinant?
3. What will be an analog of Slater determinant for bosons?

N-electron basis

If $\{\psi_i, i \in \mathbb{A}\}$ is a complete basis of one-electron functions then

$$\mathcal{C}_N(\mathbb{A}) = \{\ |\psi_{i_1}, \ldots, \psi_{i_N}\rangle, \quad i_1 < i_2 < \ldots < i_N\}$$

is a complete N-electron basis

Notations

$$|\psi_{i_1}, \ldots, \psi_{i_N}\rangle \equiv |i_1, \ldots, i_N\rangle \equiv |I\rangle$$

Also one can use occupation numbers $|n_1, n_2, \ldots\rangle$, where n_1 is number of electrons (0 or 1) with 1e-function ψ_1 and so forth.

example: $\left|\begin{smallmatrix} 0 & 1 \\ 1 & 0 \end{smallmatrix}\right\rangle \equiv \left|\begin{smallmatrix} 2 \\ 1 \end{smallmatrix}\right\rangle = \dfrac{1}{\sqrt{2}} \begin{vmatrix} \varphi_2(x_1)\chi_\uparrow(\sigma_1) & \varphi_1(x_1)\chi_\downarrow(\sigma_1) \\ \varphi_2(x_2)\chi_\uparrow(\sigma_2) & \varphi_1(x_2)\chi_\downarrow(\sigma_2) \end{vmatrix}$

Wave-function expansion

$$\Psi = \sum_I^{\mathcal{C}_N(\mathbb{A})} C_I |I\rangle$$

$$\sum_J^{\mathcal{C}_N(\mathbb{A})} \langle I|J\rangle C_J = N! \int \overline{\psi}_{i_1}(\xi_1) \ldots \overline{\psi}_{i_N}(\xi_N) \Psi(\xi_1, \ldots, \xi_N) \, \mathrm{d}\xi_1 \ldots \mathrm{d}\xi_N$$

where $\langle I|J\rangle \equiv \det O(\psi_{i_1}, \ldots, \psi_{i_N}; \psi_{j_1}, \ldots, \psi_{j_N})$

Fock space

Fock space $\mathcal{C}(\mathbb{A}) = \bigoplus_{N=0}^{|\mathbb{A}|} \mathcal{C}_N(\mathbb{A})$

Notations: an operator A in coordinate representation will be denoted A in $\mathcal{C}(\mathbb{A})$ so that e.g. Hamiltonian reads $\mathsf{H} = \mathsf{H}^{\mathsf{1e}} + \mathsf{W}$

Now let's introduce operators $\mathsf{c}_i|I\rangle = P(i, I)\ |I \backslash i\rangle$, where

$$P(i,I) = \begin{cases} 1, & i \text{ occupies odd position in } I, \\ -1, & i \text{ occupies even position in } I, \\ 0, & i \notin I. \end{cases}$$

Example: $\mathsf{c}_1|125\rangle = |25\rangle$, $\mathsf{c}_2|125\rangle = -|15\rangle$, $\mathsf{c}_3|125\rangle = 0$

Note that these operators anticommute: $\{\mathsf{c}_i, \mathsf{c}_j\} = 0$

Now all many-body objects can be written in compact form

(using c_i and their hermitian conjugates c_i^+)

$$\langle I|c_i^+ c_k|J\rangle = P(i,I)P(k,J)\det O^{(i,k)} \equiv \left(O^{-1}\right)_{ki}\det O$$

$$\langle I|c_i^+ c_j^+ c_l c_k|J\rangle = \begin{vmatrix} \left(O^{-1}\right)_{ki} & \left(O^{-1}\right)_{kj} \\ \left(O^{-1}\right)_{li} & \left(O^{-1}\right)_{lj} \end{vmatrix} \det O$$

$$\mathrm{H} = \sum_{i,k}^{\mathbb{A}} c_i^+ H_{ik}^{1e} c_k + \frac{1}{2}\sum_{i,j,k,l}^{\mathbb{A}} c_i^+ c_j^+ W_{ikjl} c_l c_k$$

$$\left(\rho_{\Psi\Phi}^{1e}\right)_{ki} = \langle\Phi|c_i^+ c_k|\Psi\rangle, \qquad \left(\rho_{\Psi\Phi}^{2e}\right)_{kilj} = \langle\Phi|c_i^+ c_j^+ c_l c_k|\Psi\rangle$$

$$E = \sum_{i,k}^{\mathbb{A}} H_{ik}^{1e}\rho_{ki}^{1e} + \frac{1}{2}\sum_{i,j,k,l}^{\mathbb{A}} W_{ikjl}\rho_{kilj}^{2e}$$

