



Second quantization

Applications

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Insight from [Crawford & Schaefer, Rev. Comp. Chem. **14** (2000) 33] is acknowledged.

Where we stopped last time

- Second quantization starts from **field operators** $\hat{\psi}^\dagger(1)$, $\hat{\psi}(1)$ sampling the electron field in space. It provides a very convenient language for the formulation and implementation of quantum chemical methods.
- **Occupation number vectors** (ONVs) are defined with respect to some (orthonormal) orbital set $\{\varphi_p(\mathbf{r})\}_{p=1}^M$
- Their occupation numbers are manipulated using **creation- and annihilation operators**, $\hat{a}_p^\dagger$ and $\hat{a}_p$, which are conjugates of each other.
- The algebra of these operators is summarized by **anti-commutator relations**

$$\left[\hat{a}_p^\dagger, \hat{a}_q^\dagger\right]_+ = 0; \quad \left[\hat{a}_p, \hat{a}_q\right]_+ = 0; \quad \left[\hat{a}_p, \hat{a}_q^\dagger\right]_+ = \delta_{pq}$$

and reflects the fermionic nature of electrons.

What about spin ?

- By convention, the z-axis is chosen as spin-axis such that the electron spin functions $|s, m_s\rangle$ are eigenfunctions of $\hat{s}^2$ and $\hat{s}_z$

$$\hat{s}^2 |s, m_s\rangle = s(s+1) |s, m_s\rangle; \quad \hat{s}_z |s, m_s\rangle = m_s |s, m_s\rangle$$

- It is also convenient to introduce **step operators**

$$\hat{s}_+ = \hat{s}_x + i\hat{s}_y \quad \text{and} \quad \hat{s}_- = \hat{s}_x - i\hat{s}_y$$

$$\hat{s}_\pm |s, m_s\rangle = \sqrt{s(s+1) - m_s(m_s \pm 1)} |s, m_s \pm 1\rangle$$

- Electrons are spin- $\frac{1}{2}$ particles with spin functions denoted $|\alpha\rangle = |\frac{1}{2}, \frac{1}{2}\rangle$ and $|\beta\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle$. The action of the spin operators is summarized by

	$\hat{s}^2$	$\hat{s}_z$	$\hat{s}_+$	$\hat{s}_-$
$ \alpha\rangle$	$\frac{3}{4} \alpha\rangle$	$\frac{1}{2} \alpha\rangle$	0	$ \beta\rangle$
$ \beta\rangle$	$\frac{3}{4} \beta\rangle$	$-\frac{1}{2} \beta\rangle$	$ \alpha\rangle$	0

Spin in second quantization

- We may separate out spin from spatial parts of the creation- and annihilation operators, giving

$$\left[\hat{a}_{p\sigma}^\dagger, \hat{a}_{q\sigma'}^\dagger\right]_+ = 0; \quad \left[\hat{a}_{p\sigma}, \hat{a}_{q\sigma'}\right]_+ = 0; \quad \left[\hat{a}_{p\sigma}, \hat{a}_{q\sigma'}^\dagger\right]_+ = \delta_{pq}\delta_{\sigma\sigma'}; \quad \sigma, \sigma' = \alpha \text{ or } \beta$$

- We may also separate out spin in the electronic Hamiltonian. For the (non-relativistic) one-electron part we obtain

$$\begin{aligned}\hat{H}_1 &= \sum_{pq} \sum_{\sigma, \sigma'} \langle \varphi_p \sigma | \hat{h} | \varphi_q \sigma' \rangle \hat{a}_{p\sigma}^\dagger \hat{a}_{q\sigma'} \\ &= \sum_{pq} \sum_{\sigma, \sigma'} \langle \varphi_p | \hat{h} | \varphi_q \rangle \langle \sigma | \sigma' \rangle \hat{a}_{p\sigma}^\dagger \hat{a}_{q\sigma'} \\ &= \sum_{pq} \sum_{\sigma, \sigma'} \langle \varphi_p | \hat{h} | \varphi_q \rangle \delta_{\sigma\sigma'} \hat{a}_{p\sigma}^\dagger \hat{a}_{q\sigma'} \\ &= \sum_{pq} \langle \varphi_p | \hat{h} | \varphi_q \rangle E_{pq}; \quad E_{pq} = \sum_{\sigma} \hat{a}_{p\sigma}^\dagger \hat{a}_{q\sigma}\end{aligned}$$

