SECOND QUANTIZATION

INTRODUCES NO NEW PHYSICS!

IT IS JUST NEW AND VERY ELEGANT WAY OF TREATING MANY-PARTICLE SYSTEMS

AXIOM OF QUANTUM MECHANICS: ANTISYMMETRY PRINCIPLE

SATISFIED BY SLATER DETERMINANTS AND THEIR LINEAR COMBINATIONS

CAN WE SATISFY THE ANTISYMMETRY PRINCIPLE WITHOUT USING SLATER DETERMINANTS?

FORMALISM IN WHICH THE ANTISYMMETRY PROPERTY OF THE WAVE FUNCTION HAS BEEN TRANSFERRED ONTO THE ALGEBRAIC PROPERTIES OF CERTAIN OPERATORS

WHY SECOND QUANTIZATION?

$$\mathcal{H}|i\rangle = \hbar\omega_i|i\rangle \qquad \mathcal{H} = \mathcal{H}^+$$

„FIRST QUANTIZATION"

$$\sum_i |i\rangle\langle i| = \mathbb{1}$$

$$\mathcal{H} = \mathbb{1}\cdot\mathcal{H}\cdot\mathbb{1} = \sum_i\sum_j |i\rangle\langle i|\mathcal{H}|j\rangle\langle j| \quad , \langle i|j\rangle = \delta_{ij}$$

$$= \sum_i \hbar\omega_i |i\rangle\langle i|$$

$|i\rangle\langle j|$?

$$|i\rangle\langle j|l\rangle = |i\rangle\delta_{jl}$$

$$b_i^+ b_j|l\rangle = |i\rangle\delta_{jl}$$

STATE i IS CREATED

STATE j IS ANNIHILATED

$$\mathcal{H} = \sum_i \hbar\omega_i b_i^+ b_i$$

SECOND QUANTIZATION

$\left.\begin{array}{l}\text{CREATION}\\ \text{ANNIHILATION}\end{array}\right\}$ OF STATE!

$b_i^+ \; : \; \chi_i \, , \; i \equiv n l s m_l m_s$

SPIN-ORBITAL

CREATION OF ONE-PARTICLE STATE

ARBITRARY SLATER DETERMINANT: $|\chi_k, \dots \chi_l\rangle$

$$b_i^+ |\chi_k, \dots \chi_l\rangle = |\chi_i, \chi_k, \dots \chi_l\rangle$$

THE ORDER IN WHICH TWO CREATION OPERATORS ACT IS IMPORTANT!

$$b_i^+ b_j^+ |\chi_k, \dots \chi_l\rangle = b_i^+ |\chi_j, \chi_k, \dots \chi_l\rangle = |\chi_i, \chi_j, \chi_k, \dots \chi_l\rangle$$

+

$$b_j^+ b_i^+ |\chi_k, \dots \chi_l\rangle = |\chi_j, \chi_i, \chi_k, \dots \chi_l\rangle = -|\chi_i, \chi_j, \chi_k, \dots \chi_l\rangle$$

$$(b_i^+ b_j^+ + b_j^+ b_i^+) |\chi_k, \dots \chi_l\rangle = 0$$

OPERATOR RELATION:

$$b_i^+ b_j^+ + b_j^+ b_i^+ = 0 = \{b_i^+, b_j^+\}$$

ANTICOMMUTATOR

$$b_i^+ b_j^+ = - b_j^+ b_i^+$$

IF $i = j$ $\quad b_i^+ b_i^+ = - b_i^+ b_i^+ = 0$ PAULI EXCLUSION PRINCIPLE!

EXAMPLE:

$$b_1^+ b_1^+ |\chi_2 \chi_3\rangle = b_1^+ |\chi_1 \chi_2 \chi_3\rangle = |\underbrace{\chi_1 \chi_1} \chi_2 \chi_3\rangle = 0$$

IN GENERAL

$$b_i^+ |\chi_k, \dots \chi_l\rangle = 0 \quad \text{IF} \quad i \in \{k, \dots l\}$$

b_i ANNIHILATION, ADJOINT OF b_i^+ : $(b_i^+)^+ = b_i$

$$b_i |\chi_i \chi_k, \dots \chi_l\rangle = |\chi_k, \dots \chi_l\rangle$$

ACTS ONLY IF SPIN ORBITAL IS IMMEDIATELY TO THE LEFT OTHERWISE:

EXAMPLE:

$$b_i|x_k x_i x_l\rangle = -b_i|x_k x_i x_l\rangle = b_i|x_i x_k x_l\rangle = |x_k x_l\rangle$$

WHY $b_i = (b_i^+)^+$?

$$|\mathcal{K}\rangle = |x_i x_j\rangle = b_i^+|x_j\rangle$$

$$\langle\mathcal{K}| = \langle x_j|(b_i^+)^+ = \langle x_j|b_i \quad / |\mathcal{K}\rangle$$