Many-body problem has been reduced to matrix diagonalization

Creation and annihilation operators

Now let's consider orthonormalized 1e basis. Then

$$\left(\rho^{1e}_{\Psi\Phi}\right)_{ik} \equiv \int \overline{\psi}_i(\xi)\rho^{1e}_{\Psi\Phi}(\xi;\eta)\psi_k(\eta)\,\mathrm{d}\xi\,\mathrm{d}\eta$$

and

$$c_i^{+}|I\rangle = P(i, I \cup i)\;|I \cup i\rangle$$

so that we can call c_i^{+} creation operator* and c_i is annihilation operator.

Properties

- Anticommute: $\{c_i, c_j\} = 0$, $\{c_i^{+}, c_j^{+}\} = 0$, $\{c_i^{+}, c_j\} = \delta_{ij}$
- Generate basis: $|I\rangle = \prod_{i \in I} c_i^{+}\;|\rangle$
- $n_i = c_i^{+}c_i$ is electron number operator: $n_i|I\rangle = \mathcal{I}\left\{i \in I\right\}|I\rangle$

Often denoted as $c_i^{\dagger}$ – reasonable if it is not hermitian conjugate of c_i

Hamiltonian becomes sparse

$< I|\mathrm{H}|J >$ is nonzero only in three cases:

- $I = J$, then

$$\sum_i^I H_{ii}^{1\mathrm{e}} + \frac{1}{2}\sum_{i,j}^I (W_{iijj} - W_{ijji})$$

- I and J differ by $i \in I$ and $k \in J$, then

$$(-1)^m H_{ik}^{1\mathrm{e}} + (-1)^m \sum_j^{I \setminus i} (W_{ikjj} - W_{ijjk})$$

  where m is number of indices in $I \cap J$ between i and k

- I and J differ by $\{i < j\} \in I$ and $\{k < l\} \in J$, then

$$(-1)^m (W_{ikjl} - W_{iljk})$$

  where m is sum of number of indices in $I \cap J$ between i and j, and between k and l

Questions

1. Complete the formula: if $\psi_i = \sum_{j \in \mathbb{A}} T_{ij} \varphi_j$ then $|I\rangle_\psi = \sum_{J:|J|=|I|} ? \qquad ?\ |J\rangle_\varphi$. What is the name of this formula in mathematics?
2. Why do we need Fock space if N is fixed?
3. What will change in case of bosons?

Spin-orbitals

Let's separate spatial and spin coordinates $\psi(\xi) \to \psi(x)\chi(\sigma)$

Let's consider spin-independent Hamiltonian, then S^2 and S_z are integrals of motion, and separation of x and σ variables is exact

Notice: in general

- Ψ is not a product of coordinate and spin part
- Slater determinant is not an eigenfunction of S^2

$$\mathsf{S}^2 = S_z^2 + \frac{1}{2} N_{\text{unpair}} + \sum_{i \in \uparrow} \sum_{j \in \downarrow} \mathrm{flip}_i \, \mathrm{flip}_j$$

But

- S_z can be easily diagonalized by fixing $N_\uparrow$ and $N_\downarrow$ so that

$$N = N_\uparrow + N_\downarrow, \qquad S_z = (N_\uparrow - N_\downarrow)/2$$

- matrix elements are diagonal in spin

Spin-orbitals: wave-function

$$\Psi \equiv \left| \begin{smallmatrix} i_1' & i_2' & \cdots \\ i_1'' & i_2'' & \cdots \end{smallmatrix} \right\rangle \equiv |I^{\uparrow}, I^{\downarrow}\rangle$$

corresponds to Slater determinant on

$$\{\psi_{i_1'}\chi_{\uparrow}, \psi_{i_2'}\chi_{\uparrow}, \ldots, \psi_{i_1''}\chi_{\downarrow}, \psi_{i_2''}\chi_{\downarrow}, \ldots\}$$

Then the spin-flip operator multiplies $|I^{\uparrow}, I^{\downarrow}\rangle$ by $(-1)^m$, where m is the number of transpositions required to reorder 1e functions

Basis transformation:

$$|I^{\uparrow}, I^{\downarrow}\rangle_{\psi} = \sum_{J:|J^{\uparrow}|=|I^{\uparrow}|,|J^{\downarrow}|=|I^{\downarrow}|} \det T_{I^{\uparrow}J^{\uparrow}} \det T_{I^{\downarrow}J^{\downarrow}}\ |J^{\uparrow}, J^{\downarrow}\rangle_{\varphi}$$