Spin in second quantization

- For the (non-relativistic) two-electron part we obtain

$$\begin{aligned}
 \hat{H}_2 &= \frac{1}{2} \sum_{pqrs} \sum_{\sigma\tau\sigma'\tau'} \langle \varphi_p \sigma \varphi_q \tau | \hat{g} | \varphi_r \sigma' \varphi_s \tau' \rangle a_{p\sigma}^\dagger a_{q\tau}^\dagger a_{s\tau'} a_{r\sigma'} \\
 &= \frac{1}{2} \sum_{pqrs} \sum_{\sigma\tau\sigma'\tau'} \langle \varphi_p \varphi_q | \hat{g} | \varphi_r \varphi_s \rangle \langle \sigma | \sigma' \rangle \langle \tau | \tau' \rangle a_{p\sigma}^\dagger a_{q\tau}^\dagger a_{s\tau'} a_{r\sigma'} \\
 &= \frac{1}{2} \sum_{pqrs} \sum_{\sigma\tau\sigma'\tau'} \langle \varphi_p \varphi_q | \hat{g} | \varphi_r \varphi_s \rangle \delta_{\sigma\sigma'} \delta_{\tau\tau'} a_{p\sigma}^\dagger a_{q\tau}^\dagger a_{s\tau'} a_{r\sigma'} \\
 &= \frac{1}{2} \sum_{pqrs} \langle \varphi_p \varphi_q | \hat{g} | \varphi_r \varphi_s \rangle e_{pq,rs}; \quad e_{pq,rs} = \sum_{\sigma\tau} a_{p\sigma}^\dagger a_{q\tau}^\dagger a_{s\tau} a_{r\sigma}
 \end{aligned}$$

- Operator algebra

$$a_{p\sigma}^\dagger a_{q\tau}^\dagger a_{s\tau} a_{r\sigma} = -a_{p\sigma}^\dagger a_{q\tau}^\dagger a_{r\sigma} a_{s\tau} = a_{p\sigma}^\dagger a_{r\sigma} a_{q\tau}^\dagger a_{s\tau} - \delta_{qr} \delta_{\sigma\tau} a_{p\sigma}^\dagger a_{s\tau}$$

- .. shows that

$$e_{pq,rs} = E_{pr} E_{qs} - \delta_{rq} E_{ps}$$

Hartree-Fock theory in second quantization

Reference ONV and orbital classes

- In first quantization language the Hartree-Fock method employs a single Slater determinant as **trial function**.
- In second quantization we start from some orthonormal orbital basis $\{\varphi_p\}_{p=1}^M$, which defines our Fock space, and build a **reference ONV** in that space

$$|0\rangle = \hat{a}_1^\dagger \hat{a}_2^\dagger \dots \hat{a}_N^\dagger |vac\rangle = \underbrace{|1, 1, 1, 1, \dots, 1\rangle}_N \underbrace{|0, \dots, 0\rangle}_{M-N}$$

- For further manipulations it is useful to introduce **orbital classes**:
 - ▶ occupied orbitals: $i, j, k, l, \dots$
 - ▶ virtual (unoccupied) orbitals: $a, b, c, d, \dots$
 - ▶ general orbitals: $p, q, r, s, \dots$

Hartree-Fock theory in second quantization

Hartree-Fock energy

$$E^{HF} = \langle 0 | \hat{H} | 0 \rangle = \langle 0 | \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pq,rs} V_{pq,rs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r | 0 \rangle + V_{nn}$$

- One-electron energy

$$E_1^{HF} = \sum_{pq} h_{pq} \langle 0 | \hat{a}_p^\dagger \hat{a}_q | 0 \rangle$$

- ▶ The operator $\hat{a}_q$ tries to remove an electron to the right; this is only possible if orbital q is occupied.
- ▶ Likewise, the operator $\hat{a}_p^\dagger$ tries to remove an electron to the left; this is only possible if orbital p is occupied.
- ▶ The final ONVs created left and right by these processes must be the same (to within a phase) for a non-zero inner product.

- We conclude

$$E_1^{HF} = \sum_i h_{ii}$$

Hartree-Fock theory in second quantization

Hartree-Fock energy

- Two-electron energy

$$E_2^{HF} = \frac{1}{2} \sum_{pq,rs} V_{pq,rs} \langle 0 | \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r | 0 \rangle$$

- ▶ Operators $\hat{a}_r$ and $\hat{a}_s$ both try to remove an electron to the right; orbitals r and s must be occupied, but not identical
- ▶ Operators $\hat{a}_p^\dagger$ and $\hat{a}_q^\dagger$ both try to remove an electron to the left; orbitals p and q must be occupied, but not identical
- ▶ The final ONVs created left and right by these processes must be the same (to within a phase) for a non-zero inner product.
- ▶ There are two possibilities

$$E_2^{HF} = \frac{1}{2} \sum_{i \neq j} \left\{ V_{ij,ij} \langle 0 | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_j \hat{a}_i | 0 \rangle + V_{ij,ji} \langle 0 | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_i \hat{a}_j | 0 \rangle \right\}$$

- The final expression is

$$E_2^{HF} = \frac{1}{2} \sum_{i \neq j} \{ V_{ij,ij} - V_{ij,ji} \} = \frac{1}{2} \sum_{ij} \langle \varphi_i \varphi_j \parallel \varphi_i \varphi_j \rangle$$

Hartree-Fock theory in second quantization

Stationarity condition

- The Hartree-Fock energy is a **functional** of the occupied orbitals

$$E^{HF} [\{\varphi_i\}] = \sum_i \langle \varphi_i | \hat{h} | \varphi_i \rangle + \frac{1}{2} \sum_{ij} \langle \varphi_i \varphi_j | | \varphi_i \varphi_j \rangle + V_{nn}$$

- .. and is minimized under the **constraint** of orthonormal orbitals

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$$

- This is normally done by the introduction of **Lagrange multipliers**

$$L^{HF} [\{\varphi_i\}] = E^{HF} [\{\varphi_i\}] - \sum_{ij} \lambda_{ij} \{ \langle \varphi_i | \varphi_j \rangle - \delta_{ij} \}$$

- Is it possible to achieve minimization without constraints ?



