Second quantization

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Introduction

- In the first quantization formulation of quantum mechanics, observables are represented by operators and states by functions.
- In the second quantization formulation, the wavefunctions are also expressed in terms of operators — the creation and annihilation operators working on the vacuum state.
- Operators (*e.g.*, the Hamiltonian) and wavefunctions are described by a single set of elementary creation and annihilation operators.
- The antisymmetry of the electronic wavefunction follows from the algebra of the creation and annihilation operators.

The Fock space

- Let $\{\phi_P(\mathbf{x})\}$ be a basis of M orthonormal spin orbitals, where $\mathbf{x}$ represents the electron's spatial ($\mathbf{r}$) and spin ($m_\mathbf{s}$) coordinates.
- A Slater determinant is a normalized, antisymmetrized product of spin orbitals,

$$|\phi_{P_1}\phi_{P_2}\cdots\phi_{P_N}| = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_{P_1}(\mathbf{x}_1) & \phi_{P_2}(\mathbf{x}_1) & \cdots & \phi_{P_N}(\mathbf{x}_1) \\ \phi_{P_1}(\mathbf{x}_2) & \phi_{P_2}(\mathbf{x}_2) & \cdots & \phi_{P_N}(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{P_1}(\mathbf{x}_N) & \phi_{P_2}(\mathbf{x}_N) & \cdots & \phi_{P_N}(\mathbf{x}_N) \end{vmatrix}$$

- In Fock space (a linear vector space), a determinant is represented by an *occupation-number (ON) vector* $|\mathbf{k}\rangle$,

$$|\mathbf{k}\rangle = |k_1, k_2, \ldots, k_M\rangle, \quad k_P = \begin{cases} 1 & \phi_P(\mathbf{x}) \text{ occupied} \\ 0 & \phi_P(\mathbf{x}) \text{ unoccupied} \end{cases}$$

The inner product

- Inner product between two ON vectors $|\mathbf{k}\rangle$ and $|\mathbf{m}\rangle$:

$$\langle\mathbf{k}|\mathbf{m}\rangle = \delta_{\mathbf{k},\mathbf{m}} = \prod_{P=1}^{M} \delta_{k_P m_P}$$

- Applies also to the product between states with different electron numbers.
- Resolution of the identity: $1 = \sum_\mathbf{k} |\mathbf{k}\rangle\langle\mathbf{k}|$
- For two general vectors in Fock space:

$$|\mathbf{c}\rangle = \sum_\mathbf{k} c_\mathbf{k}|\mathbf{k}\rangle, \quad |\mathbf{d}\rangle = \sum_\mathbf{k} d_\mathbf{k}|\mathbf{k}\rangle, \quad \langle\mathbf{c}|\mathbf{d}\rangle = \sum_\mathbf{k} c_\mathbf{k}^* d_\mathbf{k}$$

The 2^M-dimensional Fock space

- The Fock space $F(M)$ may be decomposed as a direct sum of subspaces $F(M,N)$,

$$F(M) = F(M,0) \oplus F(M,1) \oplus \cdots \oplus F(M,M)$$

- $F(M,N)$ contains all $\binom{M}{N}$ vectors for which the sum of the occupation numbers is N.
- The subspace $F(M,0)$ is the true vacuum state,

$$F(M,0) \equiv |\text{vac}\rangle = |0_1, 0_2, \ldots, 0_M\rangle, \quad \langle\text{vac}|\text{vac}\rangle = 1$$

Creation operators

- The M elementary *creation operators* are defined by

$$a_P^\dagger |k_1, k_2, \ldots, 0_P, \ldots, k_M\rangle = \Gamma_p^{\mathbf{k}} |k_1, k_2, \ldots, 1_P, \ldots, k_M\rangle$$
$$a_P^\dagger |k_1, k_2, \ldots, 1_P, \ldots, k_M\rangle = 0$$

with the phase factor $\Gamma_p^{\mathbf{k}} = \prod_{Q=1}^{P-1} (-1)^{k_Q}$

- Anticommutation relations take care of the phase factor.
- An ON vector can be expressed as a string of creation operators (in canonical order) working on the vacuum,

$$|\mathbf{k}\rangle = \left[\prod_{P=1}^{M} (a_P^\dagger)^{k_P} \right] |\text{vac}\rangle$$

Annihilation operators

- The M elementary *annihilation operators* are defined by

$$a_P|k_1, k_2, \ldots, 1_P, \ldots, k_M\rangle = \Gamma_p^{\mathbf{k}}|k_1, k_2, \ldots, 0_P, \ldots, k_M\rangle$$
$$a_P|k_1, k_2, \ldots, 0_P, \ldots, k_M\rangle = 0$$
$$a_P|\text{vac}\rangle = 0$$

  with the same phase factor as before.

- Again, anticommutation relations take care of the phase factor.
- $a_P^\dagger$ is the Hermitian adjoint to a_P. These operators are distinct operators and are not self-adjoint (Hermitian).

Anticommutation relations

- The *anticommutation relations* constitute the fundamental properties of the creation and annihilation operators:

$$[a_P, a_Q]_+ = a_P a_Q + a_Q a_P = 0$$
$$[a_P^\dagger, a_Q^\dagger]_+ = a_P^\dagger a_Q^\dagger + a_Q^\dagger a_P^\dagger = 0$$
$$[a_P^\dagger, a_Q]_+ = a_P^\dagger a_Q + a_Q a_P^\dagger = \delta_{PQ}$$

- All other algebraic properties of the second quantization formalism follow from these simple equations.
- The anticommutation relations follow from the definitions of a_P and $a_P^\dagger$ given on the previous slides.

Occupation-number operators

- The *occupation-number (ON) operator* is defined as

$$\hat{N}_P = a_P^\dagger a_P$$
$$\hat{N}_P|\mathbf{k}\rangle = a_P^\dagger a_P|\mathbf{k}\rangle = \delta_{k_p 1}|\mathbf{k}\rangle = k_P|\mathbf{k}\rangle$$

- ON operators are Hermitian ($\hat{N}_P^\dagger = \hat{N}_P$) and commute among themselves, $[\hat{N}_P, \hat{N}_Q] = 0$.
- The ON vectors are simultaneous eigenvectors of the commuting set of Hermitian operators $\hat{N}_P$.
- The ON operators are idempotent projection operators,

$$\hat{N}_P^2 = a_P^\dagger a_P a_P^\dagger a_P = a_P^\dagger (1 - a_P^\dagger a_P) a_P = a_P^\dagger a_P = \hat{N}_P$$

The number operator

- The Hermitian *number operator* $\hat{N}$ is obtained by adding together all ON operators,

$$\hat{N} = \sum_{P=1}^{M} \hat{N}_P = \sum_{P=1}^{M} a_P^\dagger a_P, \qquad \hat{N}|\mathbf{k}\rangle = \sum_{P=1}^{M} k_P|\mathbf{k}\rangle = N|\mathbf{k}\rangle$$

- Let $\hat{X}$ be a string with creation and annihilation operators with more creation than annihilation operators (the excess being N^X, which can be negative). Then,

$$[\hat{N}, \hat{X}] = N^X \hat{X}$$

- $\hat{N}$ commutes with a number-conserving string for which $N^X = 0$.

