Introduction to Second-quantization I

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What is Second Quantization?

- Another representation of Quantum Mechanics
- Operators and wavefunctions are described by a common set of elementary operators (creation and annihilation operators)

Advantages

- Antisymmetry is built automatically in
- The use of a common set of elementaty operators for wavefunctions and operators allows manipulations not easily realized in the standard formulation

Disdvantages

- Yet another formalism to learn

Slater-determinants and occupation number vectors

Slater-determinant

- A Slater-determinant is an antisymmetric combination of some spin-orbitals

Occupation number vector (ONV)

- Assume a space of m spin-orbitals are given
- An ONV is a vector of m integers, each integer may be 0 or 1

$$|\mathbf{n}\rangle = |n_1, n_2, \cdots, n_m\rangle, \quad n_i = 0, 1 \qquad \text{for } i = 1, 2, \cdots, m \tag{1}$$

- Each occupation number vector gives the occupation of a given Slater-determinant

Slater-determinant → ONV

- Assume we have a given Slater-determinant, how do we find the corresponding ONV ?
- Entry i in the ONV set
  1. 1 if spin-orbital i is occupied
  2. 0 if spin-orbital i is un-occupied
- (The total number of spin-orbitals m must also be known)

Example(m=4)

- Slater-determinant : $\frac{1}{2!}\begin{vmatrix} \phi_2(1) & \phi_4(1) \\ \phi_2(2) & \phi_4(2) \end{vmatrix}$
- ONV : $|0, 1, 0, 1\rangle$

Other Examples

Slater-determinant	ONV	# of elecs.
$\phi_3(1)$	$\|0,0,1,0\rangle$	1
$\frac{1}{2!}\begin{vmatrix} \phi_1(1) & \phi_3(1) \\ \phi_1(2) & \phi_3(2) \end{vmatrix}$	$\|1,0,1,0\rangle$	2
$\frac{1}{3!}\begin{vmatrix} \phi_1(1) & \phi_3(1) & \phi_4(1) \\ \phi_1(2) & \phi_3(2) & \phi_4(2) \\ \phi_1(3) & \phi_3(3) & \phi_4(3) \end{vmatrix}$	$\|1,0,1,1\rangle$	3
1	$\|0,0,0,0\rangle$	0

Nomenclature for ONV's

Uses correspondance between ONV and SD

- n_i is occupation number for spin-orbital i
- If $n_i = 1$, spin-orbital/level i is occupied
- If $n_i = 0$, spin-orbital/level i is unoccupied
- $\sum_{i=1,m} n_i$ is the total number of electrons in the ONV
- The ONV with zero electrons is the vacuum state $|vac\rangle = |0, 0, \cdots, 0\rangle$

ONV's represents SD's, but ONV's are not SD's

- We have a one-to-one mapping between ONV's and SD's
- But they are not identical
  - SD's are functions of space-coordinates of electrons
  - In SD's there is explicit reference to electron 1, electron 2, ...
  - ONV's a just vectors in an abstract vector space

The Fock-space

- Defined by the total number of spin-orbitals, m
- Abstract vector space
- The ONV's are unit-vectors
- Each unit-vector corresponds thus to a SD, combination of several determinants corresponds to $|0\rangle = \sum_i c_i |ONV_i\rangle$
- Contains ONV's with 0,1,... m electrons
- We thus map SD's in real cartesian space to ONV's in the Fock-space.

Inner product between ONV's

- We will **define** an inner product between ONV's, so it includes the standard inner product of SD's for orthonormal orbitals

$$\langle \mathbf{n} | \mathbf{k} \rangle = \delta_{\mathbf{n},\mathbf{k}} = \prod_{i=1,m} \delta_{n_i,k_i} \tag{2}$$

1. = 1 if the two ONV's are identical
2. = 0 if the two ONV's differ in one or more occupation numbers