Hartree-Fock theory in second quantization

Parametrization

- Suppose that we generate the optimized orbitals by transforming the initial orthonormal set $\{\varphi_p\}_{p=1}^M$

$$\tilde{\varphi}_p = \sum_q \varphi_q c_{qp}$$

and use the expansion coefficients $\{c_{qp}\}$ as variational parameters ?

- In order to preserve orthonormality the expansion coefficients must obey

$$\langle \tilde{\varphi}_p | \tilde{\varphi}_q \rangle = \sum_{rs} \langle \varphi_r c_{rp} | \varphi_s c_{sq} \rangle = \sum_{rs} \underbrace{\langle \varphi_r | \varphi_s \rangle}_{\delta_{rs}} c_{rp}^* c_{sq} = \sum_r c_{rp}^* c_{rq} = \delta_{pq}$$

- ..which means that they must form a unitary (orthogonal) matrix for complex (real) orbitals: $C^\dagger C = I$
- This adds $\frac{1}{2}M(M+1)$ constraints, and so we can not vary the coefficients **freely**.

Hartree-Fock theory in second quantization

Matrix exponentials

- We can, however, circumvent these constraints by writing the matrix as an **exponential** of another matrix

$$U = \exp(A)$$

- You recall (I hope) that the exponential of a (complex or real) number is

$$\exp(a) = e^a = \sum_{k=0}^{\infty} \frac{a^k}{k!}$$

- We have some simple rules, e.g.

$$e^a e^b = e^{a+b}; \quad \Rightarrow e^{-a} e^a = 1$$

- With matrices we have to be more careful, because, like operators, they generally do not commute.

Hartree-Fock theory in second quantization

Matrix exponentials

- In perfect analogy with numbers we define

$$\exp(A) = \sum_{k=0}^{\infty} \frac{A^k}{k!}$$

- We next consider the product

$$\exp(A) \exp(B) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{A^m}{m!} \frac{B^n}{n!}$$

- We rearrange to collect contribution of order $k = m + n$

$$\exp(A) \exp(B) = \sum_{k=0}^{\infty} \sum_{m=0}^k \frac{A^m}{m!} \frac{B^{k-m}}{(k-m)!} = \sum_{k=0}^{\infty} \frac{1}{k!} \sum_{m=0}^k \binom{k}{m} A^m B^{k-m}$$

- With numbers, we obtain our desired result $e^a e^b = e^{a+b}$ by recognizing that

$$(a + b)^k = \sum_{m=0}^k \binom{k}{m} a^m b^{k-m}; \quad \binom{k}{m} = \frac{k!}{m! (k-m)!}$$

Hartree-Fock theory in second quantization

Matrix exponentials

- With matrices this does not work, for instance

$$(A + B)^2 = A^2 + AB + BA + B^2 \neq A^2 + 2AB + B^2$$

since, generally $[A, B] \neq 0$

- However, $[A, (-A)] = 0$, so we can use this rule to obtain that

$$\exp(A) \exp(-A) = I; \quad [\exp(A)]^{-1} = \exp(-A)$$

- It is also straightforward to show that

$$\exp(A)^\dagger = \exp(A^\dagger)$$

- A unitary matrix is defined by $U^{-1} = U^\dagger$ which is obtained by using an **anti-Hermitian** A

$$A^\dagger = -A$$

Hartree-Fock theory in second quantization

Exponential parametrization

- We avoid Lagrange multipliers (constraints) by expressing the optimized orbitals as

$$\tilde{\varphi}_p = \sum_q \varphi_q U_{qp}; \quad U = \exp(-\kappa); \quad \kappa^\dagger = -\kappa$$

- I will now show that this corresponds to writing the optimized HF occupation-number vector as

$$|\tilde{0}\rangle = \exp(-\hat{\kappa}) |0\rangle$$

- where $\hat{\kappa}$ is an **orbital rotation operator** with amplitudes κ_{pq}

$$\hat{\kappa} = \sum_{pq} \kappa_{pq} \hat{a}_p^\dagger \hat{a}_q; \quad \kappa_{pq} = -\kappa_{qp}^*$$

Hartree-Fock theory in second quantization

Exponential parametrization

- We start by the expansion

$$|\tilde{0}\rangle = \exp(-\hat{\kappa})|0\rangle = \exp(-\hat{\kappa})a_1^\dagger a_2^\dagger \dots a_N^\dagger |vac\rangle$$