Excitation operators

- The simplest number-conserving operators are the elementary *excitation operators*

$$\hat{X}_Q^P = a_P^\dagger a_Q$$

- $\hat{X}_Q^P$ applied to $|\mathbf{k}\rangle$:

$$\begin{aligned} P < Q \qquad & \hat{X}_Q^P|\mathbf{k}\rangle = \delta_{P0}\delta_{Q1}\Gamma_P^{\mathbf{k}}\Gamma_Q^{\mathbf{k}}|\ldots,1_P,\ldots,0_Q,\ldots\rangle \\ P > Q \qquad & \hat{X}_Q^P|\mathbf{k}\rangle = -\delta_{P0}\delta_{Q1}\Gamma_P^{\mathbf{k}}\Gamma_Q^{\mathbf{k}}|\ldots,0_Q,\ldots,1_P,\ldots\rangle \\ P = Q \qquad & \hat{X}_Q^P|\mathbf{k}\rangle = k_P|\mathbf{k}\rangle \end{aligned}$$

Wavefunctions represented by operators

- Let $\{\phi_P(\mathbf{x})\}$ be a basis of M orthonormal spin orbitals.
- An arbitrary wavefunction (within the space spanned by all Slater determinants that can be formed using these M spin orbitals) can be written as

$$|\mathbf{c}\rangle = \sum_{\mathbf{k}} c_{\mathbf{k}}|\mathbf{k}\rangle = \sum_{\mathbf{k}} c_{\mathbf{k}} \left[\prod_{P=1}^{M} (a_P^\dagger)^{k_P}\right] |\text{vac}\rangle = \sum_{\mathbf{k}} c_{\mathbf{k}}\hat{X}_{\mathbf{k}}|\text{vac}\rangle$$

- An excitation operator can be applied to the above wavefunction to yield another function,

$$\hat{X}_Q^P|\mathbf{c}\rangle = |\mathbf{c}'\rangle$$

One-electron operators

- In first quantization, *one-electron operators* are written as

$$f^c = \sum_{i=1}^{N} f^c(\mathbf{x}_i)$$

- The second-quantization analogue has the structure

$$\hat{f} = \sum_{PQ} f_{PQ} a_P^\dagger a_Q, \qquad f_{PQ} = \int \phi_P^*(\mathbf{x}) f^c(\mathbf{x}) \phi_Q(\mathbf{x}) \mathrm{d}\mathbf{x}$$

- The order of the creation and annihilation operators ensures that the one-electron operator $\hat{f}$ produces zero when it works on the vacuum state.

One-electron operators: Slater–Condon rules

$$\langle \mathbf{k}|\hat{f}|\mathbf{k}\rangle = \sum_P f_{PP} \langle \mathbf{k}|a_P^\dagger a_P|\mathbf{k}\rangle = \sum_P k_P f_{PP} \equiv \sum_I^{\text{occupied}} f_{II}$$

$|\mathbf{k}_1\rangle$ and $|\mathbf{k}_2\rangle$ differ in one pair of occupation numbers:

$|\mathbf{k}_1\rangle = |k_1, k_2, \ldots, 0_I, \ldots, 1_J, \ldots, k_M\rangle$

$|\mathbf{k}_2\rangle = |k_1, k_2, \ldots, 1_I, \ldots, 0_J, \ldots, k_M\rangle$

$$\langle \mathbf{k}_2|\hat{f}|\mathbf{k}_1\rangle = \Gamma_I^{\mathbf{k}_2} \Gamma_J^{\mathbf{k}_1} f_{IJ}$$

$|\mathbf{k}_1\rangle$ and $|\mathbf{k}_2\rangle$ differ in more than one pair of occupation numbers:

$$\langle \mathbf{k}_2|\hat{f}|\mathbf{k}_1\rangle = 0$$

Two-electron operators

- In first quantization, *one-electron operators* are written as

$$g^c = \tfrac{1}{2} \sum_{i \neq j}^{N} g^c(\mathbf{x}_i, \mathbf{x}_j)$$

- The second-quantization analogue has the structure

$$\hat{g} = \tfrac{1}{2} \sum_{PQRS} g_{PQRS} a_P^\dagger a_R^\dagger a_S a_Q$$

- The two-electron integral is

$$g_{PQRS} = \int \int \phi_P^*(\mathbf{x}_1) \phi_R^*(\mathbf{x}_2) g^c(\mathbf{x}_1, \mathbf{x}_2) \phi_Q(\mathbf{x}_1) \phi_S(\mathbf{x}_2) \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2$$

The molecular electronic Hamiltonian

$$\hat{H} = h_{\text{nuc}} + \sum_{PQ} h_{PQ} a_P^\dagger a_Q + \tfrac{1}{2} \sum_{PQRS} g_{PQRS} a_P^\dagger a_R^\dagger a_S a_Q$$

with

$$h_{\text{nuc}} = \tfrac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}}$$

$$h_{PQ} = \int \phi_P^*(\mathbf{x}) \left(-\tfrac{1}{2} \Delta - \sum_\alpha \frac{Z_\alpha}{r_\alpha} \right) \phi_Q(\mathbf{x}) \mathrm{d}\mathbf{x}$$

$$g_{PQRS} = \int \int \phi_P^*(\mathbf{x}_1) \phi_R^*(\mathbf{x}_2) \frac{1}{r_{12}} \phi_Q(\mathbf{x}_1) \phi_S(\mathbf{x}_2) \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2$$

First- and second-quantization operators compared

First quantization	Second quantization
→ one-electron operator: $\sum_i f^c(\mathbf{x}_i)$	→ one-electron operator: $\sum_{PQ} f_{PQ} a_P^\dagger a_Q$
→ two-electron operator: $\frac{1}{2}\sum_{i\neq j} g^c(\mathbf{x}_i, \mathbf{x}_j)$	→ two-electron operator: $\frac{1}{2}\sum_{PQRS} g_{PQRS} a_P^\dagger a_R^\dagger a_S a_Q$
→ operator independent of spin-orbital basis	→ operator depends on spin-orbital basis
→ operator depends on number of electrons	→ operator independent of number of electrons
→ exact operator	→ projected operator

Matrix elements in 2nd quantization

- Let

$$|\mathbf{c}\rangle = \sum_{\mathbf{k}} c_{\mathbf{k}} |\mathbf{k}\rangle = \sum_{\mathbf{k}} c_{\mathbf{k}} \hat{X}_{\mathbf{k}} |\text{vac}\rangle$$
$$|\mathbf{d}\rangle = \sum_{\mathbf{k}} d_{\mathbf{k}} |\mathbf{k}\rangle = \sum_{\mathbf{k}} d_{\mathbf{k}} \hat{X}_{\mathbf{k}} |\text{vac}\rangle$$

- Then,

$$\langle \mathbf{c}|\hat{O}|\mathbf{d}\rangle = \sum_{\mathbf{k}}\sum_{\mathbf{k}'} c_{\mathbf{k}}^* d_{\mathbf{k}'} \langle \text{vac}|\hat{X}_{\mathbf{k}}^\dagger \hat{O} \hat{X}_{\mathbf{k}'}|\text{vac}\rangle$$

- Matrix elements become linear combinations of *vacuum expectation values*. Note that $\hat{X}_{\mathbf{k}}$ and $\hat{O}$ consist of strings of the same elementary creation and annihilation operators.