Spin-orbitals: operators

Matrix elements are similar but acquire spin indices:

$$A_{ik}^{\sigma\tau} = \delta_{\sigma\tau} \ \langle \varphi_i^\sigma | A | \psi_k^\sigma \rangle \equiv \delta_{\sigma\tau} A_{ik}^\sigma$$

$$W_{ikjl}^{\sigma\upsilon\tau\phi} = \delta_{\sigma\upsilon}\delta_{\tau\phi} \ \langle \varphi_i^\sigma(x)\varphi_j^\tau(y) | W | \psi_k^\sigma(x)\psi_l^\tau(y) \rangle \equiv \delta_{\sigma\upsilon}\delta_{\tau\phi} W_{ikjl}^{\sigma\tau}$$

Many-body matrix elements acquire spin summations:

$$O_\sigma \equiv O(\varphi_1^\sigma, \ldots, \varphi_{N_\sigma}^\sigma; \psi_1^\sigma, \ldots, \psi_{N_\sigma}^\sigma)$$

$$\det O = \prod_\sigma \det O_\sigma, \qquad \operatorname{tr} AO^{-1} = \sum_\sigma \operatorname{tr} A^\sigma O_\sigma^{-1}$$

$$\sum_{i,j}^{\Phi} \sum_{k,l}^{\Psi} (W_{ikjl} - W_{iljk}) \left(O^{-1}\right)_{ki} \left(O^{-1}\right)_{lj} \to$$

$$\to \sum_{\sigma,\tau} \sum_i^{\Phi^\sigma} \sum_j^{\Phi^\tau} \sum_k^{\Psi^\sigma} \sum_l^{\Psi^\tau} \left(W_{ikjl}^{\sigma\tau} - \delta_{\sigma\tau} W_{iljk}^{\sigma\sigma}\right) \left(O_\sigma^{-1}\right)_{ki} \left(O_\tau^{-1}\right)_{lj}$$

Spin-orbitals: Fock-space operators

$$\mathrm{c}_{i\uparrow}|I^{\uparrow},I^{\downarrow}\rangle = P(i,I^{\uparrow})\ |(I^{\uparrow}\backslash i),I^{\downarrow}\rangle$$

$$\mathrm{c}_{i\downarrow}|I^{\uparrow},I^{\downarrow}\rangle = (-1)^{|I^{\uparrow}|}P(i,I^{\downarrow})\ |I^{\uparrow},(I^{\downarrow}\backslash i)\rangle$$

$$\langle I^{\uparrow},I^{\downarrow}|J^{\uparrow},J^{\downarrow}\rangle = \langle I^{\uparrow}|J^{\uparrow}\rangle\langle I^{\downarrow}|J^{\downarrow}\rangle \equiv \det O_{\uparrow}\det O_{\downarrow} \equiv \det O$$

$$\langle I^{\uparrow},I^{\downarrow}|\mathrm{c}^{+}_{i\sigma}\mathrm{c}_{k\tau}|J^{\uparrow},J^{\downarrow}\rangle = \delta_{\sigma\tau}\left(O_{\sigma}^{-1}\right)_{ki}\det O$$

$$\langle I^{\uparrow},I^{\downarrow}|\mathrm{c}^{+}_{i\sigma}\mathrm{c}^{+}_{j\tau}\mathrm{c}_{l\phi}\mathrm{c}_{k\upsilon}|J^{\uparrow},J^{\downarrow}\rangle = \begin{vmatrix} \delta_{\sigma\upsilon}\left(O_{\sigma}^{-1}\right)_{ki} & \delta_{\tau\upsilon}\left(O_{\tau}^{-1}\right)_{kj} \\ \delta_{\sigma\phi}\left(O_{\sigma}^{-1}\right)_{li} & \delta_{\tau\phi}\left(O_{\tau}^{-1}\right)_{lj} \end{vmatrix}\det O$$

$$\mathrm{H} = \sum_{i,k}^{\mathbb{A}}\sum_{\sigma}^{\uparrow\downarrow}\mathrm{c}^{+}_{i\sigma}H^{1\mathrm{e}}_{ik}\mathrm{c}_{k\sigma} + \frac{1}{2}\sum_{i,j,k,l}^{\mathbb{A}}\sum_{\sigma\tau}^{\uparrow\downarrow}\mathrm{c}^{+}_{i\sigma}\mathrm{c}^{+}_{j\tau}W_{ikjl}\mathrm{c}_{l\tau}\mathrm{c}_{k\sigma}$$

Spin indices are absent if spin-up and -down orbitals are spatially the same

Questions

1. When Slater determinant is an eigenfunction of S^2?
2. What is origin of spin contamination in UHF/UDFT?
3. Diagonalization of S^2 is algebraic (as an angular momentum of a spherically symmetric problem). What is the name of formula/coefficients solving this problem for the case of two particles?