- Next, we insert $\exp(\hat{\kappa})\exp(-\hat{\kappa}) = 1$ everywhere

$$\begin{aligned} |\tilde{0}\rangle &= \exp(-\hat{\kappa})a_1^\dagger \exp(\hat{\kappa})\exp(-\hat{\kappa})a_2^\dagger \exp(\hat{\kappa}) \dots \exp(-\hat{\kappa})a_N^\dagger \exp(\hat{\kappa})\exp(-\hat{\kappa})|vac\rangle \\ &= \tilde{a}_1^\dagger \tilde{a}_2^\dagger \dots \tilde{a}_N^\dagger \exp(-\hat{\kappa})|vac\rangle; \quad \tilde{a}_r^\dagger = \exp(-\hat{\kappa})a_r^\dagger \exp(\hat{\kappa}) \end{aligned}$$

- First, we note that

$$\begin{aligned} \hat{\kappa}|vac\rangle &= \sum_{pq} \kappa_{pq} a_p^\dagger a_q |vac\rangle = 0; \\ \Rightarrow \exp(-\hat{\kappa})|vac\rangle &= \left(1 - \hat{\kappa} + \frac{1}{2}\hat{\kappa}^2 - \dots\right)|vac\rangle = |vac\rangle \end{aligned}$$

Hartree-Fock theory in second quantization

Baker-Campbell-Hausdorff expansion



Baker



Campbell



Hausdorff

- We next use the **Baker-Campbell-Hausdorff expansion**

$$\exp(A)B \exp(-A) = B + [A, B] + \frac{1}{2} [A, [A, B]] + \dots = \sum_{k=0}^{\infty} \frac{1}{k!} [A, B]^{(k)}$$

- **Proof:** We introduce $f(\lambda) = \exp(\lambda A)B \exp(-\lambda A)$ and note that
 - ▶ $f(0) = B$
 - ▶ $f(1) = \exp(A)B \exp(-A)$
 - ▶ Taylor expand: $f(1) = f(0) + f'(0) + \frac{1}{2}f''(0) + \dots$

Hartree-Fock theory in second quantization

Transformed creation operator

- Using the BCH expansion with $A = -\hat{\kappa}$ and $B = a_r^\dagger$ we get

$$\tilde{a}_r^\dagger = \exp(-\hat{\kappa}) a_r^\dagger \exp(\hat{\kappa}) = a_r^\dagger - [\hat{\kappa}, a_r^\dagger] + \frac{1}{2} [\hat{\kappa}, [\hat{\kappa}, a_r^\dagger]] - \dots$$

- To evaluate the commutator $[\hat{\kappa}, a_r^\dagger]$ we use our rule

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

- ..which gives

$$[\hat{\kappa}, a_r^\dagger] = \sum_{pq} \kappa_{pq} [a_p^\dagger a_q, a_r^\dagger] = \sum_{pq} \kappa_{pq} \left\{ a_p^\dagger \underbrace{[a_q, a_r^\dagger]_+}_{\delta_{qr}} - \underbrace{[a_p^\dagger, a_r^\dagger]_+}_0 a_q \right\} = \sum_p \kappa_{pr} a_p^\dagger$$

Hartree-Fock theory in second quantization

Transformed creation operator

- We proceed to the next commutator

$$\left[\hat{\kappa}, \left[\hat{\kappa}, a_r^\dagger \right] \right] = \sum_p \kappa_{pr} \left[\hat{\kappa}, a_p^\dagger \right] = \sum_{pq} \kappa_{pr} \kappa_{qp} a_q^\dagger = \sum_q (\kappa^2)_{qr} a_q^\dagger$$

- We start to see a pattern

$$\begin{aligned} \tilde{a}_r^\dagger &= a_r^\dagger - \left[\hat{\kappa}, a_r^\dagger \right] + \frac{1}{2} \left[\hat{\kappa}, \left[\hat{\kappa}, a_r^\dagger \right] \right] - \dots \\ &= a_r^\dagger - \sum_p \kappa_{pr} a_p^\dagger + \frac{1}{2} \sum_q (\kappa^2)_{qr} a_q^\dagger - \dots \\ &= \sum_p \left(\delta_{pr} - \kappa_{pr} + \frac{1}{2} (\kappa^2)_{pr} - \dots \right) a_p^\dagger \\ &= \sum_p a_p^\dagger \{ \exp [-\kappa] \}_{pr} \end{aligned}$$

Hartree-Fock theory in second quantization

Transformed creation operator

- To connect to orbital rotations we recall the formula

$$a_p^\dagger = \int \hat{\psi}^\dagger(\mathbf{r}) \varphi_p(\mathbf{r}) d^3\mathbf{r}$$

- ...from which we obtain

$$\tilde{a}_r^\dagger = \sum_p a_p^\dagger \{\exp[-\kappa]\}_{pr} = \sum_p \int \hat{\psi}^\dagger(\mathbf{r}) \varphi_p(\mathbf{r}) \{\exp[-\kappa]\}_{pr} d^3\mathbf{r} = \int \hat{\psi}^\dagger(\mathbf{r}) \tilde{\varphi}_r(\mathbf{r}) d^3\mathbf{r}$$