Products of operators in 2nd quantization

- Recall: The (finite) matrix representation $\mathbf{P}$ of the operator product $P^c(\mathbf{x}) = A^c(\mathbf{x})B^c(\mathbf{x})$ is *not* equal to the product of the matrices $\mathbf{A}$ and $\mathbf{B}$,

$$\mathbf{P} \neq \mathbf{AB}$$

- Similarly, the product of the operators $\hat{A}$ and $\hat{B}$ in second quantization requires special attention,

$$\begin{aligned} A^c &= \sum_i A^c(\mathbf{x}_i), & \hat{A} &= \sum_{PQ} A_{PQ} a_P^\dagger a_Q \\ B^c &= \sum_i B^c(\mathbf{x}_i), & \hat{B} &= \sum_{PQ} A_{PQ} a_P^\dagger a_Q \\ P^c &= A^c B^c, & \hat{P} &= ? \end{aligned}$$

Products in 2nd quantization (continued)

$$\begin{aligned} P^c &= A^c B^c = O^c + T^c = \sum_i A^c(\mathbf{x}_i) B^c(\mathbf{x}_i) \\ &+ \tfrac{1}{2} \sum_{i \neq j} [A^c(\mathbf{x}_i) B^c(\mathbf{x}_j) + A^c(\mathbf{x}_j) B^c(\mathbf{x}_i)] \end{aligned}$$

$$\hat{P} = \hat{O} + \hat{T} = \sum_{PQ} O_{PQ} a_P^\dagger a_Q + \tfrac{1}{2} \sum_{PQRS} T_{PQRS} a_P^\dagger a_R^\dagger a_S a_Q$$

$$O_{PQ} = \int \phi_P^*(\mathbf{x}) A^c(\mathbf{x}) B^c(\mathbf{x}) \phi_Q(\mathbf{x}) \mathrm{d}\mathbf{x}$$

$$T_{PQRS} = A_{PQ} B_{RS} + A_{RS} B_{PQ}$$

Using the anticommutation relations

$$
\begin{aligned}
\hat{T} &= \tfrac{1}{2} \sum_{PQRS} (A_{PQ}B_{RS} + A_{RS}B_{PQ}) a_P^\dagger a_R^\dagger a_S a_Q \\
&= \sum_{PQRS} A_{PQ}B_{RS} a_P^\dagger a_R^\dagger a_S a_Q \\
&= \sum_{PQRS} A_{PQ}B_{RS} (a_P^\dagger a_Q a_R^\dagger a_S - \delta_{RQ} a_P^\dagger a_S) \\
&= \left(\sum_{PQ} A_{PQ} a_P^\dagger a_Q \right) \left(\sum_{RS} B_{RS} a_R^\dagger a_S \right) - \sum_{PS} \left(\sum_{R} A_{PR}B_{RS} \right) a_P^\dagger a_S \\
&= \hat{A}\hat{B} - \sum_{PQ} \left(\sum_{R} A_{PR}B_{RQ} \right) a_P^\dagger a_Q
\end{aligned}
$$

Operators in 2nd quantization are projections

- The final result for the representation of P^c in second quantization is

$$\hat{P} = \hat{A}\hat{B} + \sum_{PQ} \left(O_{PQ} - \sum_{R} A_{PR}B_{RQ} \right) a_P^\dagger a_Q$$

- In a complete basis: $\sum_{R=1}^{\infty} A_{PR}B_{RQ} = O_{PQ}$.
- The second quantization operators are projections of the exact operators onto a basis of spin orbitals. For an incomplete basis, the second quantization representation depends on when the projection is made.

Heisenberg uncertainty principle

- Position and momentum do not commute: $[x^c, p_x^c] = iN$. Note that x^c and p_x^c contain sums over N electrons, and only the observables of the same electron do not commute.
- What happens with $[\hat{x}, \hat{p}_x]$ in second quantization?
- It follows that

$$[\hat{x}, \hat{p}_x] = \sum_{PQ} \left(\sum_{R} \{ x_{PR}(p_x)_{RQ} - (p_x)_{PR} x_{RQ} \} \right) a_P^\dagger a_Q$$

- In a *complete basis*, we find: $[\hat{x}, \hat{p}_x] = i\hat{N}$.

Expectation values

- We are interested in the expectation value of a general one- and two-electron Hermitian operator $\hat{\Omega}$ with respect to a normalized reference state $|0\rangle$.

$$\hat{\Omega} = \Omega_0 + \sum_{PQ} \Omega_{PQ} a_P^\dagger a_Q + \tfrac{1}{2} \sum_{PQRS} \Omega_{PQRS} a_P^\dagger a_R^\dagger a_S a_Q$$

$$|0\rangle = \sum_{\mathbf{k}} c_{\mathbf{k}} |\mathbf{k}\rangle, \qquad \langle 0|0\rangle = 1, \qquad \langle 0|\hat{\Omega}|0\rangle = ?$$

- We write the expectation value as follows:

$$\langle 0|\hat{\Omega}|0\rangle = \Omega_0 + \sum_{PQ} \Omega_{PQ} \langle 0|a_P^\dagger a_Q|0\rangle + \tfrac{1}{2} \sum_{PQRS} \Omega_{PQRS} \langle 0|a_P^\dagger a_R^\dagger a_S a_Q|0\rangle$$

Density matrices

$$\begin{aligned}\langle 0|\hat{\Omega}|0\rangle &= \Omega_0 + \sum_{PQ} \Omega_{PQ}\langle 0|a_P^\dagger a_Q|0\rangle + \tfrac{1}{2}\sum_{PQRS}\Omega_{PQRS}\langle 0|a_P^\dagger a_R^\dagger a_S a_Q|0\rangle \\ &= \Omega_0 + \sum_{PQ}\bar{D}_{PQ}\Omega_{PQ} + \tfrac{1}{2}\sum_{PQRS}\bar{d}_{PQRS}\Omega_{PQRS}\end{aligned}$$

- One-electron density-matrix elements:

$$\bar{D}_{PQ} = \langle 0|a_P^\dagger a_Q|0\rangle$$

- Two-electron density-matrix elements:

$$\bar{d}_{PQRS} = \langle 0|a_P^\dagger a_R^\dagger a_S a_Q|0\rangle$$

Properties of the one-electron density matrix

- $\bar{\mathbf{D}}$ is an $M \times M$ positive semidefinite, Hermitian matrix.
- A diagonal element is referred to as the occupation number $\bar{\omega}_P$ of the spin orbital $\phi_P(\mathbf{x})$ in the electronic state $|0\rangle$,

$$\bar{\omega}_P = \bar{D}_{PP} = \langle 0|a_P^\dagger a_P|0\rangle = \langle 0|\hat{N}_P|0\rangle = \sum_{\mathbf{k}} k_P |c_{\mathbf{k}}|^2$$

- Occup. numbers are real numbers between zero and one,

$$0 \leq \bar{\omega}_P \leq 1$$

- The trace of the density matrix is equal to the number of electrons,

$$\mathrm{Tr}\bar{\mathbf{D}} = \sum_P \bar{\omega}_P = \sum_P \langle 0|\hat{N}_P|0\rangle = \langle 0|\hat{N}|0\rangle = N$$

Natural spin orbitals

- Since $\bar{\mathbf{D}}$ is a Hermitian matrix, we may diagonalize it with a unitary matrix $\mathbf{U}$,

$$\bar{\mathbf{D}} = \mathbf{U}\bar{\boldsymbol{\eta}}\mathbf{U}^{\dagger}$$

- The eigenvalues are real numbers $0 \leq \bar{\eta}_P \leq 1$, known as *natural-orbital occupation numbers*. The sum of the these numbers is again equal to the number of electrons.
- The eigenvectors $\mathbf{U}$ constitute the *natural spin orbitals*.

