

Introduction to Second-quantization II

Jeppe Olsen

Center for Theoretical Chemistry
Department of Chemistry, Aarhus

Contents, lecture II

- From spin-orbitals to spin and orbitals
Form of spin-free one- and two-electron operators
- Rotations using exponentials I : first quantization
- Rotations using exponentials II : second quantization

Spin-functions for one electron first quantization

Two spin-functions, $\alpha(m_s), \beta(m_s)$

$$\begin{aligned} S_z \alpha &= \frac{1}{2} \alpha & S^2 \alpha &= \frac{3}{4} \alpha \\ S_z \beta &= -\frac{1}{2} \beta & S^2 \beta &= \frac{3}{4} \beta \end{aligned} \tag{1}$$

- α is 'spin-up', β is 'spin-down'

α and β as functions of m_s

- m_s can take the two values $\frac{1}{2}, -\frac{1}{2}$
- $\alpha(\frac{1}{2}) = 1, \alpha(-\frac{1}{2}) = 0$
- $\beta(\frac{1}{2}) = 0, \beta(-\frac{1}{2}) = 1$

Integration over spin

- Easy : $\int dm_s f(m_s) = f(\frac{1}{2}) + f(-\frac{1}{2})$
- α, β constitute an orthonormal basis
 1. $\int dm_s \alpha^*(m_s) \alpha(m_s) =$
 $\int dm_s \beta^*(m_s) \beta(m_s) = 1$
 2. $\int dm_s \alpha^*(m_s) \beta(m_s) = 0$
- (easily checked from definitions)

Spin-orbitals in first and second quantization

- First quantization : separate functions for spatial- and spin-parts, e.g. $\phi_i(\mathbf{r})\alpha(m_s)$
- Second quantization : Both spatial and spin-parts created by one operator $a_{i\alpha}^\dagger$
- Groundstate of H_2 : $a_{1\sigma_g\alpha}^\dagger a_{1\sigma_g\beta}^\dagger |Vac\rangle$

Various types of operators

Spin-free operators

- Operator that does not change spin-functions

$$f^c \alpha = \alpha f^c \quad f^c \beta = \beta f^c \quad (2)$$

- Operators like kinetic energy and Coulomb-repulsion depend only on spatial coordinates and are therefore spin-free

Pure spin-operators

- Operators that does not change spatial functions

$$f^c \phi_i(\mathbf{r}) = \phi_i(\mathbf{r}) f^c \quad (3)$$

- Operators like S_+ , S_- , S^2 are of this type

Mixed operators

- Changes both spatial- and spin-parts

One-electron operators in SQ

- Spin-orbital i : $i\sigma_i$ (yesterday it was just i)
- Second quantization representation of one-electron operator

$$\hat{h} = \sum_{i\sigma_i j\sigma_j} h_{i\sigma_i j\sigma_j} a_{i\sigma_i}^\dagger a_{j\sigma_j}$$
$$h_{i\sigma_i j\sigma_j} = \int d\mathbf{r} \int dm_s \phi_i(\mathbf{r})^* \sigma_i(m_s)^* h(\mathbf{r}, m_s) \phi_j(\mathbf{r}) \sigma_j(m_s)$$

Example of pure spin-operator in SQ: S_+

Form

$$S_+ = \sum_{i\sigma_i j\sigma_j} (S_+)_{i\sigma_i j\sigma_j} a_{i\sigma_i}^\dagger a_{j\sigma_j}$$

$$\underline{(S_+)_{i\sigma_i j\sigma_j} = ?}$$

- Remember of S_+ in FQ
- Use this to calculate integrals $(S_+)_{i\sigma_i j\sigma_j}$

S_+ in FQ

$$S_+\beta = \alpha \quad S_+\alpha = 0$$

$$S_+\phi_i = \phi_i S_+ \quad (S_+ \text{ is pure spin-operator})$$

The integrals $(S_+)_{i\sigma_i j\sigma_j}$

$$\begin{aligned} & (S_+)_{i\sigma_i j\sigma_j} \\ &= \int d\mathbf{r} \int dm_s \phi_i(\mathbf{r})^* \sigma_i(m_s)^* S_+(m_s) \phi_j(\mathbf{r}) \sigma_j(m_s) \\ &= \int d\mathbf{r} \phi_i(\mathbf{r})^* \phi_j(\mathbf{r}) \int dm_s \sigma_i(m_s)^* S_+(m_s) \sigma_j(m_s) \\ &= \delta_{ij} \delta_{\sigma_i \alpha} \delta_{\sigma_j \beta} \end{aligned}$$

$$((S_+)_{i\sigma_i j\sigma_j} = \delta_{ij}\delta_{\sigma_i\alpha}\delta_{\sigma_j\beta})$$