Example: spin part for two electrons

- $S = 0$

$$\Psi(\xi_1, \xi_2) = X(x_1, x_2)\frac{1}{\sqrt{2}}\left[\chi_\uparrow(\sigma_1)\chi_\downarrow(\sigma_2) - \chi_\downarrow(\sigma_1)\chi_\uparrow(\sigma_2)\right]$$

where $X(x_1, x_2)$ is symmetric function

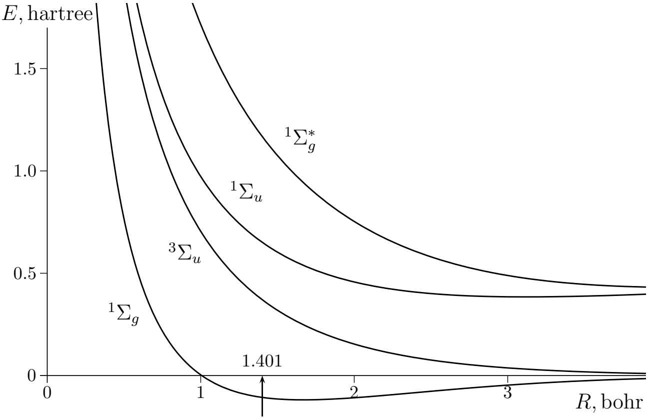
- $S = 1$

$$\Psi(\xi_1, \xi_2) = X(x_1, x_2)\begin{cases} \chi_\uparrow(\sigma_1)\chi_\uparrow(\sigma_2), & S_z = +1, \\ \chi_\downarrow(\sigma_1)\chi_\downarrow(\sigma_2), & S_z = -1, \\ \frac{1}{\sqrt{2}}\left[\chi_\uparrow(\sigma_1)\chi_\downarrow(\sigma_2) + \chi_\downarrow(\sigma_1)\chi_\uparrow(\sigma_2)\right], & S_z = 0, \end{cases}$$

where $X(x_1, x_2)$ is antisymmetric function

Notice that the last function cannot be written as single Slater determinant

Example: H_2 molecule in one-orbital approximation



H_2 molecule: basis

One-electron basis consists of two orbitals φ_1 and φ_2 centered on the 1st and 2nd hydrogens respectively. Let $s = \langle \varphi_1 | \varphi_2 \rangle$. The one-electron Hamiltonian

$$H^{1e} = \begin{pmatrix} \varepsilon_1^0 + \Lambda_{121} & t_{12}^0 \\ t_{12}^0 & \varepsilon_2^0 + \Lambda_{212} \end{pmatrix}$$

Many-body basis for $N = 2$ and $S_z = 0$ consists of 4 functions:

$$\left| \begin{smallmatrix} 1 \\ 1 \end{smallmatrix} \right\rangle, \quad \left| \begin{smallmatrix} 1 \\ 2 \end{smallmatrix} \right\rangle, \quad \left| \begin{smallmatrix} 2 \\ 1 \end{smallmatrix} \right\rangle, \quad \left| \begin{smallmatrix} 2 \\ 2 \end{smallmatrix} \right\rangle$$

The overlap matrix for this basis is

$$S = \begin{pmatrix} 1 & s & s & s^2 \\ \dots & 1 & s^2 & s \\ \dots & \dots & 1 & s \\ \dots & \dots & \dots & 1 \end{pmatrix}$$

H_2 molecule: Hamiltonian

$$H = \begin{pmatrix} 2\varepsilon_1^0 + 2\Lambda_{121} + W_{11} & s\varepsilon_1^0 + s\Lambda_{121} + t^0 + W_{112} & s\varepsilon_1^0 + s\Lambda_{121} + t^0 + W_{112} & 2st^0 + W_{12}^{\mathrm{ex}} \\ \dots & \varepsilon_1^0 + \varepsilon_2^0 + \Lambda_{121} + \Lambda_{212} + W_{12} & 2st^0 + W_{12}^{\mathrm{ex}} & s\varepsilon_2^0 + s\Lambda_{212} + t^0 + W_{122} \\ \dots & \dots & \varepsilon_1^0 + \varepsilon_2^0 + \Lambda_{121} + \Lambda_{212} + W_{12} & s\varepsilon_2^0 + s\Lambda_{212} + t^0 + W_{122} \\ \dots & \dots & \dots & 2\varepsilon_2^0 + 2\Lambda_{212} + W_{22} \end{pmatrix}$$

