



Second quantization

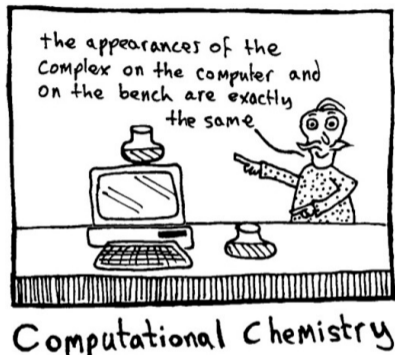
Basics

Trond Saue

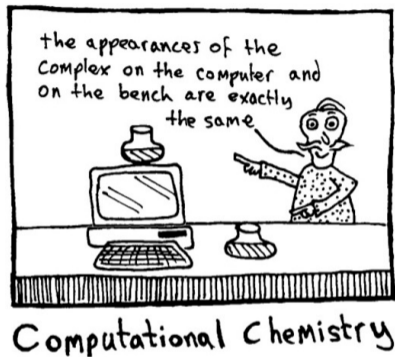
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Asking Nature ... and the computer

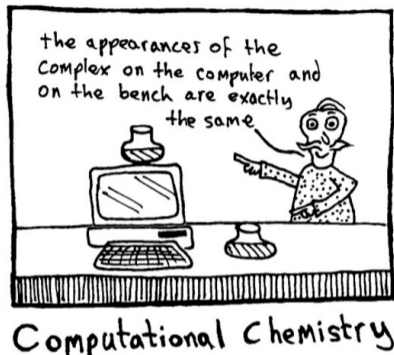


Asking Nature ... and the computer



To learn about the world

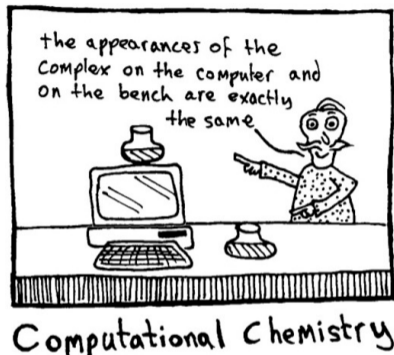
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- the **experimentalist** asks Nature using his experimental apparatus

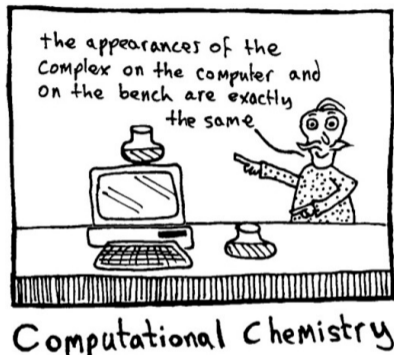
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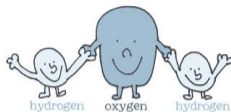
Asking Nature ... and the computer



To learn about the world

- the **experimentalist** asks Nature using his experimental apparatus
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- The most important operator is the **Hamiltonian**

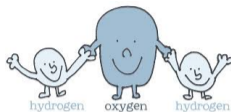
The molecular problem



- The time-independent molecular Schrödinger equation

$$\hat{H}^{mol}\Psi^{mol} = E^{tot}\Psi^{mol}$$

The molecular problem



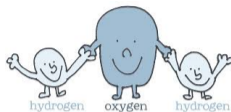
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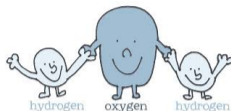
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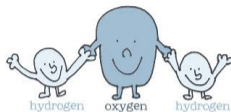
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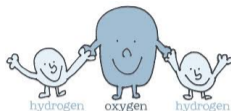
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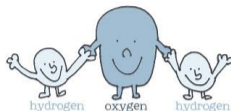
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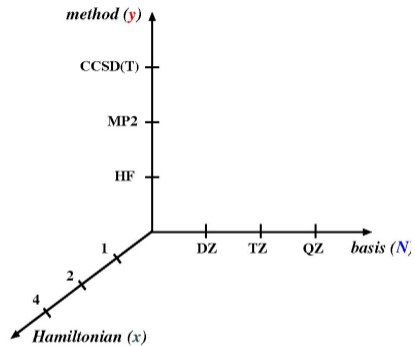
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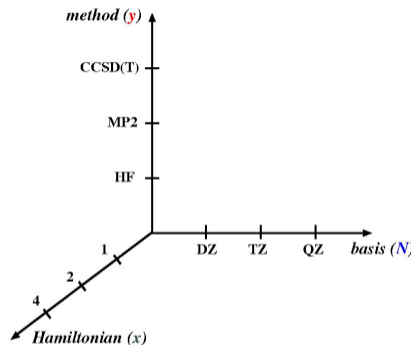
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- ... although many of us stop after the electronic part.