So

$$\begin{aligned} S_+ &= \sum_{i\sigma_i j\sigma_j} (S_+)_{i\sigma_i j\sigma_j} a_{i\sigma_i}^\dagger a_{j\sigma_j} \\ &= \sum_{i\sigma_i j\sigma_j} \delta_{ij}\delta_{\sigma_i\alpha}\delta_{\sigma_j\beta} a_{i\sigma_i}^\dagger a_{j\sigma_j} \\ &= \sum_i a_{i\alpha}^\dagger a_{i\beta} \end{aligned}$$

Corresponds to intuitive picture : changes β to α

Form of spin-free one-electron operator in SQ

The integrals $h_{i\sigma_i j\sigma_j}$

$$\begin{aligned} & h_{i\sigma_i j\sigma_j} \\ &= \int d\mathbf{r} \int dm_s \phi_i(\mathbf{r})^* \sigma_i(m_s)^* h(\mathbf{r}) \phi_j(\mathbf{r}) \sigma_j(m_s) \\ &= \int \int dm_s \sigma_i(m_s)^* \sigma_j(m_s) \int d\mathbf{r} \phi_i(\mathbf{r})^* h(\mathbf{r}) \phi_j(\mathbf{r}) \\ &= \delta_{\sigma_i \sigma_j} h_{ij} \end{aligned}$$

$$(h_{i\sigma ij\sigma_j} = \delta_{\sigma_i\sigma_j} h_{ij})$$

$$\begin{aligned}\hat{h} &= \sum_{i\sigma ij\sigma_j} h_{i\sigma ij\sigma_j} a_{i\sigma_i}^\dagger a_{j\sigma_j} \\ &= \sum_{i\sigma ij\sigma_j} \delta_{\sigma_i\sigma_j} h_{ij} a_{i\sigma_i}^\dagger a_{j\sigma_j} \\ &= \sum_{ij} h_{ij} \left(\sum_{\sigma} a_{i\sigma}^\dagger a_{j\sigma} \right)\end{aligned}$$

$$(\hat{h} = \sum_{ij} h_{ij} (\sum_{\sigma} a_{i\sigma}^{\dagger} a_{j\sigma}))$$

Introduce

$$\begin{aligned} E_{ij} &= \sum_{\sigma} a_{i\sigma}^{\dagger} a_{j\sigma} \\ &= a_{i\alpha}^{\dagger} a_{j\alpha} + a_{i\beta}^{\dagger} a_{j\beta} \end{aligned}$$

E_{ij} is an generator of the linear group

A spin-free one-electron operator then reads

- $\hat{h} = \sum_{ij} h_{ij} E_{ij}$
- h_{ij} depends on orbitals
- E_{ij} excites α - and β - spin orbitals

Spin-free Two-electron operator in SQ

General two-electron operator in SQ

$$\hat{g} = \frac{1}{2} \sum_{i\sigma_i j\sigma_j k\sigma_k l\sigma_l} g_{i\sigma_i j\sigma_j k\sigma_k l\sigma_l} a_{i\sigma_i}^\dagger a_{k\sigma_k}^\dagger a_{l\sigma_l} a_{j\sigma_j} \quad (4)$$

Simplification for spin-free two-electron operator

$$g_{i\sigma_i j\sigma_j k\sigma_k l\sigma_l} = g_{ijkl} \delta_{\sigma_i \sigma_j} \delta_{\sigma_k \sigma_l}$$

$$g_{ijkl} = \int d\mathbf{r} d\mathbf{r}' \phi_i^*(\mathbf{r}) \phi_k^*(\mathbf{r}') g^c(\mathbf{r}, \mathbf{r}') \phi_j(\mathbf{r}) \phi_l(\mathbf{r}')$$

Gives spin-free two-electron operator

$$\hat{g} = \frac{1}{2} \sum_{ijkl} g_{ijkl} \left(\sum_{\sigma\sigma'} a_{i\sigma}^\dagger a_{k\sigma'}^\dagger a_{l\sigma'} a_{j\sigma} \right)$$