After simplifications and redefinitions we obtain:

$$H = 2\varepsilon_0 + \begin{pmatrix} U & t & t & 2st' \\ \dots & V & 2st' & t \\ \dots & \dots & V & t \\ \dots & \dots & \dots & U \end{pmatrix}$$

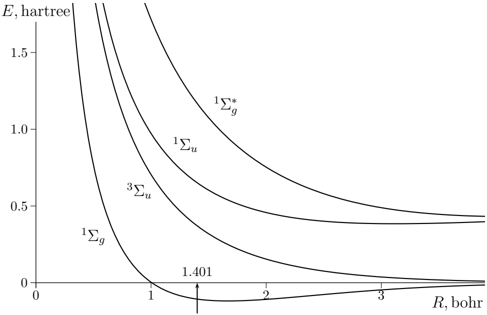
H_2 molecule: orthogonalized basis

$$\begin{aligned}
\Phi_1 &= \frac{1}{\sqrt{2(1-s^2)}}\left(\left|{1 \atop 1}\right\rangle - \left|{2 \atop 2}\right\rangle\right)\\
\Phi_2 &= \frac{1}{\sqrt{2(1-s^2)}}\left(\left|{1 \atop 1}\right\rangle + \left|{2 \atop 2}\right\rangle\right) - \frac{s}{\sqrt{2(1-s^2)}}\left(\left|{1 \atop 2}\right\rangle + \left|{2 \atop 1}\right\rangle\right)\\
\Phi_3 &= \frac{1}{\sqrt{2(1-s^2)}}\left(\left|{1 \atop 2}\right\rangle + \left|{2 \atop 1}\right\rangle\right) - \frac{s}{\sqrt{2(1-s^2)}}\left(\left|{1 \atop 1}\right\rangle + \left|{2 \atop 2}\right\rangle\right)\\
\Phi_4 &= \frac{1}{\sqrt{2(1-s^2)}}\left(\left|{1 \atop 2}\right\rangle - \left|{2 \atop 1}\right\rangle\right)
\end{aligned}$$

or in coordinate representation

$$\begin{aligned}
\frac{1}{\sqrt{2}}\left(\left|{1 \atop 1}\right\rangle \pm \left|{2 \atop 2}\right\rangle\right) &= \frac{\varphi_1(x_1)\varphi_1(x_2) \pm \varphi_2(x_1)\varphi_2(x_2)}{\sqrt{2}}\ \frac{\chi_\uparrow(\sigma_1)\chi_\downarrow(\sigma_2) - \chi_\downarrow(\sigma_1)\chi_\uparrow(\sigma_2)}{\sqrt{2}}\\
\frac{1}{\sqrt{2}}\left(\left|{1 \atop 2}\right\rangle \pm \left|{2 \atop 1}\right\rangle\right) &= \frac{\varphi_1(x_1)\varphi_2(x_2) \pm \varphi_2(x_1)\varphi_1(x_2)}{\sqrt{2}}\ \frac{\chi_\uparrow(\sigma_1)\chi_\downarrow(\sigma_2) \mp \chi_\downarrow(\sigma_1)\chi_\uparrow(\sigma_2)}{\sqrt{2}}
\end{aligned}$$

H_2 molecule: solution



- triplet $^3\Sigma_u$ can be easily identified with $\left(\left|\begin{smallmatrix}1\\2\end{smallmatrix}\right\rangle - \left|\begin{smallmatrix}2\\1\end{smallmatrix}\right\rangle\right)$
- odd singlet $^1\Sigma_u$ can be identified by symmetry: $\left(\left|\begin{smallmatrix}1\\1\end{smallmatrix}\right\rangle - \left|\begin{smallmatrix}2\\2\end{smallmatrix}\right\rangle\right)$
- other two states are given by
$$\Psi \sim \mathrm{e}^{\mp\eta}\left(\left|\begin{smallmatrix}1\\1\end{smallmatrix}\right\rangle + \left|\begin{smallmatrix}2\\2\end{smallmatrix}\right\rangle\right) \pm \mathrm{e}^{\pm\eta}\left(\left|\begin{smallmatrix}1\\2\end{smallmatrix}\right\rangle + \left|\begin{smallmatrix}2\\1\end{smallmatrix}\right\rangle\right)$$
if correlation factor $\eta = 0$ we get single Slater determinants