Theoretical model chemistries

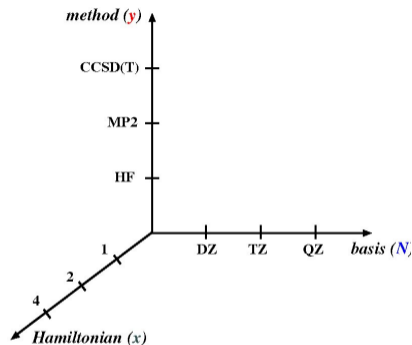


Theoretical model chemistries



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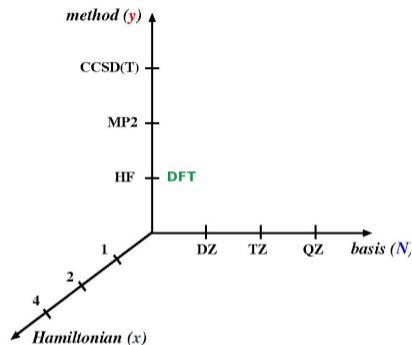
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- The constant term is

$$E_0 = \langle \Psi | V_{nn} | \Psi \rangle = V_{nn} \langle \Psi | \Psi \rangle = V_{nn}$$

which follows from the normalization of the wave function.

The electronic energy

One-electron energy

- We can simplify the one-electron energy

$$\begin{aligned} E_1 &= \sum_{i=1}^N \langle \Psi | \hat{h}(i) | \Psi \rangle \\ &= \sum_{i=1}^N \int \Psi^\dagger(1, 2, \dots, N) \hat{h}(i) \Psi(1, 2, \dots, N) d1d2 \dots dN \end{aligned}$$

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- We therefore pick one and multiply with the number N of electrons

$$E_1 = N \langle \Psi | \hat{h}(1) | \Psi \rangle$$

The electronic energy

Two-electron energy

- For the two-electron energy

$$\begin{aligned} E_2 &= \frac{1}{2} \sum_{i \neq j}^N \langle \Psi | \hat{g}(i, j) | \Psi \rangle \\ &= \frac{1}{2} \sum_{i \neq j}^N \int \Psi^\dagger(1, 2, \dots, N) \hat{g}(i, j) \Psi(1, 2, \dots, N) d1 d2 \dots dN \end{aligned}$$

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- We can therefore write

$$E_2 = \frac{1}{2} N(N - 1) \langle \Psi | \hat{g}(1, 2) | \Psi \rangle$$

where $\frac{1}{2} N(N - 1)$ is the number of electron pairs.

The electronic Hamiltonian

1-electron density matrix

- The one-electron Hamiltonian can be split into a free-electron part (kinetic energy) and a term describing the electron-nucleus interaction

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$$\begin{aligned}\langle \hat{V}_{eN} \rangle &= N \int \Psi^\dagger(1, 2, \dots, N) \hat{v}_{eN}(1) \Psi(1, 2, \dots, N) d1 d2 \dots dN \\ &= N \int \hat{v}_{eN}(1) \Psi^\dagger(1, 2, \dots, N) \Psi(1, 2, \dots, N) d1 d2 \dots dN \\ &= \int \hat{v}_{eN}(1) n_1(1; 1) d1\end{aligned}$$

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- where we have introduced the **one-electron density matrix**

$$n_1(1; 1') = N \int \Psi^\dagger(1, 2, \dots, N) \Psi(1', 2, \dots, N) d2 \dots dN$$

The electronic Hamiltonian

2-electron density matrix

- The kinetic part \hat{h}_0 is in general not multiplicative, but we can write the expectation value of kinetic energy in terms of the one-electron density matrix by a trick

$$\begin{aligned}\langle \hat{T}_e \rangle &= N \int \Psi^\dagger(1, 2, \dots, N) \hat{h}_0(1) \Psi(1, 2, \dots, N) d1 d2 \dots dN \\ &= \int [\hat{h}_0(1') n(1; 1')]_{1' \rightarrow 1} d1\end{aligned}$$

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- The expectation value of the two-electron interaction

$$\begin{aligned}\langle \hat{V}_{ee} \rangle &= \frac{1}{2} N(N-1) \int \Psi^\dagger(1, 2, \dots, N) \hat{g}(1, 2) \Psi(1, 2, \dots, N) d1 d2 \dots dN \\ &= \frac{1}{2} \int \hat{g}(1, 2) n_2(1, 2; 1, 2) d1 d2\end{aligned}$$

may be expressed in terms of the **two-electron density matrix**

$$n_2(1, 2; 1', 2') = N(N-1) \int \Psi^\dagger(1, 2, \dots, N) \Psi(1', 2', \dots, N) d3 \dots dN$$

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What is needed to calculate the energy?

