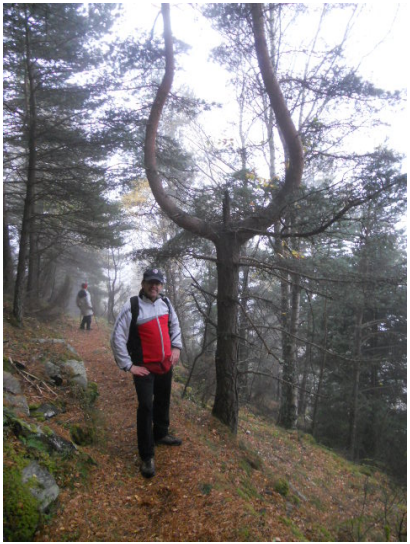

Second quantization

Applications

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

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- 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 $\hat{s}_z$

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

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- It is also convenient to introduce **step operators** $\hat{s}_+ = \hat{s}_x + i\hat{s}_y$ and $\hat{s}_- = \hat{s}_x - i\hat{s}_y$

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- 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

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

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- 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

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

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- .. shows that

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

Hartree-Fock theory in second quantization

Reference ONV and orbital classes

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  - general orbitals: $p, q, r, s, \dots$

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Hartree-Fock energy

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

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- We conclude

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

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

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- 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

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

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- Is it possible to achieve minimization without constraints ?

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

- 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 ?

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- In order to preserve orthonormality the expansion coeffients must obey

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

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- ..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.

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

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- 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

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

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

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- 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

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

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- 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

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- We start by the expansion

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

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

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- First, we note that

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

Hartree-Fock theory in second quantization

Baker-Campbell-Hausdorff expansion

Baker

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Hausdorff

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

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

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  - $f(1) = \exp(A)B\exp(-A)$
  - 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

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

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

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

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- ..which gives

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

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- We start to see a pattern

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

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Transformed creation operator

- To connect to orbital rotations we recall the formula

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

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- which provides the connection

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

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- 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

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

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

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

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- 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 ($N = 2$):

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

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- 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

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

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- .. to obtain

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

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- We next develop an analogous commutator rule

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- 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.*

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

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- A more complicated example is

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

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

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

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Only fully contracted terms contribute to vacuum expectation values.

Wick's theorem: example

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

$$
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- 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.

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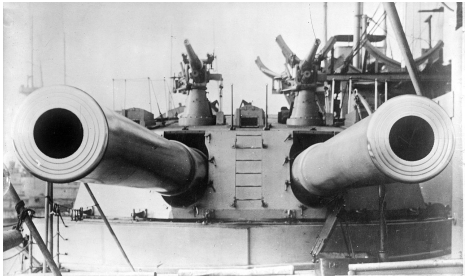
- We need even bigger guns



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

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  - $a_a^\dagger$ 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

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

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- Recall that the only non-zero contraction appears when a annihilation operator appears to the left of a creation operator

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- 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

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

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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.

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- Non-zero double contractions are

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

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The normal-ordered electronic Hamiltonian

..almost there

- From the non-zero double contractions we get

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

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+ \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

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

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

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

Final words

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