A simple rewrite

$$\begin{aligned}\hat{g} &= \frac{1}{2} \sum_{ijkl} g_{ijkl} \left(\sum_{\sigma\sigma'} a_{i\sigma}^\dagger a_{k\sigma'}^\dagger a_{l\sigma'} a_{j\sigma} \right) \\ &= -\frac{1}{2} \sum_{ijkl} g_{ijkl} \left(\sum_{\sigma\sigma'} a_{i\sigma}^\dagger a_{k\sigma'}^\dagger a_{j\sigma} a_{l\sigma'} \right) \\ &= -\frac{1}{2} \sum_{ijkl} g_{ijkl} \left(\sum_{\sigma\sigma'} a_{i\sigma}^\dagger (-a_{j\sigma} a_{k\sigma'}^\dagger + \delta_{jk} \delta_{\sigma\sigma'}) a_{l\sigma'} \right) \\ &= \frac{1}{2} \sum_{ijkl} g_{ijkl} \left(\sum_{\sigma\sigma'} a_{i\sigma}^\dagger a_{j\sigma} a_{k\sigma'}^\dagger a_{l\sigma'} - \delta_{jk} a_{i\sigma}^\dagger a_{l\sigma} \right) \\ &= \frac{1}{2} \sum_{ijkl} g_{ijkl} (E_{ij} E_{kl} - \delta_{jk} E_{il})\end{aligned}$$

The Hamiltonian in SQ

- One-electron part containing kinetic energy and nuclear attraction $\leftarrow \hat{h}$
- Two-electron part containing electron-electron repulsion $\leftarrow \hat{g}$
- Spin-free !

$$\begin{aligned}\hat{H} &= \hat{h} + \hat{g} \\ &= \sum_{ij} h_{ij} E_{ij} + \frac{1}{2} \sum_{ijkl} g_{ijkl} (E_{ij} E_{kl} - \delta_{jk} E_{il})\end{aligned}$$

And now for something completely different Orbital-rotations using exponential mappings

Problem

- A set of orthonormal spinorbitals is given ϕ
- Obtain all orthonormal orbitals $\tilde{\phi}$ that can be obtained as linear combinations of ϕ

$$\tilde{\phi} = \phi X$$
$$\langle \tilde{\phi}_i | \tilde{\phi}_j \rangle = \delta_{ij}$$

- We want a simple parameterization of all orthonormal spin-orbitals $\tilde{\phi}$
- Occurs in SCF and MCSCF optimization
- (Note : i, j refers now to spin-orbitals)

Why not use the elements of \mathbf{X} as parameters ?

- The required orthonormality of $\tilde{\phi}$ requires that \mathbf{X} is unitary

$$\mathbf{X}^\dagger \mathbf{X} = \mathbf{1}$$

- The unitary conditions on \mathbf{X} gives constraints on its elements
- The elements of \mathbf{X} can therefore not be used as independent parameters
- A parameterization of unitary matrices may be obtained in terms of exponential matrices

Exponential matrices

Definition

$$\begin{aligned}\exp(\mathbf{A}) &= \sum_{n=0, \infty} \frac{1}{n!} \mathbf{A}^n \\ &= \mathbf{1} + \mathbf{A} + \frac{1}{2} \mathbf{A}^2 + \dots\end{aligned}$$

- Straightforward extension of Taylor-expansion of $\exp(x)$, where x is a number
- Converges for any choice of finite \mathbf{A} (assuming finite dimension)

Relations

$$\exp(\mathbf{A}) \exp(-\mathbf{A}) = \mathbf{1}$$

$$\exp(\mathbf{A})^\dagger = \exp(\mathbf{A}^\dagger)$$

$$\mathbf{B} \exp(\mathbf{A}) \mathbf{B}^{-1} = \exp(\mathbf{B} \mathbf{A} \mathbf{B}^{-1})$$

$$\exp(\mathbf{A} + \mathbf{B}) = \exp(\mathbf{A}) \exp(\mathbf{B}) \text{ iff } [\mathbf{A}, \mathbf{B}] = 0$$

The Baker-Cambell-Hausdorf (BCH) expansion

$$\begin{aligned} \exp(\mathbf{A}) \mathbf{B} \exp(-\mathbf{A}) &= \mathbf{B} + [\mathbf{A}, \mathbf{B}] + \frac{1}{2}[\mathbf{A}, [\mathbf{A}, \mathbf{B}]] \\ &+ \dots + \frac{1}{n!}[\mathbf{A}, [\mathbf{A}, \dots, [\mathbf{A}, \mathbf{B}] \dots]] + \dots \end{aligned}$$

