October 30

Lecture #14

Second quantization
Normal order and expectation values
Wick's theorem

Chapters 3 and 4, pages 95-99 Lectures on Atomic Physics
Chapter 11, pages 241-246, Atomic many-body theory
I. Lindgren and J. Morrison

Second quantization: atomic electrons (fermions)

One-electron state |k>
Described by the wave function $\Psi_k(q_i)$

Vacuum state
(no electrons)

$$\langle 0|0\rangle = 1$$

$$|k\rangle = a_k^{\dagger}|0\rangle$$ Creation operator

$$\langle k| = \langle 0|a_k$$ Annihilation operator

$$a_k|0\rangle = 0:$$ "there are no electrons to annihilate in a vacuum"

$$\langle 0|a_k^{\dagger} = 0$$

Anticommutation relations

$$\{a_i^\dagger, a_j^\dagger\} = a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0$$
$$\{a_i, a_j\} = a_i a_j + a_j a_i = 0$$
$$\{a_i, a_j^\dagger\} = a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij}$$

Normal form (order) with respect to vacuum

$$a_k|0\rangle = 0$$
$$\langle 0|a_k^\dagger = 0$$

Creation operators | Annihilation operators

left ← $a_i^\dagger \; a_j^\dagger$ $\qquad$ $a_l \; a_k$ → right

Designation for normal order $\quad : a_i \; a_j \; a_k^\dagger \; a_l^\dagger :$

Normal form: example

$$a_k |0\rangle = 0$$
$$\langle 0| a_k^\dagger = 0$$

Why do we want to transform to normal order?
To calculate expectation values: expectation value of normal-ordered operators is zero.
Also, the permutations within the normal product only affect the phase.

$$a_j a_i a_k^\dagger a_l^\dagger = \delta_{ik}\delta_{jl} - \delta_{jk}\delta_{il}$$
$$- :a_l^\dagger a_j: \delta_{ik} + \delta_{jk} :a_l^\dagger a_i: + :a_k^\dagger a_j: \delta_{il} - \delta_{jl} :a_k^\dagger a_i: + :a_k^\dagger a_l^\dagger a_j a_i:$$

$$\langle 0| a_j a_i a_k^\dagger a_l^\dagger |0\rangle = \delta_{ik}\delta_{jl} - \langle 0| a_l^\dagger a_j |0\rangle \delta_{ik} - \delta_{jk}\delta_{il} + \delta_{jk} \langle 0| a_l^\dagger a_i |0\rangle$$
$$+ \langle 0| a_k^\dagger a_j |0\rangle \delta_{il} - \delta_{jl} \langle 0| a_k^\dagger a_i |0\rangle + \langle 0| a_k^\dagger a_l^\dagger a_j a_i |0\rangle$$
$$= \delta_{ik}\delta_{jl} - \delta_{jk}\delta_{il}$$

Contraction

The contraction of arbitrary creation or annihilation operators A and B designated by

$$\overbracket{A\,B}$$

is defined as the difference between the ordinary and the normal product of the operators A and B :

$$\overbracket{A\,B} = AB - :AB:$$

How to calculate a contraction?

$$\overbracket{A\,B} = AB - :AB:$$

$$\text{Already in normal form}\quad \left\{ \begin{array}{l} a_i^\dagger a_j^\dagger = :a_i^\dagger a_j^\dagger: \;\rightarrow\; \overbracket{a_i^\dagger a_j^\dagger} = 0 \\ a_i\, a_j = :a_i\, a_j: \;\rightarrow\; \overbracket{a_i\, a_j} = 0 \\ a_i^\dagger a_j = :a_i^\dagger a_j: \;\rightarrow\; \overbracket{a_i^\dagger a_j} = 0 \end{array} \right.$$

$$\overbracket{A\,B} = AB - :AB:$$

How to calculate a contraction?