- which provides the connection

$$|\tilde{0}\rangle = \exp(-\hat{\kappa})|0\rangle \quad \Rightarrow \quad \tilde{\varphi}_r(\mathbf{r}) = \sum_p \varphi_p(\mathbf{r}) \{\exp[-\kappa]\}_{pr}$$

Density functional theory in second quantization

- The central quantity of DFT is the (charge) density $\rho(\mathbf{r})$
- It is an **observable** and therefore expressible as an expectation value

$$\rho(\mathbf{r}) = -e \left\langle \Psi \left| \sum_{i=1}^N \delta^3(\mathbf{r}_i - \mathbf{r}) \right| \Psi \right\rangle$$

- In second quantization the charge density operator is

$$\begin{aligned} \hat{\rho}(\mathbf{r}) &= -e \int \hat{\psi}^\dagger(\mathbf{r}') \delta^3(\mathbf{r}' - \mathbf{r}) \hat{\psi}(\mathbf{r}') d^3\mathbf{r}' = -e \sum_{pq} \left\langle \varphi_p \left| \delta^3(\mathbf{r}' - \mathbf{r}) \right| \varphi_q \right\rangle a_p^\dagger a_q \\ &= -e \sum_{pq} \Omega_{pq}(\mathbf{r}) a_p^\dagger a_q; \quad \Omega_{pq}(\mathbf{r}) = \varphi_p^\dagger(\mathbf{r}) \varphi_q(\mathbf{r}) \end{aligned}$$

- Just as in Hartree-Fock we may choose an exponential parametrization for the Kohn-Sham determinant

$$|\tilde{0}\rangle = \exp(-\hat{\kappa}) |0\rangle$$

- such that the charge density is parametrized as

$$\tilde{\rho}(\mathbf{r}, \kappa) = -e \sum_{pq} \varphi_p^\dagger(\mathbf{r}) \varphi_q(\mathbf{r}) \left\langle \tilde{0} \left| a_p^\dagger a_q \right| \tilde{0} \right\rangle = -e \sum_{pq} \Omega_{pq}(\mathbf{r}) D_{pq}(\kappa)$$

Wave-function based correlation methods

- Hartree-Fock theory is the starting point for wave-function based correlation methods in that

$$E^{\text{"exact"}} = E^{\text{HF}} + E^{\text{corr}}$$

- This is where second quantization really shows its teeth



- The **Configuration Interaction** (CI) method employs a **linear** parametrization

$$|CI\rangle = (1 + \hat{C}) |HF\rangle; \quad \hat{C} = \sum_{ia} c_i^a a_a^\dagger a_i + \frac{1}{4} \sum_{ijab} c_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + \dots$$

- The **Coupled Cluster** (CC) method employs an **exponential** parametrization

$$|CC\rangle = \exp(\hat{T}) |HF\rangle; \quad \hat{T} = \sum_{ia} t_i^a a_a^\dagger a_i + \frac{1}{4} \sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + \dots$$

Matrix elements

- Calculating the matrix element of a one-electron operator $\hat{\Omega}$ for a two-electron system ($N = 2$):

$$\langle \mathbf{m} | \hat{\Omega} | \mathbf{n} \rangle = \sum_{pq} \Omega_{pq} \langle \mathbf{m} | a_p^\dagger a_q | \mathbf{n} \rangle; \quad |\mathbf{m}\rangle = a_r^\dagger a_s^\dagger |vac\rangle; \quad |\mathbf{n}\rangle = a_t^\dagger a_u^\dagger |vac\rangle$$

- .. amounts to evaluating the vacuum expectation value

$$\langle vac | a_s a_r a_p^\dagger a_q a_t^\dagger a_u^\dagger | vac \rangle$$

- Based on the relations

$$\hat{a}_p |vac\rangle = \mathbf{0}, \quad \forall \hat{a}_p; \quad \langle vac | \hat{a}_p^\dagger = \mathbf{0}; \quad \forall \hat{a}_p^\dagger$$

- our strategy will be to move creation operators to the left and annihilation operators to the right, that is, we bring the operator string on **normal-ordered form**.

- We start by using our commutator rule

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

- .. to obtain

$$\begin{aligned}\langle vac | a_s a_r a_p^\dagger a_q a_t^\dagger a_u^\dagger | vac \rangle &= \langle vac | \left(a_p^\dagger a_s a_r + [a_s a_r, a_p^\dagger] \right) a_q a_t^\dagger a_u^\dagger | vac \rangle \\ &= \langle vac | \left(a_s [a_r, a_p^\dagger]_+ - [a_s, a_p^\dagger]_+ a_r \right) a_q a_t^\dagger a_u^\dagger | vac \rangle \\ &= \langle vac | (a_s \delta_{rp} - \delta_{sp} a_r) a_q a_t^\dagger a_u^\dagger | vac \rangle\end{aligned}$$