Properties of the two-electron density matrix

- The elements of the two-electron density matrix $\bar{\mathbf{d}}$ are not all independent,

$$\bar{d}_{PQRS} = -\bar{d}_{RQPS} = -\bar{d}_{PSRQ} = \bar{d}_{RSPQ}$$

- We define the two-electron density matrix $\bar{\mathbf{T}}$ with elements

$$\bar{T}_{PQ,RS} = \bar{d}_{PRQS} \qquad \text{with} \quad P > Q, \quad R > S$$

- The diagonal elements $\bar{\omega}_{PQ}$ are *pair-occupation numbers*,

$$\begin{aligned} \bar{\omega}_{PQ} &= \bar{T}_{PQ,PQ} = \langle 0|a_P^{\dagger}a_Q^{\dagger}a_Q a_P|0\rangle = \langle 0|\hat{N}_P\hat{N}_Q|0\rangle \\ &= \sum_{\mathbf{k}} k_P k_Q |c_{\mathbf{k}}|^2 \end{aligned}$$

Operator rank

- In the manipulation of operators and matrix elements in second quantization, we often encounter *commutators* and *anticommutators*,

$$\begin{aligned}[\hat{A},\hat{B}] &= \hat{A}\hat{B}-\hat{B}\hat{A}\\ [\hat{A},\hat{B}]_+ &= \hat{A}\hat{B}+\hat{B}\hat{A}\end{aligned}$$

- The anticommutation relations of creation and annihilation operators can be used to simplify commutators and anticommutators of strings of operators.
- The *particle rank* of a string is the number of elementary operators divided by two (*e.g.*, the rank of a creation operator is 1/2 and the rank of a ON operator is 1).

Rank reduction

- *Rank reduction* is said to occur when the rank of a commutator or anticommutator is lower than the combined rank of the operators involved,

$$a_P^\dagger a_P + a_P a_P^\dagger = 1$$

  The rank of the operator products is 1, the rank of the anticommutator is 0.

- Simple rule:
  Rank reduction follows upon anticommutation of two strings of half-integral rank and upon commutation of all other strings.

$$[a_P^\dagger, a_R a_S] = [a_P^\dagger, a_R]_+ a_S - a_R [a_P^\dagger, a_S]_+ = \delta_{PR} a_S - \delta_{PS} a_R$$

Useful operator identities

$$[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$$

$$[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]_+\hat{C} - \hat{B}[\hat{A}, \hat{C}]_+$$

$$[\hat{A}, \hat{B}\hat{C}]_+ = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]_+ \;=\; [\hat{A}, \hat{B}]_+\hat{C} - \hat{B}[\hat{A}, \hat{C}]$$

For example:

$$\begin{aligned}
[a_P^\dagger, a_R a_S^\dagger a_T]_+ &= [a_P^\dagger, a_R]_+ a_S^\dagger a_T - a_R[a_P^\dagger, a_S^\dagger a_T] \\
&= \delta_{PR} a_S^\dagger a_T - a_R\left([a_P^\dagger, a_S^\dagger]_+ a_T - a_S^\dagger [a_P^\dagger, a_T]_+\right) \\
&= \delta_{PR} a_S^\dagger a_T + \delta_{PT} a_R a_S^\dagger
\end{aligned}$$

Normal-ordered second-quantization operators

- A normal-ordered string of second-quantization operators is one in which we find *all annihilation operators standing to the right of all creation operators*.
- As an example, consider the string $a_P a_Q^\dagger a_R a_S^\dagger$,

$$\begin{aligned}
a_P a_Q^\dagger a_R a_S^\dagger &= \delta_{PQ} a_R a_S^\dagger - a_Q^\dagger a_P a_R a_S^\dagger \\
&= \delta_{PQ}\delta_{RS} - \delta_{PQ} a_S^\dagger a_R - \delta_{RS} a_Q^\dagger a_P + a_Q^\dagger a_P a_S^\dagger a_R \\
&= \delta_{PQ}\delta_{RS} - \delta_{PQ} a_S^\dagger a_R - \delta_{RS} a_Q^\dagger a_P + \delta_{PS} a_Q^\dagger a_R - a_Q^\dagger a_S^\dagger a_P a_R
\end{aligned}$$

- All of the strings in the rearrangement are in normal order.
- None of them contribute to the vacuum expectation value,

$$\langle \text{vac} | a_P a_Q^\dagger a_R a_S^\dagger | \text{vac} \rangle = \delta_{PQ}\delta_{RS}$$

Normal-ordered operators (continued)

- Consider the two wavefunctions $|\mathbf{c}\rangle$ and $|\mathbf{d}\rangle$:

$$|\mathbf{c}\rangle = \sum_{\mathbf{k}} c_{\mathbf{k}} \hat{X}_{\mathbf{k}} |\text{vac}\rangle, \qquad |\mathbf{d}\rangle = \sum_{\mathbf{k}} d_{\mathbf{k}} \hat{X}_{\mathbf{k}} |\text{vac}\rangle$$

- The matrix element

$$\langle \mathbf{c}| a_P a_Q^\dagger a_R a_S^\dagger |\mathbf{d}\rangle = \sum_{\mathbf{k},\mathbf{k}'} c_{\mathbf{k}}^* d_{\mathbf{k}'} \langle \text{vac}| \hat{X}_{\mathbf{k}}^\dagger a_P a_Q^\dagger a_R a_S^\dagger \hat{X}_{\mathbf{k}'} |\text{vac}\rangle$$

  can be evaluated by rearranging $\hat{X}_{\mathbf{k}}^\dagger a_P a_Q^\dagger a_R a_S^\dagger \hat{X}_{\mathbf{k}'}$ into normal order.

Contractions

- A contraction between two arbitrary elementary operators, for example between a_P and and $a_Q^\dagger$ is defined as

$$\overbrace{a_P a_Q^\dagger} = a_P a_Q^\dagger - \{a_P a_Q^\dagger\}$$

  where the notation $\{a_P a_Q^\dagger\}$ indicates the normal-orderer string.
- Thus, the contraction between the operators is simply the original ordering of the pair minus the normal-ordered pair.
- The notation $\{\dots\}$ introduces a sign $(-1)^p$, where p is the number of permutations required to bring the operators into normal order.