- Inner product also defined for ONV's with different number of electrons

Creation-operators $a_i^\dagger$

- One creation operator $a_i^\dagger$ for each spin-orbital i
- Definition

$$\begin{aligned} a_i^\dagger|n_1,\cdots,0_i,\cdots,n_m\rangle &= \Gamma(\mathbf{n})_i\ |n_1,\cdots,1_i,\cdots,n_m\rangle \\ a_i^\dagger|n_1,\cdots,1_i,\cdots,n_m\rangle &= 0 \end{aligned}$$

$$\Gamma(\mathbf{n})_i = (-1)^{\left(\sum_{j=1}^{i-1} n_j\right)} \tag{3}$$

- Creates an electron in spin-orbital i if this spin-orbital is unoccupied in $|\mathbf{n}\rangle$
- Gives zero if spin-orbital i is occupied in $|\mathbf{n}\rangle$
- Phase-factor $\Gamma(\mathbf{n})_i$
  - count the number of electrons in $|\mathbf{n}\rangle$ before i
  - Even number → $\Gamma(\mathbf{n})_i = 1$, odd → $\Gamma(\mathbf{n})_i = -1$

Examples

- $a_1^\dagger|1,0,0,0\rangle = 0$
- $a_1^\dagger|0,1,0,0\rangle = |1,1,0,0\rangle$
- $a_2^\dagger|1,0,0,0\rangle = -|1,1,0,0\rangle$

Products of two creation-operators

$a_i^\dagger a_j^\dagger$

$\underline{a_i^\dagger a_i^\dagger}$

- Consider the action of $a_i^\dagger a_i^\dagger$ on an arbitrary ONV, two cases

1.

$$a_i^\dagger a_i^\dagger |\cdots, 1_i, \cdots\rangle \; = a_i^\dagger \mathbf{0} = \mathbf{0} \tag{4}$$

2.

$$\begin{aligned} a_i^\dagger a_i^\dagger |\cdots, 0_i, \cdots\rangle \; &= \Gamma(\mathbf{n})_i a_i^\dagger |\cdots, 1_i, \cdots\rangle \\ &= 0 \end{aligned} \tag{5}$$

- $a_i^\dagger a_i^\dagger$ working on any ONV gives $\mathbf{0}$, so

$$a_i^\dagger a_i^\dagger = 0 \tag{6}$$

$a_i^\dagger a_j^\dagger$ and $a_j^\dagger a_i^\dagger, i < j$

- Only nonvanishing if both spinorbitals i, j are unoccupied

$$\begin{aligned} a_i^\dagger a_j^\dagger |\cdots 0_i \cdots 0_j \cdots\rangle &= \Gamma(\mathbf{n})_j a_i^\dagger |\cdots 0_i \cdots 1_j \cdots\rangle \\ &= \Gamma(\mathbf{n})_i \Gamma(\mathbf{n})_j |\cdots 1_i \cdots 1_j \cdots\rangle \\ a_j^\dagger a_i^\dagger |\cdots 0_i \cdots 0_j \cdots\rangle &= \Gamma(\mathbf{n})_i a_j^\dagger |\cdots 1_i \cdots 0_j \cdots\rangle \\ &= -\Gamma(\mathbf{n})_i \Gamma(\mathbf{n})_j |\cdots 1_i \cdots 1_j \cdots\rangle \end{aligned} \tag{7}$$

- so $(a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger)|\cdots 0_i \cdots 0_j \cdots\rangle = \mathbf{0}$
- Same relation holds(trivially) for other ONV'S so

$$a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0 \tag{8}$$

$$a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0$$

- holds for all i, j
- Creation-operators anticommute
- The anticommutation arise from the definition of the phase-factor Γ
- Also written as $[a_i^\dagger, a_j^\dagger]_+ = 0$
  $([A, B]_+ = AB + BA)$

Annihilation-operators a_i

- The operators obtained by conjugating $a_i^\dagger$: $a_i = (a_i^\dagger)^\dagger$
- From the definition of the creationoperators it may be shown

$$\begin{aligned} a_i|\cdots\ 1_i\cdots\rangle &= \Gamma(\mathbf{n})_i\ |\cdots\ 0_i\cdots\rangle \\ a_i|\cdots\ 0_i\cdots\rangle &= 0 \end{aligned} \tag{9}$$

- Thus
  1. $a_i^\dagger$ creates an electron in spin-orbital i if possible
  2. a_i annihilates an electron in spin-orbital i if possible
- Examples
  - $a_1|0,0,0,0\rangle = 0$
  - $a_1|1,1,0,0\rangle = |0,1,0,0\rangle$
  - $a_2|1,1,0,0\rangle = -|1,0,0,0\rangle$