Matrix elements

- We next develop an analogous commutator rule

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

- .. such that

$$\begin{aligned}\langle vac | a_s a_r a_p^\dagger a_q a_t^\dagger a_u^\dagger | vac \rangle &= \langle vac | (a_s \delta_{rp} - \delta_{sp} a_r) \left(a_t^\dagger a_u^\dagger a_q + [a_q, a_t^\dagger a_u^\dagger] \right) | vac \rangle \\ &= \langle vac | (a_s \delta_{rp} - \delta_{sp} a_r) \left([a_q, a_t^\dagger]_+ a_u^\dagger - a_t^\dagger [a_q, a_u^\dagger]_+ \right) | vac \rangle \\ &= \langle vac | (a_s \delta_{rp} - \delta_{sp} a_r) \left(\delta_{qt} a_u^\dagger - a_t^\dagger \delta_{qu} \right) | vac \rangle\end{aligned}$$

- The final expression is

$$\langle vac | a_s a_r a_p^\dagger a_q a_t^\dagger a_u^\dagger | vac \rangle = \delta_{rp} \delta_{qt} \delta_{su} - \delta_{rp} \delta_{qu} \delta_{st} - \delta_{sp} \delta_{qt} \delta_{ru} + \delta_{sp} \delta_{qu} \delta_{rt}$$

- .. and the matrix element evaluates to

$$\langle \mathbf{m} | \hat{\Omega} | \mathbf{n} \rangle = \langle \varphi_r \varphi_s | \hat{\Omega} | \varphi_t \varphi_u \rangle = \Omega_{rt} \delta_{su} - \Omega_{ru} \delta_{st} - \Omega_{st} \delta_{ru} + \Omega_{su} \delta_{rt}$$

- We quickly run out of steam; we need more powerful tools !

Let us bring out some bigger guns...



(Wick'ed guys)

Normal-ordering

Definition

- Writing an operator string $\hat{O}$ on normal-ordered form $\{\hat{O}\}$ corresponds to moving all creation operators to the left and all annihilation operators to the right *as if they all anticommuted*, e.g.

$$\{a_p a_q\} = a_p a_q; \quad \{a_p^\dagger a_q^\dagger\} = a_p^\dagger a_q^\dagger$$

$$\{a_p^\dagger a_q\} = a_p^\dagger a_q; \quad \{a_p a_q^\dagger\} = -a_q^\dagger a_p$$

- A more complicated example is

$$\{a_s a_r a_p^\dagger a_q a_t^\dagger a_u^\dagger\} = \{a_{\textcolor{red}{p}}^\dagger a_s a_r a_q a_t^\dagger a_u^\dagger\} = -\{a_p^\dagger a_{\textcolor{red}{t}}^\dagger a_s a_r a_q a_u^\dagger\} = a_p^\dagger a_t^\dagger a_{\textcolor{red}{u}}^\dagger a_s a_r a_q$$

- The vacuum expectation value of a normal-ordered operator string is **zero**

$$\langle vac | \{\hat{O}\} | vac \rangle = 0$$

Contraction

- A **contraction** is defined as

$$\overline{xy} = xy - \{xy\}$$

- There are four possible combinations

$$\begin{aligned}\overline{a_p^\dagger a_q^\dagger} &= a_p^\dagger a_q^\dagger - \{a_p^\dagger a_q^\dagger\} = a_p^\dagger a_q^\dagger - a_p^\dagger a_q^\dagger = 0 \\ \overline{a_p a_q} &= a_p a_q - \{a_p a_q\} = a_p a_q - a_p a_q = 0 \\ \overline{a_p^\dagger a_q} &= a_p^\dagger a_q - \{a_p^\dagger a_q\} = a_p^\dagger a_q - a_p^\dagger a_q = 0 \\ \overline{a_p a_q^\dagger} &= a_p a_q^\dagger - \{a_p a_q^\dagger\} = a_p a_q^\dagger + a_q^\dagger a_p = \delta_{pq}\end{aligned}$$

- The only non-zero contraction occurs when an annihilation operator appears to the left of a creation operator.

Wick's theorem



An operator string may be written
as a linear combination of normal-ordered strings.

$$\begin{aligned} ABC \dots XYZ &= \{ABC \dots XYZ\} \\ &+ \sum_{\text{singles}} \left\{ \overline{A}BC \dots XYZ \right\} \\ &+ \sum_{\text{doubles}} \left\{ \overline{AB}C \dots XYZ \right\} \\ &+ \dots \end{aligned}$$

Only fully contracted terms contribute to vacuum expectation values.