$$\boxed{\overbracket{a_i\, a_j^\dagger} = ?}$$

$$a_i\, a_j^\dagger + a_j^\dagger a_i = \delta_{ij} \rightarrow a_i\, a_j^\dagger = \delta_{ij} - a_j^\dagger a_i \;\rightarrow\; a_i\, a_j^\dagger = \delta_{ij} - :a_j^\dagger a_i:$$

$$:a_j^\dagger a_i: = \delta_{ij} - a_i\, a_j^\dagger$$

$$:a_j^\dagger a_i: = -:a_i\, a_j^\dagger:$$

$$:a_i\, a_j^\dagger: = -:a_j^\dagger a_i: = -\delta_{ij} + a_i\, a_j^\dagger$$

$$\overbracket{a_i\, a_j^\dagger} = a_i\, a_j^\dagger - :a_i\, a_j^\dagger: = a_i\, a_j^\dagger - \left(-\delta_{ij} + a_i\, a_j^\dagger\right) = \delta_{ij}$$

$$\boxed{\overbracket{a_i\, a_j^\dagger} = \delta_{ij}}$$

Wick's theorem

If A is a product of creation or annihilation operators, then

$$A =: A: + :\overline{A}:$$

where $:A:$ is the normal form of A and $:\overline{A}:$ represents the sum of normal-ordered terms obtained by making all possible single, double, … contractions within A.

Application of Wick's theorem: an example

$$\boxed{A =: A: + :\overline{A}:}$$

Lets obtain this results by using Wick's theorem:

$$a_j a_i a_k^\dagger a_l^\dagger = \delta_{ik}\delta_{jl} - \delta_{jk}\delta_{il}$$
$$- :a_l^\dagger a_j: \delta_{ik} + \delta_{jk} :a_l^\dagger a_i: + :a_k^\dagger a_j: \delta_{il} - \delta_{jl} :a_k^\dagger a_i: + :a_k^\dagger a_l^\dagger a_j a_i:$$

A note on calculating contractions

The formulas we derived for the contractions of two operators are valid for consecutive operators.

$$a_i^\dagger a_j^\dagger = 0 \qquad a_i a_j = 0 \qquad a_i^\dagger a_j = 0 \qquad a_i a_j^\dagger = \delta_{ij}$$

For example, $: a_j a_i a_k^\dagger a_l^\dagger : = : a_j a_l^\dagger : \delta_{ik}$

In the operators are separated by one or more operator you must permute them until they are consecutive. It is very easy to do as the permutation inside the normal product will only affect the phase (+ for even permutations, - for odd permutations).

For example, $: a_j a_i a_k^\dagger a_l^\dagger : = - : a_j a_i a_l^\dagger a_k^\dagger : = - : a_j a_k^\dagger : \delta_{il}$ odd

$: a_j a_i a_k^\dagger a_l^\dagger : = : a_j a_l^\dagger a_i a_k^\dagger : = : a_i a_k^\dagger : \delta_{jl}$ even

Note: the intermediate step is usually skipped, just keep track on signs.

Application of Wick's theorem: an example

$$A = : A : + : A :$$

1 contraction 2 contractions

$$a_j a_i a_k^\dagger a_l^\dagger = : a_j a_i a_k^\dagger a_l^\dagger : + \sum : a_j a_i a_k^\dagger a_l^\dagger : + \sum : a_j a_i a_k^\dagger a_l^\dagger :$$

1 contraction: $: a_j a_i a_k^\dagger a_l^\dagger : = : a_j a_l^\dagger : \delta_{ik}$ $\qquad$ $: a_j a_i a_k^\dagger a_l^\dagger : = - : a_j a_k^\dagger : \delta_{il}$

$: a_j a_i a_k^\dagger a_l^\dagger : = - : a_i a_l^\dagger : \delta_{jk}$ $\qquad$ $: a_j a_i a_k^\dagger a_l^\dagger : = : a_i a_k^\dagger : \delta_{jl}$

2 contractions: $: a_j a_i a_k^\dagger a_l^\dagger : = \delta_{ik}\, \delta_{jl}$

$: a_j a_i a_k^\dagger a_l^\dagger : = - : a_j a_k^\dagger : \delta_{il} = -\delta_{il}\, \delta_{jk}$

$$a_j a_i a_k^\dagger a_l^\dagger = \delta_{ik}\delta_{jl} - \delta_{jk}\delta_{il}$$
$$+ : a_j a_l^\dagger : \delta_{ik} - \delta_{jk} : a_i a_l^\dagger : - : a_j a_k^\dagger : \delta_{il} + \delta_{jl} : a_i a_k^\dagger : + : a_j a_i\, a_k^\dagger a_l^\dagger :$$

Application of Wick's theorem: an example

$$A =: A : + : A :$$

The permutation within the normal product only affects the phase:
odd permutations introduce "-" sign.