ADJOINT

$$1 = \langle\mathcal{K}|\mathcal{K}\rangle = \langle x_j|b_i|\mathcal{K}\rangle \ ?$$

$$\langle\mathcal{K}|\mathcal{K}\rangle = 1 = \langle x_j|x_j\rangle \Rightarrow$$

FORMALISM IS CONSISTENT IF

$$b_i|\mathcal{K}\rangle \equiv b_i|x_i x_j\rangle = |x_j\rangle$$

b_i ANNIHILATES STATE i IN „KET" (ACTS TO THE RIGHT)

$$\langle x_i x_j| = \langle x_j|b_i$$

CREATES STATE i IN „BRA" (ACTS TO THE LEFT)

ADJOINT

$$\langle x_i x_j|b_i^+ = \langle\mathcal{K}|b_i^+ = \langle x_j|$$

b_i^+ ACTING ON THE LEFT ANNIHILATES STATE i

$$\{b_i^+, b_j^+\} = b_i^+ b_j^+ + b_j^+ b_i^+ = 0$$

ADJOINT $(AB)^+ = B^+A^+$

$$\{b_j, b_i\} = b_j b_i + b_i b_j = 0$$

$b_i b_j = -b_j b_i$ IT IS POSSIBLE TO INTERCHANGE THEM

IF $i=j$ $\quad b_i b_i = -b_i b_i = 0$ WE CANNOT DESTROY A STATE TWICE

$$b_i|x_k, \ldots x_l\rangle = 0 \quad \text{IF} \quad i \notin \{k, \ldots l\}$$

RELATION BETWEEN CREATION AND ANNIHILATION OPERATORS

ARBITRARY DETERMINANT: $|\chi_k, \dots \chi_l\rangle$ WITH χ_i NOT OCCUPIED

$$(b_i b_i^+ + \overset{0}{b_i^+ b_i})|\chi_k, \dots \chi_l\rangle = b_i b_i^+ |\chi_k, \dots \chi_l\rangle =$$

$i \notin \{k, \dots l\}$

$$= b_i |\chi_i \chi_k, \dots \chi_l\rangle =$$

$$= |\chi_k \dots \chi_l\rangle$$

$i \in \{k, \dots l\}$: χ_i IS OCCUPIED

$$(\underset{0}{b_i b_i^+} + b_i^+ b_i)|\chi_k, \dots \chi_i, \dots \chi_l\rangle = b_i^+ b_i |\chi_k, \dots \chi_i, \dots \chi_l\rangle =$$

$$(-1)^n b_i^+ b_i |\chi_i, \dots \chi_k, \dots \chi_l\rangle =$$

$$(-1)^n b_i^+ | \dots \chi_k, \dots \chi_l\rangle =$$

$$(-1)^n |\chi_i, \dots \chi_k, \dots \chi_l\rangle =$$

$$= |\chi_k, \dots \chi_i, \dots \chi_l\rangle$$

OPERATOR RELATION

$$b_i b_i^+ + b_i^+ b_i = 1 = \{b_i, b_i^+\}$$

$$(b_j^+ b_i + b_i b_j^+)|\chi_k, \dots \chi_l\rangle \qquad i \neq j$$

$j \notin \{k, \dots l\} \wedge i \in \{k, \dots l\}$ OTHERWISE $= 0$

BUT DUE TO THE ANTISYMMETRY OF DETERMINANT:

$$(b_i b_j^+ + b_j^+ b_i)|\chi_k, \dots \chi_i, \dots \chi_l\rangle = -(b_i b_j^+ + b_j^+ b_i)|\chi_i, \dots \chi_k, \dots \chi_l\rangle =$$

$$= -b_i |\chi_j, \chi_i, \dots \chi_k, \dots \chi_l\rangle - b_j^+ | \dots \chi_k, \dots \chi_l\rangle =$$

$$= b_i |\chi_i, \chi_j, \dots \chi_k, \dots \chi_l\rangle - |\chi_j, \dots \chi_k, \dots \chi_l\rangle =$$

$$= |\chi_j, \dots \chi_k, \dots \chi_l\rangle - |\chi_j, \dots \chi_k, \dots \chi_l\rangle = 0$$

$$b_i b_j^+ + b_j^+ b_i = 0 = \{b_i, b_j^+\}, \quad i \neq j$$

$\{b_i, b_j^+\} = \delta_{ij}$ ANTICOMMUTATOR

$b_i b_j^+ = -b_j^+ b_i \quad i \neq j$

$b_i b_i^+ = 1 - b_i^+ b_i$ (FOR THE SAME SPIN ORBITAL)