Wick's theorem: example

- Returning to our one-electron expectation value we find that

$$\begin{aligned}
 \langle vac | a_s a_r a_p^\dagger a_q a_t^\dagger a_u^\dagger | vac \rangle &= \langle vac | \overbrace{a_s a_r a_p^\dagger a_q a_t^\dagger a_u^\dagger}^{(1)} | vac \rangle \\
 &+ \langle vac | \overbrace{a_s a_r a_p^\dagger a_q a_t^\dagger}^{(2)} a_u^\dagger | vac \rangle \\
 &+ \langle vac | \overbrace{a_s a_r a_p^\dagger a_q a_t^\dagger}^{(3)} a_u^\dagger | vac \rangle \\
 &+ \langle vac | \overbrace{a_s a_r a_p^\dagger a_q a_t^\dagger}^{(4)} a_u^\dagger | vac \rangle
 \end{aligned}$$

- Signs of **fully contracted** contributions are given by $(-1)^k$ where k is the number of crossing lines.
- We again obtain

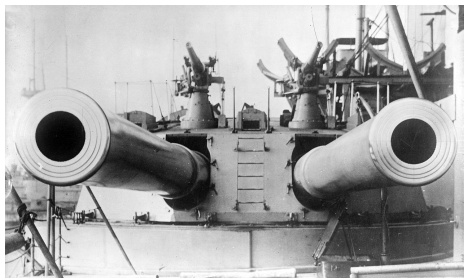
$$\langle vac | a_s a_r a_p^\dagger a_q a_t^\dagger a_u^\dagger | vac \rangle = \delta_{rp} \delta_{qt} \delta_{su} - \delta_{rp} \delta_{qu} \delta_{st} - \delta_{sp} \delta_{qt} \delta_{ru} + \delta_{sp} \delta_{qu} \delta_{rt}$$

Matrix elements

- We have seen that any matrix element over a string of creation- and annihilation operators can be expressed as a vacuum expectation value and then evaluated using Wick's theorem, e.g.

$$\langle \mathbf{m} | \hat{\Omega} | \mathbf{n} \rangle = \sum_{pq} \Omega_{pq} \langle \text{vac} | a_s a_r a_p^\dagger a_q^\dagger a_t^\dagger a_u^\dagger | \text{vac} \rangle$$

- However, with an increasing number N of electrons the operator strings become long and the evaluation tedious.
- We need even bigger guns



Let us look at the vacuum state

- We have seen that the vacuum expectation value of a normal-ordered string is zero.
- A prime example is

$$\langle vac | \hat{H} | vac \rangle = \langle vac | \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pq,rs} V_{pq,rs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r | vac \rangle = 0$$

(we dropped V_{nn})

- The vacuum state can be defined as the “empty” state

$$|vac\rangle = |0, 0, 0, \dots, 0\rangle,$$

- ..alternatively as the occupation-number vector for which

$$\hat{a}_p |vac\rangle = \mathbf{0}; \quad \forall \hat{a}_p$$

Particle-hole formalism

- Let us consider the occupation-number vector $|0\rangle$ corresponding to some reference determinant Φ_0 , e.g. the Hartree-Fock determinant.
- As before we introduce **orbital classes** with respect to this reference
 - ▶ occupied orbitals: $i, j, k, l, \dots$
 - ▶ virtual (unoccupied) orbitals: $a, b, c, d, \dots$

- We observe the following

$$a_a |0\rangle = a_i^\dagger |0\rangle = 0; \quad \forall a_a, a_i^\dagger$$

- ▶ with respect to the reference a_a and $a_i^\dagger$ act as annihilation operators
 - ▶ their conjugates $a_a^\dagger$ and a_i act as creation operators
 - ▶ $a_a^\dagger$ creates an electron (particle), whereas a_i creates a vacancy (hole)
- Using Wick's theorem, we will express all operators in terms of normal-ordering with respect to the new reference, the **Fermi vacuum**. This also changes the zero of energy.

The normal-ordered electronic Hamiltonian

One-electron part

- Using Wick's theorem the one-electron part of the Hamiltonian becomes

$$\hat{H}_1 = \sum_{pq} h_{pq} a_p^\dagger a_q = \sum_{pq} h_{pq} \left(\{a_p^\dagger a_q\}_0 + \{\overline{a_p^\dagger} a_q\}_0 \right)$$

- Recall that the only non-zero contraction appears when an annihilation operator appears to the left of a creation operator
- This only happens when both p and q refer to occupied orbitals, giving

$$\hat{H}_1 = \sum_{pq} h_{pq} \left(\{a_p^\dagger a_q\}_0 + \delta_{pq} \delta_{p \in i} \right) = \sum_{pq} h_{pq} \{a_p^\dagger a_q\}_0 + \sum_i h_{ii}$$

The normal-ordered electronic Hamiltonian

Two-electron part

- For the two-electron part

$$\hat{H} = \frac{1}{2} \sum_{pq,rs} V_{pq,rs} a_p^\dagger a_q^\dagger a_s a_r$$

non-zero contractions only occur if p or q refer to occupied orbitals such that the corresponding operators $\hat{a}_p^\dagger$ and $\hat{a}_q^\dagger$ are annihilators with respect to the Fermi vacuum.