Contractions (continued)

- Examples with two elementary operators:

$$\overbracket{a_P a_Q} = 0, \quad \overbracket{a_P^\dagger a_Q^\dagger} = 0, \quad \overbracket{a_P^\dagger a_Q} = 0,$$

$$\overbracket{a_P a_Q^\dagger} = a_P a_Q^\dagger - \{a_P a_Q^\dagger\} = a_P a_Q^\dagger + a_Q^\dagger a_P = \delta_{PQ}$$

- An example with more than two elementary operators:

$$\overbracket{a_P a_R a_Q^\dagger} a_S^\dagger = -\delta_{PQ} a_R a_S^\dagger$$

- A sign change occurs for every permutation that is required until the contracted operators are adjacent to one another.

Full contractions

- A string of operators is *fully contracted*, if all operators are pairwise contracted. Only full contractions contribute to the vacuum expectation value.
- An example with two contractions:

$$\overbracket{a_P a_R a_Q^\dagger} a_S^\dagger = -\overbracket{a_P a_R a_S^\dagger} a_Q^\dagger = -\overbracket{a_P a_Q^\dagger}\, \delta_{RS} = -\delta_{PQ}\delta_{RS}$$

- Rule of thumb: the sign of a full contraction is negative if the number of crossings is odd, else positive.

Wick's theorem

Wick's theorem provides a recipe by which an arbitrary string of annihilation and creation operators, $ABC...XYZ$, may be written as a linear combination of normal-ordered strings. Schematically, Wick's theorem is:

$$
\begin{aligned}
ABC...XYZ &= \{ABC...XYZ\} \\
&+ \sum_{\text{singles}} \{\overbrace{AB}C...XYZ\} \\
&+ \sum_{\text{doubles}} \{ABC...XYZ\} \quad + \quad ...
\end{aligned}
$$

where "singles", "doubles", etc. refer to the number of pairwise contractions.

Wick's theorem (continued)

Applying Wick's theorem to $a_P a_Q^\dagger a_R a_S^\dagger$ yields:

$$
\begin{aligned}
a_P a_Q^\dagger a_R a_S^\dagger &= \{a_P a_Q^\dagger a_R a_S^\dagger\} + \{\overbrace{a_P a_Q^\dagger} a_R a_S^\dagger\} \\
&+ \{a_P a_Q^\dagger a_R a_S^\dagger\} + \{a_P a_Q^\dagger \overbrace{a_R a_S^\dagger}\} \\
&+ \{\overbrace{a_P a_Q^\dagger}\,\overbrace{a_R a_S^\dagger}\} \\
&= -a_Q^\dagger a_S^\dagger a_P a_R - \delta_{PQ} a_S^\dagger a_R + \delta_{PS} a_Q^\dagger a_R \\
&- \delta_{RS} a_Q^\dagger a_P + \delta_{PQ}\delta_{RS}
\end{aligned}
$$

This result is identical to that obtained using the anticommutation relations.

Wick's theorem (continued)

Another example:

$$\begin{aligned} a_P^\dagger a_Q a_S a_R^\dagger &= \{a_P^\dagger a_Q a_S a_R^\dagger\} + \{a_P^\dagger a_Q \overbrace{a_S a_R^\dagger}\} + \{a_P^\dagger \overbrace{a_Q a_S a_R^\dagger}\} \\ &= a_P^\dagger a_R^\dagger a_Q a_S + \delta_{SR} a_P^\dagger a_Q - \delta_{QR} a_P^\dagger a_S \end{aligned}$$

This result is also easily obtained using the anticommutation relations:

$$\begin{aligned} a_P^\dagger a_Q a_S a_R^\dagger &= a_P^\dagger a_Q \delta_{SR} - a_P^\dagger a_Q a_R^\dagger a_S \\ &= a_P^\dagger a_Q \delta_{SR} - a_P^\dagger \delta_{QR} a_S + a_P^\dagger a_R^\dagger a_Q a_S \end{aligned}$$

Application of Wick's theorem

- Consider the two one-electron states $|T\rangle = a_T^\dagger|\text{vac}\rangle$ and $|U\rangle = a_U^\dagger|\text{vac}\rangle$. The matrix element $\langle T|a_P a_Q^\dagger a_R a_S^\dagger|U\rangle$ is evaluated by retaining only the *fully contracted* terms,

$$\langle T|a_P a_Q^\dagger a_R a_S^\dagger|U\rangle = \langle \text{vac}|a_T a_P a_Q^\dagger a_R a_S^\dagger a_U^\dagger|\text{vac}\rangle$$

$$= \langle \text{vac}|\{\overbrace{a_T a_P a_Q^\dagger a_R a_S^\dagger a_U^\dagger}\} + \{\overbrace{a_T a_P a_Q^\dagger a_R a_S^\dagger a_U^\dagger}\}$$

$$+ \{\overbrace{a_T a_P a_Q^\dagger a_R a_S^\dagger a_U^\dagger}\} + \{\overbrace{a_T a_P a_Q^\dagger a_R a_S^\dagger a_U^\dagger}\}|\text{vac}\rangle$$

$$= \delta_{TU}\delta_{PQ}\delta_{RS} + \delta_{TQ}\delta_{PS}\delta_{RU} - \delta_{TQ}\delta_{PU}\delta_{RS} - \delta_{TS}\delta_{PQ}\delta_{RU}$$

Generalized Wick's theorem

The generalized Wick's theorem provides a recipe by which we can evaluate a product of two normal-ordered strings,

$$\begin{aligned}\{ABC...\}\{XYZ...\} &= \{ABC...XYZ...\} \\ &+ \sum_{\text{singles}} \{\overbrace{ABC...XY}Z...\} \\ &+ \sum_{\text{doubles}} \{\overbrace{AB\overbrace{C...XY}Z...}\} + \ ...\end{aligned}$$

Contractions need only be evaluated between normal-ordered strings and not within them.

Application of the generalized Wick's theorem

Let us consider the product of the the strings $a_P^\dagger a_Q$ and $a_R^\dagger a_S$, which both are in normal order:

$$\begin{aligned}a_P^\dagger a_Q a_R^\dagger a_S &= \{a_P^\dagger a_Q a_R^\dagger a_S\} + \{a_P^\dagger \overbrace{a_Q a_R^\dagger} a_S\} \\ &= -a_P^\dagger a_R^\dagger a_Q a_S + \delta_{QR} a_P^\dagger a_S\end{aligned}$$

Of course, the same result is also obtained by inserting the anticommutation relation $a_Q a_R^\dagger = \delta_{QR} - a_R^\dagger a_Q$ into the product $a_P^\dagger a_Q a_R^\dagger a_S$.

Fermi vacuum

- In configuration-interaction or coupled-cluster theories, it is more convenient to deal with the N-electron reference determinant $|\text{HF}\rangle$ than with the true vacuum state $|\text{vac}\rangle$.
- The evaluation of matrix elements using Wick's theorem were very tedious if one had to include the whole set of creation operators to generate $|\text{HF}\rangle$ from the true vacuum,

$$|\text{HF}\rangle = a_I^\dagger a_J^\dagger a_K^\dagger a_L^\dagger ... |\text{vac}\rangle$$

- We alter the definition of normal ordering from one given relative to the true vacuum to one given relative to the reference state $|\text{HF}\rangle$ (*Fermi vacuum*).