Unitary matrices as exponentials of antihermitian matrices

$$\mathbf{X} = \exp(i\boldsymbol{\kappa})$$

$$\mathbf{X}^\dagger \mathbf{X} = \mathbf{1} (\mathbf{X} \text{ is unitary})$$

$$\boldsymbol{\kappa}^\dagger = \boldsymbol{\kappa} (\boldsymbol{\kappa} \text{ is Hermitian})$$

1 : $\exp(i\boldsymbol{\kappa})$ is unitary

$$\begin{aligned} \exp(i\boldsymbol{\kappa})^\dagger \exp(i\boldsymbol{\kappa}) &= \exp(-i\boldsymbol{\kappa}) \exp(i\boldsymbol{\kappa}) \\ &= \mathbf{1} \end{aligned}$$

2 All unitary matrices may be written as $\exp(i\boldsymbol{\kappa})$

- A unitary matrix \mathbf{X} may be diagonalized $\mathbf{X} = \mathbf{U}\boldsymbol{\epsilon}\mathbf{U}^\dagger$, $\mathbf{U}\mathbf{U}^\dagger = \mathbf{1}$
- $\boldsymbol{\epsilon}$ is a diagonal matrix and $|\epsilon_i| = 1$
- $|\epsilon_i| = 1 \rightarrow \epsilon_i = \exp(i\delta_i)$, δ_i is real
- Therefore $\mathbf{X} = \mathbf{U} \exp(i\boldsymbol{\delta})\mathbf{U}^\dagger = \exp(i\mathbf{U}\boldsymbol{\delta}\mathbf{U}^\dagger)$
- $\mathbf{U}\boldsymbol{\delta}\mathbf{U}^\dagger$ is Hermitian, $(\mathbf{U}\boldsymbol{\delta}\mathbf{U}^\dagger)^\dagger = \mathbf{U}\boldsymbol{\delta}\mathbf{U}^\dagger$
- We have therefore proved that any unitary matrix can be written in the stated form

What is so great about $\mathbf{X} = \exp(i\boldsymbol{\kappa})$

- It is as easy to obtain an independent set of parameters for an Hermitian matrix
 1. Take the elements at or below the diagonal as the independent parameters
 2. Obtain the elements above the diagonal as

$$\kappa_{ji} = \kappa_{ij}^*, i > j$$

A parameterization of all sets of orthonormal orbitals

- $\kappa_{ij}, i > j \rightarrow \boldsymbol{\kappa} \rightarrow \mathbf{X} \rightarrow \tilde{\phi}$

The energy as a function of orbitals

- $E = E(\tilde{\phi}) = E(\boldsymbol{\kappa}_{low})$, for example the SCF energy
- The energy is now a function of a set of independent parameters
- Standard numerical methods like Quasi-Newton methods or the Newton method may then be used to optimize energy
- If some use for SCF, essential for MCSCF

Rotation of creation-operators

- Rotated orbitals : $\tilde{\phi}_i = \sum_j X_{ji} \phi_j$, $\mathbf{X} = \exp(i\boldsymbol{\kappa})$
- A creation operator creating on electron in spin-orbital $\tilde{\phi}_i$: $\tilde{a}_i^\dagger = \sum_j a_j^\dagger X_{ji}$
- An ONV of rotated spin-orbitals $\tilde{a}_1^\dagger \tilde{a}_2^\dagger \cdots |vac\rangle = \sum_{j_1 j_2 \cdots} a_{j_1}^\dagger a_{j_2}^\dagger \cdots |vac\rangle X_{j_1 1} X_{j_2 2} \cdots$
- Complicated form

An operator form of \tilde{a}^\dagger

- $\tilde{a}_i^\dagger = \sum_k a_k^\dagger (\exp(i\boldsymbol{\kappa}))_{ki}$
- We will show that $\tilde{a}_i^\dagger = \exp(i\hat{\kappa})a_i^\dagger \exp(-i\hat{\kappa})$
- $\hat{\kappa} = \sum_{ij} \kappa_{ij} a_i^\dagger a_j$ ($\hat{\kappa}$ is an Hermitian one-electron operator)
- Exponential of operator is defined as exponential of matrix and have the same properties and relations.