$$a_j a_i a_k^\dagger a_l^\dagger = \delta_{ik}\delta_{jl} - \delta_{jk}\delta_{il}$$
$$+ : a_j a_l^\dagger : \delta_{ik} - \delta_{jk} : a_i a_l^\dagger : - : a_j a_k^\dagger : \delta_{il} + \delta_{jl} : a_i a_k^\dagger : + : a_j a_i \, a_k^\dagger a_l^\dagger : =$$
$$= \delta_{ik}\delta_{jl} - \delta_{jk}\delta_{il}$$
$$- : a_l^\dagger a_j : \delta_{ik} + \delta_{jk} : a_l^\dagger a_i : + : a_k^\dagger a_j : \delta_{il} - \delta_{jl} : a_k^\dagger a_i : + : a_k^\dagger a_l^\dagger a_j a_i :$$

SAME RESULT

$$a_j a_i a_k^\dagger a_l^\dagger = \delta_{ik}\delta_{jl} - \delta_{jk}\delta_{il}$$
$$- : a_l^\dagger a_j : \delta_{ik} + \delta_{jk} : a_l^\dagger a_i : + : a_k^\dagger a_j : \delta_{il} - \delta_{jl} : a_k^\dagger a_i : + : a_k^\dagger a_l^\dagger a_j a_i :$$

Expectation values: application of Wick's theorem:

$$A =: A : + : A :$$

1. All matrix elements (expectation values) will contain an even number of operators.
2. The expectation value of normal-ordered operators vanishes.
3. Therefore, the expectation value is equal to sum of the terms with maximum number of contractions (N/2 for the product of N operators).

In our example: $a_j a_i a_k^\dagger a_l^\dagger \quad N = 4$

Maximum number of contractions: 2

$$\langle 0 | a_j a_i a_k^\dagger a_l^\dagger | 0 \rangle = \langle 0 | : a_j a_i a_k^\dagger a_l^\dagger : | 0 \rangle + \langle 0 | : a_j a_i a_k^\dagger a_l^\dagger : | 0 \rangle = \delta_{ik}\delta_{jl} - \delta_{jk}\delta_{il}$$

Lets re-define our vacuum

Example: atom with single (valence) electron outside a closed core.

Na Z=11

core → $1s^2 2s^2 2p^6$ $3s$ ← valence electron

$$|0_C\rangle = a_a^\dagger a_b^\dagger \dots a_n^\dagger |0\rangle$$

$$a_v^\dagger |0_C\rangle$$

Creation operator for state v

Core wave function

Lets re-define our vacuum

$$|0_C\rangle = \underbrace{a_a^\dagger a_b^\dagger \dots a_n^\dagger}_{\text{filled subshells}} |0\rangle$$

Lets designate core and "above core" or excited state operators differently

↑ operators with a,b,c,d,… indices

↑ operators with m,n,r,s,… indices (v,w for valence electrons)

operators with i,j,k,l indicies: any states (either core or above core)

Normal form with respect to "new vacuum"

$a_m \left| 0_C \right\rangle = 0 \longrightarrow$ We can not annihilate excited state from the core: there is none. $\left\langle 0_C \right| a_m^\dagger = 0$

$a_a^\dagger \left| 0_C \right\rangle = 0 \longrightarrow$ We can not create one more core electron: it is entirely occupied and creating one more core electron will violate Pauli exclusion principle. $\left\langle 0_C \right| a_a = 0$

Normal order

$$\xleftarrow{\text{left}} \quad \underbrace{a_a\ a_b\ a_m^\dagger\ a_n^\dagger} \qquad \underbrace{a_a^\dagger\ a_b^\dagger\ a_m\ a_n} \quad \xrightarrow{\text{right}}$$

Order inside these groups does not matter

Normal form with respect to "new vacuum"

Normal order

$$\xleftarrow{\text{left}} \quad \underbrace{a_a\ a_b\ a_m^\dagger\ a_n^\dagger} \qquad \underbrace{a_a^\dagger\ a_b^\dagger\ a_m\ a_n} \quad \xrightarrow{\text{right}}$$

Order inside these groups does not matter

Wick's theorem is applicable in exactly the same way, only with the normal order defined above.

The expectation value of the normal-ordered operator product with respect to "new vacuum" $|0_C>$ also vanishes.