ALL THE PROPERTIES OF SLATER DETERMINANTS ARE REPRESENTED BY THE ANTICOMMUTATION RELATIONS OF CREATION AND ANNIHILATION OP.

$$\boxed{\begin{aligned} \{b_i^+, b_j^+\} &= 0 \\ \{b_i, b_j\} &= 0 \\ \{b_i, b_j^+\} &= \delta_{ij} \end{aligned}}$$

VACUUM STATE = STATE OF A SYSTEM THAT CONTAINS NO PARTICLES

$| \ \rangle$

IT IS NORMALIZED $\langle \ | \ \rangle = 1$

PROPERTIES:

$$b_i | \ \rangle = 0$$

$$\langle \ | b_i^+ = 0$$

APPLYING A SEQUENCE OF b^+ => ANY STATE OF THE SYSTEM

$$|\chi_i\rangle = b_i^+ | \ \rangle$$

$$b_i^+ b_k^+ \dots b_l^+ | \ \rangle = |\chi_i \chi_k, \dots \chi_l\rangle$$

SECOND-QUANTIZED REPRESENTATION OF A SLATER DETERMINANT

EXAMPLE: EVALUATE THE OVERLAP BETWEEN THE TWO DETERMINANTS

$$|\mathcal{K}\rangle = |\chi_i \chi_j\rangle = b_i^+ b_j^+ |\ \rangle$$
$$|\mathcal{L}\rangle = |\chi_k \chi_l\rangle = b_k^+ b_l^+ |\ \rangle$$

STANDARD WAY:

$$\langle \mathcal{K}|\mathcal{L}\rangle = \langle \chi_i \chi_j | \chi_k \chi_l \rangle =$$

$$\frac{1}{\sqrt{2}} \begin{vmatrix} \chi_i(1) & \chi_j(1) \\ \chi_i(2) & \chi_j(2) \end{vmatrix} \qquad \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_k(1) & \chi_l(1) \\ \chi_k(2) & \chi_l(2) \end{vmatrix}$$

$$= \frac{1}{2} \langle \chi_i(1)\chi_j(2) - \chi_j(1)\chi_i(2) | \chi_k(1)\chi_l(2) - \chi_l(1)\chi_k(2) \rangle =$$

$$= \frac{1}{2} \{ \langle \chi_i(1)\chi_j(2) | \chi_k(1)\chi_l(2) \rangle \qquad \delta(ik)\,\delta(jl)$$
$$- \langle \chi_i(1)\chi_j(2) | \chi_l(1)\chi_k(2) \rangle \qquad \delta(il)\,\delta(jk)$$
$$- \langle \chi_j(1)\chi_i(2) | \chi_k(1)\chi_l(2) \rangle \qquad \delta(jk)\,\delta(il)$$
$$+ \langle \chi_j(1)\chi_i(2) | \chi_l(1)\chi_k(2) \rangle \} \qquad \delta(jl)\,\delta(ik)$$

$$= \delta(ik)\delta(jl) - \delta(il)\delta(jk)$$

SECOND QUANTIZATION:

$$|\mathcal{K}\rangle = |\chi_i \chi_j\rangle = b_i^+ b_j^+ |\ \rangle \qquad \langle \mathcal{K}| = \langle\ |(b_i^+ b_j^+)^+ \equiv$$
$$|\mathcal{L}\rangle = |\chi_k \chi_l\rangle = b_k^+ b_l^+ |\ \rangle \qquad \langle\ | b_j b_i$$

$$\langle \mathcal{K}|\mathcal{L}\rangle = \langle\ | b_j b_i b_k^+ b_l^+ | 0 \rangle$$

HOW TO EVALUATE SUCH INTEGRAL?

GENERAL STRATEGY: USING THE ANTICOMMUTATION RELATIONS MOVE THE ANNIHILATION OPERATORS TO THE RIGHT UNTIL THEY OPERATE DIRECTLY ON THE VACUUM STATE

$$\langle \, | b_j b_i b_k^+ b_l^+ | \, \rangle =$$

$b_i b_k^+ = \delta_{ik} - b_k^+ b_i$

$$= \langle \, | b_j (\delta_{ik} - b_k^+ b_i) b_l^+ | \, \rangle =$$

$$= \langle \, | b_j b_k^+ b_i b_l^+ | \, \rangle + \delta_{ik} \langle \, | b_j b_l^+ | \, \rangle =$$

$b_i b_l^+ = \delta_{il} - b_l^+ b_i$ $\qquad$ $b_j b_l^+ = \delta_{jl} - b_l^+ b_j$

$$= -\delta_{il} \langle \, | b_j b_k^+ | \, \rangle + \langle \, | b_j \cancel{b_k^+ b_l^+} b_i | \, \rangle + \delta_{ik}\delta_{jl} - \delta_{ik} \langle \, | \cancel{b_l^+ b_j} | \, \rangle$$