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Fermi vacuum and particle–hole formalism

- When working on the Fermi vacuum, a hole is created by the operator a_I while a particle is created by $a_A^\dagger$.
- We refer to operators that create or destroy holes and particles as *quasiparticle operators* (q-operators). That is, q-annihilation operators are those that annihilate holes and particles (*e.g.*, $a_I^\dagger$ and a_A), and q-creation operators are those that create holes and particles (*e.g.*, a_I and $a_A^\dagger$).
- A string of second-quantization operators is normal ordered relative to the Fermi vaccuum if all q-annihilation operators are standing to the right of all q-creation operators.

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Contractions in the particle–hole formalism

- The definition of normal ordering relative to the Fermi vacuum (denoted as ":...:") changes the application of Wick's theorem only slightly. The only nonzero contractions take place between q-annihilation operators that stand to the left of q-creation operators,

$$\overbracket{a_I^\dagger a_J} = a_I^\dagger a_J \; - :a_I^\dagger a_J: \; = a_I^\dagger a_J + a_J a_I^\dagger = \delta_{IJ}$$

$$\overbracket{a_A a_B^\dagger} = a_A a_B^\dagger \; - :a_A a_B^\dagger: \; = a_A a_B^\dagger + a_B^\dagger a_A = \delta_{AB}$$

$$\overbracket{a_A^\dagger a_B} = \overbracket{a_I a_J^\dagger} = 0$$

- All other combinations involve mixed hole and particle indices for which the Kronecker delta functions give zero.

Wick's theorem in the particle–hole formalism

Consider the overlap between two doubly-substituted determinants:

$$\left\langle \begin{smallmatrix} CD \\ KL \end{smallmatrix} \middle| \begin{smallmatrix} AB \\ IJ \end{smallmatrix} \right\rangle = \langle \mathsf{HF} | a_K^\dagger a_L^\dagger a_D a_C a_A^\dagger a_B^\dagger a_J a_I | \mathsf{HF} \rangle$$

$$= \langle \mathsf{HF} | \overbracket{a_K^\dagger a_L^\dagger a_D a_C a_A^\dagger a_B^\dagger a_J a_I} + \overbracket{a_K^\dagger a_L^\dagger a_D a_C a_A^\dagger a_B^\dagger a_J a_I}$$

$$+ \overbracket{a_K^\dagger a_L^\dagger a_D a_C a_A^\dagger a_B^\dagger a_J a_I} + \overbracket{a_K^\dagger a_L^\dagger a_D a_C a_A^\dagger a_B^\dagger a_J a_I} | \mathsf{HF} \rangle$$

$$= (\delta_{IK}\delta_{JL} - \delta_{IL}\delta_{JK})(\delta_{AC}\delta_{BD} - \delta_{AD}\delta_{BC})$$

Normal-ordered one-electron operator

- The molecular electronic Hamiltonian reads:

$$\hat{H} = h_{\text{nuc}} + \sum_{PQ} h_{PQ} a_P^\dagger a_Q + \tfrac{1}{2} \sum_{PQRS} g_{PQRS} a_P^\dagger a_R^\dagger a_S a_Q$$

- Applying Wick's theorem to its one-electron term yields:

$$\begin{aligned} \sum_{PQ} h_{PQ} a_P^\dagger a_Q &= \sum_{PQ} h_{PQ} :a_P^\dagger a_Q: + \sum_{PQ} h_{PQ} :\overbracket{a_P^\dagger a_Q}: \\ &= \sum_{PQ} h_{PQ} :a_P^\dagger a_Q: + \sum_{I} h_{II} \end{aligned}$$

Normal-ordered two-electron operator

- We rewrite $a_P^\dagger a_R^\dagger a_S a_Q$ as:

$$\begin{aligned} a_P^\dagger a_R^\dagger a_S a_Q &= :a_P^\dagger a_R^\dagger a_S a_Q: \\ &+ :\overbracket{a_P^\dagger a_R^\dagger} a_S a_Q: + :\overbracket{a_P^\dagger a_R^\dagger a_S} a_Q: + :a_P^\dagger \overbracket{a_R^\dagger a_S} a_Q: \\ &+ :a_P^\dagger \overbracket{a_R^\dagger a_S a_Q}: + :\overbracket{a_P^\dagger \overbracket{a_R^\dagger} a_S} a_Q: + :\overbracket{a_P^\dagger \overbracket{a_R^\dagger a_S a_Q}}: \end{aligned}$$

- Hence,

$$\begin{aligned} \tfrac{1}{2} \sum_{PQRS} g_{PQRS} a_P^\dagger a_R^\dagger a_S a_Q &= \tfrac{1}{2} \sum_{PQRS} g_{PQRS} :a_P^\dagger a_R^\dagger a_S a_Q: \\ + \sum_{IPQ} (g_{IIPQ} - g_{IPQI}) :a_P^\dagger a_Q: &+ \tfrac{1}{2} \sum_{IJ} (g_{IIJJ} - g_{IJJI}) \end{aligned}$$

The normal-ordered electronic Hamiltonian

- We note that:

$$\sum_I h_{II} + \tfrac{1}{2}\sum_{IJ}(g_{IIJJ} - g_{IJJI}) = E_{\text{HF}} \qquad \text{(Hartree–Fock energy)}$$

$$h_{PQ} + \sum_I (g_{IIPQ} - g_{IPQI}) = f_{PQ} \qquad \text{(Fock-matrix element)}$$

- We obtain:

$$\hat{H} = \sum_{PQ} f_{PQ} {:}a_P^\dagger a_Q{:} + \tfrac{1}{2}\sum_{PQRS} g_{PQRS} {:}a_P^\dagger a_R^\dagger a_S a_Q{:} + E_{\text{HF}}$$

$$\hat{H} = \hat{F}_N + \hat{V}_N + E_{\text{HF}}$$

$$\hat{H}_N = \hat{F}_N + \hat{V}_N = \hat{H} - E_{\text{HF}}$$

Brillouin's theorem

- Let $\left|\begin{smallmatrix} A \\ I \end{smallmatrix}\right\rangle = a_A^\dagger a_I |\text{HF}\rangle$ be a singly-substituted determinant. The matrix element $\langle \text{HF}|\hat{H}|\begin{smallmatrix} A \\ I \end{smallmatrix}\rangle$ can be computed using Wick's theorem,

$$\langle \text{HF}|\hat{H}|\begin{smallmatrix} A \\ I \end{smallmatrix}\rangle = \langle \text{HF}|\hat{H} a_A^\dagger a_I|\text{HF}\rangle = \langle \text{HF}|\hat{F}_N a_A^\dagger a_I|\text{HF}\rangle$$

$$= \sum_{PQ} f_{PQ} \langle \text{HF}| {:}a_P^\dagger a_Q{:} a_A^\dagger a_I|\text{HF}\rangle$$

$$= \sum_{PQ} f_{PQ} \langle \text{HF}| \overbrace{a_P^\dagger a_Q a_A^\dagger}\, a_I\, |\text{HF}\rangle$$

$$= f_{IA} = 0 \qquad \text{(if Brillouin condition fulfilled)}$$

First-order interacting space

- Similarly, for $\left|\begin{smallmatrix} AB \\ IJ \end{smallmatrix}\right\rangle = a_A^\dagger a_I |\mathrm{HF}\rangle$ we obtain:

$$\langle \mathrm{HF}|\hat{H}\left|\begin{smallmatrix} AB \\ IJ \end{smallmatrix}\right\rangle = \langle \mathrm{HF}|\hat{V}_N a_A^\dagger a_B^\dagger a_J a_I|\mathrm{HF}\rangle$$

$$= \frac{1}{2}\sum_{PQRS} g_{PQRS}\langle \mathrm{HF}|:a_P^\dagger a_R^\dagger a_S a_Q: a_A^\dagger a_B^\dagger a_J a_I|\mathrm{HF}\rangle$$

$$= \frac{1}{2}\sum_{PQRS} g_{PQRS}\langle \mathrm{HF}|\overbrace{a_P^\dagger a_R^\dagger a_S a_Q a_A^\dagger a_B^\dagger a_J a_I}$$

$$+ a_P^\dagger a_R^\dagger a_S a_Q a_A^\dagger a_B^\dagger a_J a_I + a_P^\dagger a_R^\dagger a_S a_Q a_A^\dagger a_B^\dagger a_J a_I$$

$$+ a_P^\dagger a_R^\dagger a_S a_Q a_A^\dagger a_B^\dagger a_J a_I\,|\mathrm{HF}\rangle = g_{IAJB} - g_{IBJA}$$

Spin in second quantization

- So far, we have used the upper-case index P to count spin orbitals of the form

$$\phi_P(\mathbf{x}) = \phi_{p\sigma}(\mathbf{r}, m_\mathsf{s}) = \phi_p(\mathbf{r})\sigma(m_\mathsf{s})$$

- m_s is the spin coordinate and the spin function $\sigma(m_\mathsf{s})$ is either $\alpha(m_\mathsf{s})$ or $\beta(m_\mathsf{s})$.
- The theory of second quantization can also be formulated using the composite index $p\sigma$. For example, the anti-commutator between creation and annihilation operators can be written as

$$[a_{p\sigma}^\dagger, a_{q\tau}]_+ = \delta_{p\sigma,q\tau} = \delta_{pq}\delta_{\sigma\tau}$$

- With lower-case indices p, we count spatial orbitals $\phi_p(\mathbf{r})$.

Spinfree one-electron operators

- Consider the following spinfree (or spinless) operator:

$$f^c = \sum_{i=1}^{N} f^c(\mathbf{r}_i), \qquad \hat{f} = \sum_{p\sigma q\tau} f_{p\sigma,q\tau} a^\dagger_{p\sigma} a_{q\tau}$$

$$\begin{aligned} f_{p\sigma,q\tau} &= \int\int \phi^*_p(\mathbf{r})\sigma^*(m_\mathsf{s}) f^c(\mathbf{r}) \phi_q(\mathbf{r})\tau(m_\mathsf{s}) \mathrm{d}\mathbf{r}\, \mathrm{d}m_\mathsf{s} \\ &= \delta_{\sigma\tau} \int \phi^*_p(\mathbf{r}) f^c(\mathbf{r}) \phi_q(\mathbf{r}) \mathrm{d}\mathbf{r} = \delta_{\sigma\tau} f_{pq} \end{aligned}$$

- The sum over spin functions in the second quantization operator $\hat{f}$ can be accounted for in the *singlet excitation operator*

$$E_{pq} = a^\dagger_{p\alpha} a_{q\alpha} + a^\dagger_{p\beta} a_{q\beta}, \qquad \hat{f} = \sum_{pq} f_{pq} E_{pq}$$

Spinfree two-electron operators

The spinfree two-electron operator

$$g^c = \tfrac{1}{2} \sum_{i \neq j} g^c(\mathbf{r}_i, \mathbf{r}_j)$$

gives

$$\begin{aligned} \hat{g} &= \tfrac{1}{2} \sum_{pqrs} \sum_{\sigma\tau\mu\nu} g_{p\sigma,q\tau,r\mu,s\nu}\, a^\dagger_{p\sigma} a^\dagger_{r\mu} a_{s\nu} a_{q\tau} \\ &= \tfrac{1}{2} \sum_{pqrs} \sum_{\sigma\tau} g_{pqrs}\, a^\dagger_{p\sigma} a^\dagger_{r\tau} a_{s\tau} a_{q\sigma} \\ &= \tfrac{1}{2} \sum_{pqrs} g_{pqrs}\, e_{pqrs}, \qquad \text{with} \quad e_{pqrs} = E_{pq} E_{rs} - \delta_{qr} E_{ps} \end{aligned}$$

Pure spin operators

The representation of first-quantization operators f^c that work in spin space only may be written in the general form

$$\begin{aligned}\hat{f} &= \sum_{p\sigma q\tau} \int \phi_p^*(\mathbf{r})\sigma^*(m_s) f^c(m_s)\phi_q(\mathbf{r})\tau(m_s)\mathrm{d}\mathbf{r}\,\mathrm{d}m_s\, a_{p\sigma}^\dagger a_{q\tau} \\ &= \sum_{\sigma\tau} \int \sigma^*(m_s) f^c(m_s)\tau(m_s)\mathrm{d}m_s \sum_p a_{p\sigma}^\dagger a_{p\tau}\end{aligned}$$

Consider the operators S_z^c, S_+^c and S_-^c (the latter are known as *step-up and step-down operators* or ladder operators).

$$S_z^c(m_s)\alpha(m_s) = \tfrac{1}{2}\alpha(m_s), \qquad S_z^c(m_s)\beta(m_s) = -\tfrac{1}{2}\beta(m_s)$$

$$S_-^c(m_s)\alpha(m_s) = \beta(m_s), \qquad S_-^c(m_s)\beta(m_s) = 0$$

$$S_+^c(m_s)\alpha(m_s) = 0, \qquad S_+^c(m_s)\beta(m_s) = \alpha(m_s)$$

Pure spin operators (continued)

$$\hat{S}_z = \tfrac{1}{2}\sum_p \left(a_{p\alpha}^\dagger a_{p\alpha} - a_{p\beta}^\dagger a_{p\beta}\right), \quad \hat{S}_+ = \sum_p a_{p\alpha}^\dagger a_{p\beta}, \quad \hat{S}_- = \sum_p a_{p\beta}^\dagger a_{p\alpha}$$

From these operators, it follows:

$$\hat{S}_+^\dagger = \hat{S}_-, \quad \hat{S}_-^\dagger = \hat{S}_+$$

$$\hat{S}_x = \tfrac{1}{2}\left(\hat{S}_+ + \hat{S}_-\right) = \tfrac{1}{2}\sum_p \left(a_{p\alpha}^\dagger a_{p\beta} + a_{p\beta}^\dagger a_{p\alpha}\right)$$

$$\hat{S}_y = \tfrac{1}{2i}\left(\hat{S}_+ - \hat{S}_-\right) = \tfrac{1}{2i}\sum_p \left(a_{p\alpha}^\dagger a_{p\beta} - a_{p\beta}^\dagger a_{p\alpha}\right)$$

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \hat{S}_+\hat{S}_- + \hat{S}_z\left(\hat{S}_z - 1\right) = \hat{S}_-\hat{S}_+ + \hat{S}_z\left(\hat{S}_z + 1\right)$$

$$[\hat{S}_+, \hat{S}_-] = 2\hat{S}_z$$

ROHF expectation value of $\hat{S}^2$

The expectation value of $\hat{S}^2$ with respect to a restricted open-shell Hartree–Fock (ROHF) reference state can easily be evaluated using Wick's theorem in the particle–hole formalism.