Products of annihilation-operators

- From the anticommutation of the creation operators $a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0$
- We obtain by conjugation

$$\begin{aligned}(a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger)^\dagger &= \\ a_j a_i + a_i a_j &= 0\end{aligned} \tag{10}$$

- Thus annihilation-operators are also anticommuting $[a_i, a_j]_+ = 0$

Anticommutation of creation- and annihilation-operator

$$a_i^\dagger a_j + a_j a_i^\dagger = \,?$$

- From examining the action on various ONV's one obtains
  1. $i \neq j : a_i^\dagger a_j + a_j a_i^\dagger = 0$
  2. $i = j : a_i^\dagger a_i + a_i a_i^\dagger = 1$
- Collecting the two gives $a_i^\dagger a_j + a_j a_i^\dagger = \delta_{ij}$
- δ_{ij} is the Kronecker delta-function

$$\delta_{ij} = \begin{cases} 1 & \text{for} \quad i = j \\ 0 & \text{for} \quad i \neq j \end{cases} \tag{11}$$

The operator $a_i^\dagger a_i$

- Two cases :

$$\begin{aligned} a_i^\dagger a_i|\cdots 1_i \cdots\rangle &= \Gamma(\mathbf{n})_i a_i^\dagger|\cdots 0_i \cdots\rangle \\ &= \Gamma(\mathbf{n})_i^2|\cdots 1_i \cdots\rangle = |\cdots 1_i \cdots\rangle \\ a_i^\dagger a_i|\cdots 0_i \cdots\rangle &= 0 \end{aligned} \tag{12}$$

- The two cases may be combined as

$$a_i^\dagger a_i|\cdots n_i \cdots\rangle = n_i|\cdots n_i \cdots\rangle \tag{13}$$

- When $a_i^\dagger a_i$ works on a ONV, it thus gives the ONV multiplied with the occupation number
- $\hat{n}_i = a_i^\dagger a_i$ is thus the **number-operator** for spin-orbital i
- $\hat{N} = \sum_i \hat{n}_i$ gives the total number of electrons, $\sum_i n_i$ of an ONV

Excitation-operators

$$a_i^\dagger a_j (i \neq j)$$

- $a_i^\dagger a_j | \cdots 0_i \cdots 1_j \cdots \rangle = \pm | \cdots 1_i \cdots 0_j \cdots \rangle$
- Removes one electron in spin-orbital j and creates one electron i
- In other words : Excites one electron from j to i
- $a_i^\dagger a_j (i \neq j)$ is therefore a **single-electron excitation**
- Two-electron excitations may be obtained as $a_i^\dagger a_j^\dagger a_k a_l$

Table 1: Elements of second quantization

Basis vectors	$\lvert\mathbf{n}\rangle = \lvert n_1, n_2, \cdots, n_m\rangle, n_i = 0, 1$
Inner product	$\langle\mathbf{n}\vert\mathbf{k}\rangle = \prod_i \delta_{n_i k_i}$
Creation operators	$a_i^\dagger \lvert n_1, \cdots, 0_i, \cdots, n_m\rangle = \Gamma(\mathbf{n})_i \lvert n_1, \cdots, 1_i, \cdots, n_m\rangle$ $\Gamma(\mathbf{n})_i = -1^{(\sum_{j=1}^{i-1} n_j)}$ $a_i^\dagger \lvert n_1, \cdots, 1_i, \cdots, n_m\rangle = 0$
Annihilation operators	$a_i \lvert n_1, \cdots, 1_i, \cdots, n_m\rangle = \Gamma(\mathbf{n})_i \lvert n_1, \cdots, 0_i, \cdots, n_m\rangle$ $a_i \lvert n_1, \cdots, 0_i, \cdots, n_m\rangle = 0$
Anticommutation relations	$a_i^\dagger a_j + a_j a_i^\dagger = \delta_{ij}$ $a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0$ $a_i a_j + a_j a_i = 0$
Number operators	$a_i^\dagger a_i \lvert\mathbf{n}\rangle = n_i \lvert\mathbf{n}\rangle$ $(\sum_i a_i^\dagger a_i)\lvert\mathbf{n}\rangle = (\sum_i n_i)\lvert\mathbf{n}\rangle$
Vacuum state	$\lvert vac\rangle = \lvert 0_1, 0_2, \cdots, 0_m\rangle$ $\langle vac\vert vac\rangle = 1$ $a_i \lvert vac\rangle = 0$