$\delta_{jk} - b_k^+ b_j$

$$= -\delta_{il}\delta_{jk} + \delta_{il} \langle \, | \cancel{b_k^+ b_j} | \, \rangle + \delta_{ik}\delta_{jl}$$

$$= \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}$$

(MANIPULATIONS WITHOUT ANY KNOWLEDGE OF THE PROPERTIES OF DETERMINANTS

ONLY ALGEBRAIC PROPERTIES OF b AND b^+ ARE USED

SECOND-QUANTIZED OPERATORS AND THEIR MATRIX ELEMENTS

$$H = \underbrace{\sum_i h(i)}_{O_1} + \underbrace{\frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}}_{O_2}$$

$$O_1 = \sum_{ij} \langle i | h | j \rangle b_i^+ b_j$$

$$O_2 = \frac{1}{2} \sum_{ijkl} \langle ij | kl \rangle b_i^+ b_j^+ b_l b_k$$

$\qquad \langle ij | kl \rangle = \langle ij | \frac{1}{r_{\alpha\beta}} | kl \rangle$

THE DEFINITION IS INDEPENDENT OF THE NUMBER OF PARTICLES

THE SUMS RUN OVER THE SET OF SPIN ORBITALS

ILLUSTRATION OF EQUIVALENCE OF SECOND QUANTIZATION WITH THE PROCEDURE BASED ON SLATER DETERMINANTS

$$|\Psi_0\rangle = |\chi_1, \dots \chi_a, \chi_b, \dots \chi_N\rangle$$

$$\langle\Psi_0|O_1|\Psi_0\rangle = \sum_{ij} \langle i|h|j\rangle \langle\Psi_0| b_i^+ b_j |\Psi_0\rangle$$

$i=a,\ j=b$

$i,j \in \{1, \dots a, b, \dots N\}$

a, b - OCCUPIED

$$= \sum_{ab} \langle a|h|b\rangle \langle\Psi_0| b_a^+ b_b |\Psi_0\rangle$$

$$b_a^+ b_b = \delta_{ab} - b_b b_a^+$$

$$= \sum_{ab} \langle a|h|b\rangle \delta_{ab} \langle\Psi_0|\Psi_0\rangle - \sum_{ab} \langle a|h|b\rangle \cancel{\langle\Psi_0| b_b b_a^+ |\Psi_0\rangle}$$

$$\boxed{= \sum_a \langle a|h|a\rangle}$$ (SEE I.19)

$$\langle\Psi_0|O_2|\Psi_0\rangle = \frac{1}{2} \sum_{abcd} \langle ab|cd\rangle \langle\Psi_0| b_a^+ \underbrace{b_b^+ b_d}_{\delta_{bd} - b_d b_b^+} b_c |\Psi_0\rangle =$$

$$= \frac{1}{2} \sum_{abcd} \langle ab|cd\rangle \left\{ \langle\Psi_0| \delta_{bd} \underbrace{b_a^+ b_c}_{\delta_{ac} - b_c b_a^+} |\Psi_0\rangle - \langle\Psi_0| b_a^+ b_d \underbrace{b_b^+ b_c}_{\delta_{bc} - b_c b_b^+} |\Psi_0\rangle \right\}$$

$$= \frac{1}{2} \sum_{abcd} \langle ab|cd\rangle \left\{ \delta_{bd}\delta_{ac} \overset{1}{\langle\Psi_0|\Psi_0\rangle} - \delta_{bd} \cancel{\langle\Psi_0| b_c b_a^+ |\Psi_0\rangle} - \right.$$

$$\left. - \delta_{bc} \langle\Psi_0| b_a^+ b_d |\Psi_0\rangle + \cancel{\langle\Psi_0| b_a^+ b_d b_c b_b^+ |\Psi_0\rangle} \right\} =$$

$$= \frac{1}{2} \sum_{abcd} \langle ab|cd\rangle \left\{ \delta_{bd}\delta_{ac} - \delta_{bc}\delta_{ad} \overset{1}{\langle\Psi_0|\Psi_0\rangle} + \cancel{\langle\Psi_0| b_d b_a^+ |\Psi_0\rangle} \delta_{bc} \right\}$$

$$= \frac{1}{2} \sum_{abcd} \langle ab|cd\rangle \left\{ \delta_{bd}\delta_{ac} - \delta_{bc}\delta_{ad} \right\} =$$

$$\boxed{= \frac{1}{2} \sum_{ab} [\underbrace{\langle ab|ab\rangle}_{\text{DIRECT}} - \underbrace{\langle ab|ba\rangle}_{\text{EXCHANGE}}]}$$ (SEE I.20)

THERE IS NO NEW PHYSICS!