$$\langle \mathsf{HF}|\hat{S}_+\hat{S}_-|\mathsf{HF}\rangle = \sum_{pq}\langle \mathsf{HF}|\, \overbrace{a^\dagger_{p\alpha}\overbrace{a_{p\beta}a^\dagger_{q\beta}}a_{q\alpha}}\,|\mathsf{HF}\rangle = N_\alpha - N_\beta$$

$$\langle \mathsf{HF}|\hat{S}_-\hat{S}_+|\mathsf{HF}\rangle = \sum_{pq}\langle \mathsf{HF}|\, \overbrace{a^\dagger_{p\beta}\overbrace{a_{p\alpha}a^\dagger_{q\alpha}}a_{q\beta}}\,|\mathsf{HF}\rangle = 0$$

$$\langle \mathsf{HF}|\hat{S}_z|\mathsf{HF}\rangle = \tfrac{1}{2}\sum_{p}\langle \mathsf{HF}|\, \overbrace{a^\dagger_{p\alpha}a_{p\alpha}} - \overbrace{a^\dagger_{p\beta}a_{p\beta}}\,|\mathsf{HF}\rangle = \tfrac{1}{2}\,(N_\alpha - N_\beta)$$

$$\langle \mathsf{HF}|\hat{S}_z^2|\mathsf{HF}\rangle = \tfrac{1}{4}\sum_{pq}\langle \mathsf{HF}|\, \overbrace{a^\dagger_{p\alpha}a_{p\alpha}}\overbrace{a^\dagger_{q\alpha}a_{q\alpha}} + \ldots\,|\mathsf{HF}\rangle = \tfrac{1}{4}\,(N_\alpha - N_\beta)^2$$

$$\langle \mathsf{HF}|\hat{S}^2|\mathsf{HF}\rangle = \tfrac{1}{2}\,(N_\alpha - N_\beta)\left\{\tfrac{1}{2}\,(N_\alpha - N_\beta) + 1\right\}$$

Mixed operators

Consider the (atomic) first-quantization spin–orbit operator,

$$V^c_{\mathsf{SO}} = \sum_{i=1}^{N} V^c_{\mathsf{SO}}(\mathbf{r}_i, m_{\mathsf{s}i}) = \sum_{i=1}^{N} \xi(r_i)\,\boldsymbol{\ell}^c(\mathbf{r}_i)\cdot\mathbf{S}^c(m_{\mathsf{s}i})$$

which in second quantization takes the form:

$$\hat{V}_{\mathsf{SO}} = \sum_{pq}\left(V^x_{pq}\hat{T}^x_{pq} + V^y_{pq}\hat{T}^y_{pq} + V^z_{pq}\hat{T}^z_{pq}\right)$$

with

$$V^\mu_{pq} = \int \phi^*_p(\mathbf{r})\xi(r)\,\ell^c_\mu(\mathbf{r})\,\phi_q(\mathbf{r})\,\mathrm{d}\mathbf{r}, \qquad (\mu = x, y, z)$$

and the *triplet excitation operators*

$$T^x_{pq} = \tfrac{1}{2}(a^\dagger_{p\alpha}a_{q\beta} + a^\dagger_{p\beta}a_{q\alpha}), \qquad T^y_{pq} = \tfrac{1}{2i}(a^\dagger_{p\alpha}a_{q\beta} - a^\dagger_{p\beta}a_{q\alpha})$$

$$T^z_{pq} = \tfrac{1}{2}(a^\dagger_{p\alpha}a_{q\alpha} - a^\dagger_{p\beta}a_{q\beta})$$

One-electron density matrix

$$\begin{aligned}\langle 0|\hat{\Omega}|0\rangle &= \Omega_0 + \sum_{pq}\Omega_{pq}\langle 0|E_{pq}|0\rangle + \tfrac{1}{2}\sum_{pqrs}\Omega_{pqrs}\langle 0|e_{pqrs}|0\rangle \\ &= \Omega_0 + \sum_{pq} D_{pq}\Omega_{PQ} + \tfrac{1}{2}\sum_{pqrs} d_{pqrs}\Omega_{pqrs}\end{aligned}$$

- One-electron density matrix,

$$D_{pq} = \langle 0|E_{pq}|0\rangle = \bar{D}_{p\alpha,q\alpha} + \bar{D}_{p\beta,q\beta}, \qquad D_{pq} = D^*_{qp}$$

- Orbital occupation numbers,

$$D_{pp} = \omega_p = \bar{\omega}_{p\alpha} + \bar{\omega}_{p\beta}, \qquad 0 \leq \omega_p \leq 2$$

- Natural occupation numbers,

$$\mathbf{D} = \mathbf{U}\boldsymbol{\eta}\mathbf{U}^\dagger, \qquad 0 \leq \eta_p \leq 2$$

Two-electron density matrix

$$\begin{aligned}\langle 0|\hat{\Omega}|0\rangle &= \Omega_0 + \sum_{pq}\Omega_{pq}\langle 0|E_{pq}|0\rangle + \tfrac{1}{2}\sum_{pqrs}\Omega_{pqrs}\langle 0|e_{pqrs}|0\rangle \\ &= \Omega_0 + \sum_{pq} D_{pq}\Omega_{PQ} + \tfrac{1}{2}\sum_{pqrs} d_{pqrs}\Omega_{pqrs}\end{aligned}$$

- Two-electron density matrix,

$$d_{pqrs} = \langle 0|e_{pqrs}|0\rangle = \sum_{\sigma\tau}\langle 0|a^\dagger_{p\sigma}a^\dagger_{r\tau}a_{s\tau}a_{q\sigma}|0\rangle = \sum_{\sigma\tau}\bar{d}_{p\sigma,q\sigma,r\tau,s\tau}$$

- Pair occupation numbers,

$$d_{ppqq} = \omega_{pq} = \sum_{\sigma\tau}\bar{\omega}_{p\sigma,q\tau}, \qquad 0 \leq \omega_{pq} \leq 2(2-\delta_{pq})$$

The spin-density matrix

- The spin-density matrix is defined as

$$D^T_{pq} = \tfrac{1}{2}\langle 0|a^\dagger_{p\alpha}a_{q\alpha} - a^\dagger_{p\beta}a_{q\beta}|0\rangle = \tfrac{1}{2}(\bar{D}_{p\alpha,q\alpha} - \bar{D}_{p\beta,q\beta})$$

- The spin-density matrix measures the excess of the density of alpha electrons over beta electrons.
- Similarly, the spin occupation number

$$\omega^T_p = \tfrac{1}{2}(\bar{\omega}_{p\alpha} - \bar{\omega}_{p\beta})$$

  measures the excess of alpha over beta electrons in ϕ_p.
- The trace of $\mathbf{D}^T$ yields the total spin projection,

$$\mathrm{Tr}\mathbf{D}^T = \tfrac{1}{2}\sum_p \langle 0|a^\dagger_{p\alpha}a_{p\alpha} - a^\dagger_{p\beta}a_{p\beta}|0\rangle = \langle 0|\hat{S}_z|0\rangle$$