- Non-zero double contractions are

$$\left\{ \overbrace{a_p^\dagger a_q^\dagger a_s a_r} \right\}_0 = -\delta_{p \in i} \delta_{ps} \delta_{q \in j} \delta_{qr}$$

$$\left\{ \overbrace{a_p^\dagger a_q^\dagger a_s a_r} \right\}_0 = \delta_{p \in i} \delta_{pr} \delta_{q \in j} \delta_{qs}$$

The normal-ordered electronic Hamiltonian

Two-electron part

- Non-zero single contractions are

$$\left\{ \overline{a_p^\dagger a_q^\dagger} a_s a_r \right\}_0 = - \left\{ \overline{a_p^\dagger a_s} a_q^\dagger a_r \right\}_0 = -\delta_{p \in i} \delta_{ps} \left\{ a_q^\dagger a_r \right\}_0$$

$$\left\{ \overline{a_p^\dagger a_q^\dagger} a_s a_r \right\}_0 = \left\{ \overline{a_p^\dagger a_r} a_q^\dagger a_s \right\}_0 = \delta_{p \in i} \delta_{pr} \left\{ a_q^\dagger a_s \right\}_0$$

$$\left\{ a_p^\dagger \overline{a_q^\dagger} a_s a_r \right\}_0 = \delta_{q \in i} \delta_{qs} \left\{ a_p^\dagger a_r \right\}_0$$

$$\left\{ a_p^\dagger \overline{a_q^\dagger} a_s a_r \right\}_0 = - \left\{ a_p^\dagger \overline{a_q^\dagger} a_r a_s \right\}_0 = -\delta_{q \in i} \delta_{qr} \left\{ a_p^\dagger a_s \right\}_0$$

The normal-ordered electronic Hamiltonian

..almost there

- From the non-zero double contractions we get

$$\frac{1}{2} \sum_{pq,rs} V_{pq,rs} (\delta_{p \in i} \delta_{pr} \delta_{q \in j} \delta_{qs} - \delta_{p \in i} \delta_{ps} \delta_{q \in j} \delta_{qr}) = \frac{1}{2} \sum_{ij} (V_{ij,ij} - V_{ij,ji}) = E_2^{HF}$$

- From the non-zero single contractions we get

$$\begin{aligned} & \frac{1}{2} \sum_{pq,rs} V_{pq,rs} \left(\delta_{p \in i} \delta_{pr} \left\{ a_q^\dagger a_s \right\}_0 - \delta_{p \in i} \delta_{ps} \left\{ a_q^\dagger a_r \right\}_0 \right) \\ & + \frac{1}{2} \sum_{pq,rs} V_{pq,rs} \left(\delta_{q \in i} \delta_{qs} \left\{ a_p^\dagger a_r \right\}_0 - \delta_{q \in i} \delta_{qr} \left\{ a_p^\dagger a_s \right\}_0 \right) \\ & = \frac{1}{2} \sum_{iq,s} V_{iq,is} \left\{ a_q^\dagger a_s \right\}_0 - \frac{1}{2} \sum_{iq,r} V_{iq,ri} \left\{ a_q^\dagger a_r \right\}_0 \\ & + \frac{1}{2} \sum_{pi,r} V_{pi,ri} \left\{ a_p^\dagger a_r \right\}_0 - \frac{1}{2} \sum_{pi,s} V_{pi,is} \left\{ a_p^\dagger a_s \right\}_0 \\ & = \sum_{pq,i} (V_{pi,qi} - V_{pi,iq}) \left\{ a_p^\dagger a_q \right\}_0 \end{aligned}$$

The normal-ordered electronic Hamiltonian

Final form

- The final form of the electronic Hamiltonian is

$$\begin{aligned}\hat{H} &= E^{HF} + \sum_{pq} \left(h_{pq} + \sum_i (V_{pi,qi} - V_{pi,iq}) \right) \{a_p^\dagger a_q\}_0 + \frac{1}{2} \sum_{pq,rs} V_{pq,rs} \{a_p^\dagger a_q^\dagger a_s a_r\}_0 \\ &= E^{HF} + \hat{H}_N\end{aligned}$$

- where appears the HF energy

$$E^{HF} = \langle 0 | \hat{H} | 0 \rangle = \sum_i h_{ii} + \frac{1}{2} \sum_{ij} (V_{ij,ij} - V_{ij,ji})$$

- and the **normal-ordered electronic Hamiltonian**

$$\hat{H}_N = \sum_{pq} f_{pq} \{a_p^\dagger a_q\}_0 + \frac{1}{2} \sum_{pq,rs} V_{pq,rs} \{a_p^\dagger a_q^\dagger a_s a_r\}_0 = \hat{H} - \langle 0 | \hat{H} | 0 \rangle$$

- This result can be generalized: $\hat{\Omega}_N = \hat{\Omega} - \langle 0 | \hat{\Omega} | 0 \rangle$

Final words

- The second quantization formalism provides a powerful language for the formulation and implementation of quantum chemical methods
- Matrix elements over second quantized operators split into integrals over the operator in the chosen orbital basis and a vacuum expectation value.
- For the formulation of wave-function based electron correlation methods second quantization becomes an indispensable tool.
- Further sophistication is provided by Wick's theorem, the particle-hole formalism and ...

