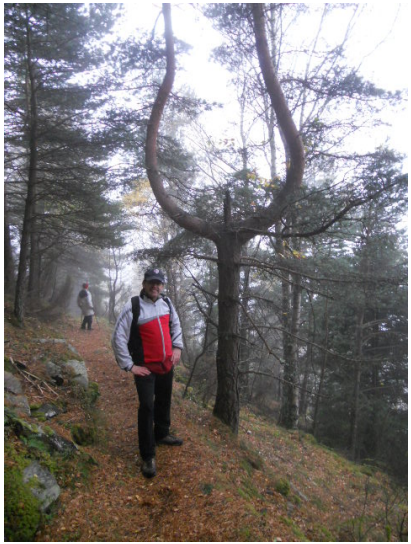

Second quantization

Applications

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Where we stopped last time

- Second quantization starts from **field operators** $\psi^\dagger(1)$, $\psi(1)$ 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**

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

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

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

- Electrons are spin-$\frac{1}{2}$ particles with spin functions denoted $|\alpha\rangle = \left|\frac{1}{2}, \frac{1}{2}\right\rangle$ and $|\beta\rangle = \left|\frac{1}{2}, -\frac{1}{2}\right\rangle$. 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

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

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

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

Spin in second quantization

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

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

- Operator algebra

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

- .. 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

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

- 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 possibilites

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

- 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

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

- .. 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

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

- 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 coeffients 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 $k = m + n$

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

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

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

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

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

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

$$A^\dagger = -A$$

- 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

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

- 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

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

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

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

- First, we note that

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

Hartree-Fock theory in second quantization

Baker-Campbell-Hausdorff expansion

Baker

Campbell

Hausdorff

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

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

- **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: $f(1) = f(0) + f'(0) + \frac{1}{2}f''(0) + \ldots$

Hartree-Fock theory in second quantization

Transformed creation operator

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

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

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

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

- ..which gives

$$\left[\hat{\kappa}, a_r^\dagger\right] = \sum_{pq} \kappa_{pq}\left[a_p^\dagger a_q, a_r^\dagger\right] = \sum_{pq} \kappa_{pq}\left\{a_p^\dagger \underbrace{\left[a_q, a_r^\dagger\right]_+}_{\delta_{qr}} - \underbrace{\left[a_p^\dagger, a_r^\dagger\right]_+}_{0} a_q\right\} = \sum_p \kappa_{pr} a_p^\dagger$$

Hartree-Fock theory in second quantization

Transformed creation operator

- We proceed to the next commutator

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

- We start to see a pattern

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

Hartree-Fock theory in second quantization

Transformed creation operator

- To connect to orbital rotations we recall the formula

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

- ...from which we obtain

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

- which provides the connection

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

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

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

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

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

- 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

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

- This is where second quantization really shows its teeth

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

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

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

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

Matrix elements

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

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

- .. 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**.

Matrix elements

- We start by using our commutator rule

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

- .. to obtain

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

Matrix elements

- We next develop an analogous commutator rule

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

- .. such that

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

- The final expression is

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

- The final expression is

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

- 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 $\left\{\hat{O}\right\}$ corresponds to moving all creation operators to the left and all annihilation operators to the left *as if they all anticommuted, e.g.*

$$\{a_p a_q\} = a_p a_q; \qquad \left\{a_p^\dagger a_q^\dagger\right\} = a_p^\dagger a_q^\dagger$$

$$\left\{a_p^\dagger a_q\right\} = a_p^\dagger a_q; \qquad \left\{a_p a_q^\dagger\right\} = -a_q^\dagger a_p$$

- A more complicated example is

$$\left\{a_s a_r a_p^\dagger a_q a_t^\dagger a_u^\dagger\right\} = \left\{a_p^\dagger a_s a_r a_q a_t^\dagger a_u^\dagger\right\} = -\left\{a_p^\dagger a_t^\dagger a_s a_r a_q a_u^\dagger\right\} = a_p^\dagger a_t^\dagger a_u^\dagger a_s a_r a_q$$

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

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

Contraction

- A **contraction** is defined as

$$\overbracket{xy} = xy - \{xy\}$$

- There are four possible combinations

$$\begin{aligned}
\overbracket{a_p^\dagger a_q^\dagger} &= a_p^\dagger a_q^\dagger - \left\{a_p^\dagger a_q^\dagger\right\} = a_p^\dagger a_q^\dagger - a_p^\dagger a_q^\dagger = 0 \\
\overbracket{a_p a_q} &= a_p a_q - \{a_p a_q\}_v = a_p a_q - a_p a_q = 0 \\
\overbracket{a_p^\dagger a_q} &= a_p^\dagger a_q - \left\{a_p^\dagger a_q\right\} = a_p^\dagger a_q - a_p^\dagger a_q = 0 \\
\overbracket{a_p a_q^\dagger} &= a_p a_q^\dagger - \left\{a_p a_q^\dagger\right\} = a_p a_q^\dagger + a_q^\dagger a_p = \delta_{pq}
\end{aligned}$$

- 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.

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

Only fully contracted terms contribute to vacuum expectation values.

Wick's theorem: example

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

$$\begin{aligned}
\langle vac|a_s a_r a_p^\dagger a_q a_t^\dagger a_u^\dagger|vac\rangle &= \langle vac|\overbrace{a_s a_r a_p^\dagger a_q a_t^\dagger a_u^\dagger}|vac\rangle \\
&+ \langle vac|\overbrace{a_s a_r a_p^\dagger a_q a_t^\dagger a_u^\dagger}|vac\rangle \\
&+ \langle vac|\overbrace{a_s a_r a_p^\dagger a_q a_t^\dagger a_u^\dagger}|vac\rangle \\
&+ \langle vac|\overbrace{a_s a_r a_p^\dagger a_q a_t^\dagger a_u^\dagger}|vac\rangle
\end{aligned}$$

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

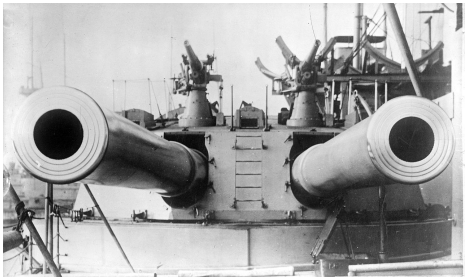
$$\langle vac|a_s a_r a_p^\dagger a_q a_t^\dagger a_u^\dagger|vac\rangle = \delta_{rp}\delta_{qt}\delta_{su} - \delta_{rp}\delta_{qu}\delta_{st} - \delta_{sp}\delta_{qt}\delta_{ru} + \delta_{sp}\delta_{qu}\delta_{rt}$$

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.

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

- 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

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

- ..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: $i, j, k, l, \ldots$
  - virtual (unoccupied) orbitals: $a, b, c, d, \ldots$
- 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

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

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

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

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

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

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

The normal-ordered electronic Hamiltonian

Two-electron part

- Non-zero single contractions are

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

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

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

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

The normal-ordered electronic Hamiltonian

..almost there

- From the non-zero double contractions we get

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

- From the non-zero single contractions we get

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

The normal-ordered electronic Hamiltonian

Final form

- The final form of the electronic Hamiltonian is

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

- 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**

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

- 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 ...