Operators in second quantization

- In the Fock-space, we could define very simple operators like the number-operator
- We need representations of quantum mechanical operators, for example the kinetic-energy operator
- Procedure
  1. We know the mapping $|SD_i\rangle \rightarrow |ONV_i\rangle$
  2. We know the mapping $|SD_j\rangle \rightarrow |ONV_j\rangle$
  3. Obtain the second quantization representation, $\hat{f}$ of a given first-quantization operator f^c by requiring

$$\langle ONV_i|\hat{f}|ONV_j\rangle = \langle SD_i|f^c|SD_j\rangle \tag{14}$$

- It is only then we have obtained an alternative representation of quantum chemistry

One-electron operators

Examples

- kinetic energy operator, nuclear-electron attraction operator

First-quantization form

- Form : $f^c = \sum_{i=1,N} f^c(i)$, N : number of electrons
- Properties :
  1. Works on SD's with at least one electron
  2. Connects Slater-determinants differing in atmost one set of occupations

Implies form of second quantization operator

- $\hat{f} = \sum_{rs} f_{rs} a_r^\dagger a_s$ where f_{rs} pt are unknowns

$f_{rs} = ?$

- Setting $f_{rs} = \int d\mathbf{x}\phi_r(\mathbf{x})^\star f^c(\mathbf{x})\phi_s(\mathbf{x})$ gives the same matrix-elements in first- and second quantization
- Example : Diagonal elements
  - First quantization (from elementary QM)
    $\langle SD_i|f^c|SD_i\rangle = \sum_r n_r \int d\mathbf{x}\phi_r(\mathbf{x})^\star f^c(\mathbf{x})\phi_r(\mathbf{x})$
  - Second quantization :

$$\langle ONV_i|\sum_{rs} f_{rs}a_r^\dagger a_s|ONV_i\rangle =$$

$$\langle ONV_i|\sum_{r} f_{rr}a_r^\dagger a_r|ONV_i\rangle = \langle ONV_i|\sum_{r} f_{rr}n_r|ONV_i\rangle$$

$$= \sum_r n_r \int d\mathbf{x}\phi_r(\mathbf{x})^\star f^c(\mathbf{x})\phi_r(\mathbf{x}) \tag{15}$$

- The phase-factor $\Gamma(\mathbf{n})$ is essential for agreement

Two-electron operators

Examples

- Electron-electron repulsion, two-electron spin-orbit

First-quantization form

- Form : $g^c = \frac{1}{2} \sum'_{i,j=1,N} g^c(i,j)$,
- Properties :
  1. Works on SD's with at least two electron
  2. Connects Slater-determinants differing in atmost two sets of occupations

Implies form of second quantization operator

- $\hat{g} = \frac{1}{2} \sum_{ijkl} g_{ijkl} a_i^\dagger a_k^\dagger a_l a_j$ where g_{ijkl} pt are unknowns

$g_{ijkl} = ?$

- Equivalence is obtained between first and second quantization by setting

$$g_{ijkl} = \int d\mathbf{x} d\mathbf{x}' \phi_i^\star(\mathbf{x}) \phi_k^\star(\mathbf{x}') g^c(\mathbf{x},\mathbf{x}') \phi_j(\mathbf{x}) \phi_l(\mathbf{x}') \tag{16}$$

- Shown by going through the various cases
- The phase-factor $\Gamma(\mathbf{n})$ is essential for obtaining agreement

Conclusion

We have now

- Obtained a new way of representing antisymmetric wave-functions
- Obtained a new way of representing operators

So that

- Expectation values are identical to the standard formulation

In other words

- We have obtained a new representation of quantum mechanics for electrons

Table 2: Operators in first and second quantization

First quantization	Second quantization
One-electron operator $\sum_i f(\mathbf{r_i}, \sigma_i)$	One-electron operator $\sum_{ij} h_{ij} a_i^\dagger a_j$
Two-electron operator $frac12 \sum_{i \neq j} g(\mathbf{r_i}, \sigma_i, \mathbf{r_j}, \sigma_j)$	Two-electron operator $frac12 \sum_{ijkl} g_{ijkl} a_i^\dagger a_k^\dagger a_l a_j$
Operators are independent of spin-orbital basis	Operators depend on spin-orbital basis
Operators depend in the number of electrons	Operators are independent of the number of electrons
Exact operators	Projected operators