- This exercise has shown that in order to calculate the electronic energy we do not need the full wave function in terms of N electron coordinates

The electronic energy

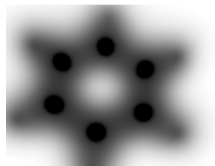
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 - ▶ It suffices to have:
 - ★ the near-diagonal elements of the one-electron density matrix
 - ★ the diagonal elements of the two-electron density matrix.

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 - ★ the diagonal elements of the two-electron density matrix.
- Density functional theory goes a big step further and proposes that we only need the electron density $\rho(\mathbf{r}) = -e \sum_{\text{spin}} n(1; 1)$



The electronic problem

- The generic form of the electronic Hamiltonian, relativistic or not, is

$$\hat{H} = \sum_{i=1}^n \hat{h}(i) + \frac{1}{2} \sum_{i \neq j}^n \hat{g}(i, j) + V_{NN}$$

and is supposed to specify our system.

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- The problematic term is the two-electron interaction $\hat{g}(i, j)$.
- Let us for a moment drop this term, as well as V_{NN} (a number), and consider a two-electron system

$$\left[\hat{h}(1) + \hat{h}(2) \right] \Psi(1, 2) = E\Psi(1, 2)$$

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Separation of variables

- We write the two-electron wave function as

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- Division by $\Psi(1, 2)$ gives

$$\frac{\{h(1)\varphi_a(1)\}}{\varphi_a(1)} + \frac{\{h(2)\varphi_b(2)\}}{\varphi_b(2)} = E$$

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- In order for this relation to hold for any choice of electron coordinates 1 and 2, we must have

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- ... is thereby converted into two wave equations for single electrons

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- The situation is even simpler ...

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Indistinguishability

- Electrons can not be distinguished,
so it suffices to solve a single wave equation

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- ▶ electrons are identical particles

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The exact wave function for a system of N *non-interacting* electrons is an antisymmetrized product of one-electron wave functions (orbitals).

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- This is achieved with **second quantization** !

First quantization

- The quantum-mechanical Hamiltonian \hat{H} is obtained from its classical counterpart, the Hamiltonian function $H \equiv H(\mathbf{r}, \mathbf{p})$, by replacing the dynamical variables (position \mathbf{r} and momentum \mathbf{p}) by operators:

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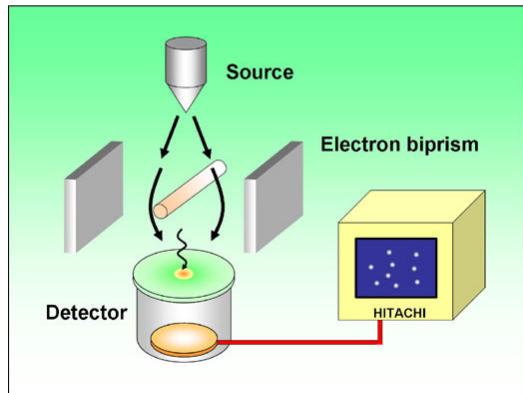
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- Quantization leads to discrete values of the energy E (as well as angular momentum etc.)