Proof of operator form

- The BCH expansion gives

$$\exp(i\hat{\kappa})a_i^\dagger \exp(-i\hat{\kappa}) = a_i^\dagger + i[\hat{\kappa}, a_i^\dagger] + \frac{i^2}{2}[\hat{\kappa}, [\hat{\kappa}, a_i^\dagger]] + \dots$$

- Calculating the commutators gives

$$\begin{aligned} & \exp(i\hat{\kappa})a_i^\dagger \exp(-i\hat{\kappa}) \\ &= a_i^\dagger + i \sum_k \kappa_{ki} a_k^\dagger + \sum_k \frac{i^2}{2!} (\kappa)_{ki}^2 a_k^\dagger + \dots \\ &= \sum_k a_k^\dagger (\mathbf{1} + i\boldsymbol{\kappa} + \frac{i^2}{2!} (\boldsymbol{\kappa})^2 + \dots)_{ki} \\ &= \sum_k \exp(i\boldsymbol{\kappa})_{ki} a_k^\dagger \end{aligned}$$

$$\begin{aligned} |\widetilde{ONV}\rangle &= \tilde{a}_1^\dagger \tilde{a}_2^\dagger \cdots \tilde{a}_n^\dagger |vac\rangle \\ &= \exp(i\hat{\kappa}) a_1^\dagger \exp(-i\hat{\kappa}) \exp(i\hat{\kappa}) a_2^\dagger \exp(-i\hat{\kappa}) \\ &\quad \cdots \exp(i\hat{\kappa}) a_n^\dagger \exp(-i\hat{\kappa}) |vac\rangle \\ &= \exp(i\hat{\kappa}) a_1^\dagger a_2^\dagger \cdots a_n^\dagger |vac\rangle \\ &= \exp(i\hat{\kappa}) |ONV\rangle \end{aligned}$$

- Applying a single exponential operator rotates all the spin-orbitals !!

Unrestricted $\hat{\kappa}$

- $i\hat{\kappa} = i \sum_{ij} \kappa_{ij} a_i^\dagger a_j$ with $\boldsymbol{\kappa}$ general Hermitian matrix \rightarrow complete general spin-orbital transformation
 1. Allows the orbital to become complex (elements of $i\boldsymbol{\kappa}$ may be complex)
 2. α - and β -spinorbitals are allowed to get different spatial parts
 3. α - and β -spinorbitals are allowed to mix

Restriction to real orbitals

- Restrict $i\hat{\kappa}$ to real elements
- Corresponds to restricting $\boldsymbol{\kappa}$ to be an purely imaginary antisymmetric matrix

$$\kappa_{ij} = i^A \kappa_{ij}, \quad A \kappa_{ij} = -A \kappa_{ji}$$

- Then

$$\begin{aligned} i\hat{\kappa} &= i \sum_{ij} i^A \kappa_{ij} a_i^\dagger a_j \\ &= - \sum_{i>j} A \kappa_{ij} a_i^\dagger a_j - \sum_{i<j} A \kappa_{ij} a_i^\dagger a_j \\ &= - \sum_{i>j} A \kappa_{ij} a_i^\dagger a_j - \sum_{i>j} A \kappa_{ji} a_j^\dagger a_i \\ &= - \sum_{i>j} A \kappa_{ij} (a_i^\dagger a_j - a_j^\dagger a_i) \end{aligned}$$

Restrictions on spin-orbitals

- α - and β -spin-orbitals should not mix :
 $A_{\kappa_{i\alpha j\beta}} = A_{\kappa_{i\alpha j\beta}} = 0$
- α - and β -spin-orbitals should rotate in the same way $A_{\kappa_{i\alpha j\alpha}} = A_{\kappa_{i\beta j\beta}} = A_{\kappa_{ij}}$
- Restricted form of $i\hat{\kappa}$ become

$$\begin{aligned} i\hat{\kappa} &= - \sum_{i>j} A_{\kappa_{ij}} (a_{i\alpha}^\dagger a_{j\alpha} + a_{i\beta}^\dagger a_{j\beta} - a_{j\alpha}^\dagger a_{i\alpha} - a_{j\beta}^\dagger a_{i\beta}) \\ &= \sum_{ij} A_{\kappa_{ij}} (E_{ij} - E_{ji}) \end{aligned}$$

(sum over i, j are now over orbitals)

Restricted rotation of ONV

$$\begin{aligned} |\widetilde{ONV}\rangle &= \exp(i\hat{\kappa})|ONV\rangle \\ &= \exp\left(-\sum_{ij}^A \kappa_{ij}(E_{ij} - E_{ji})\right)|ONV\rangle \end{aligned}$$

This is -with small notational differences, the form B. Roos will use in the MCSCF lectures