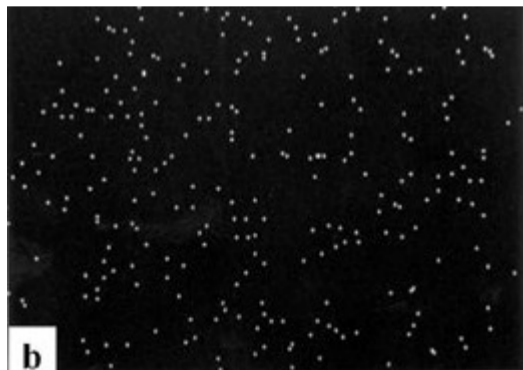
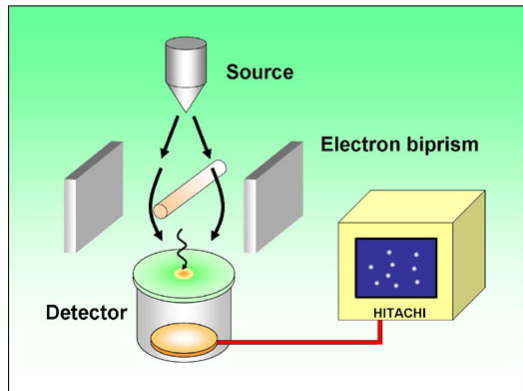
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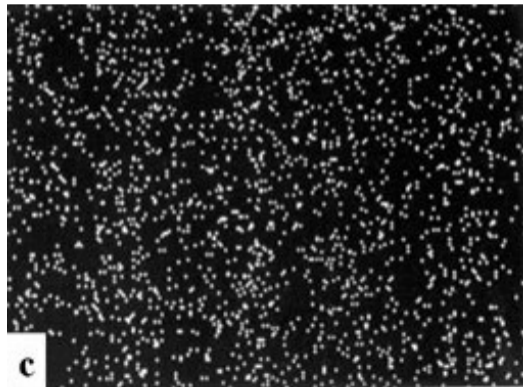
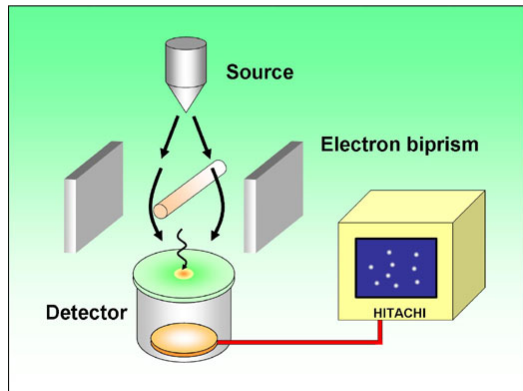
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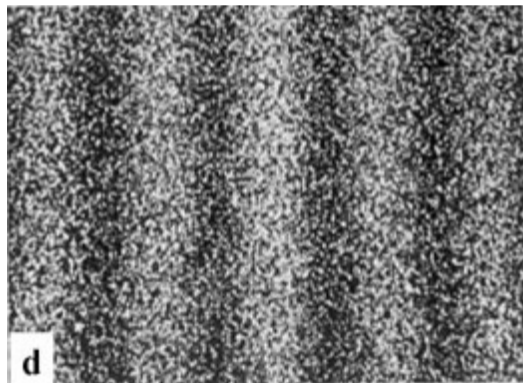
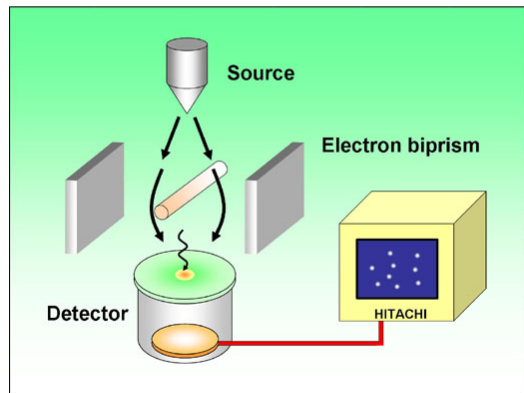
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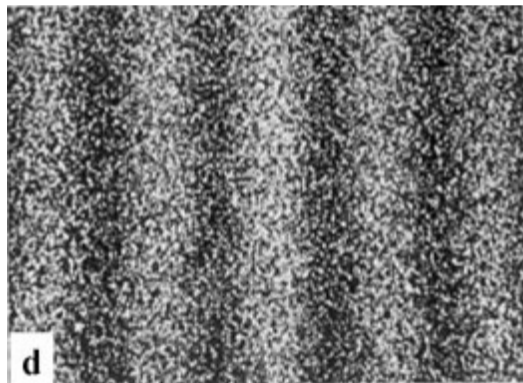
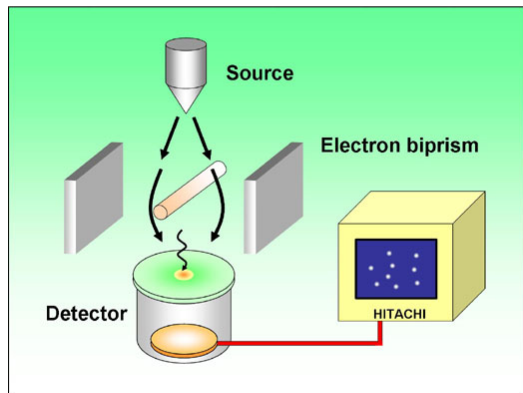
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- This leads to the normalization condition

$$\int \Psi^\dagger(1, 2, \dots, N) \Psi(1, 2, \dots, N) d1 d2 \dots dN = 1$$

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- ... in terms of operators $\hat{\psi}^\dagger(1)$ and $\hat{\psi}(1)$, creating and annihilating electron density amplitude at position 1, respectively.
- We want the total operator \hat{N} to return the particle number N , when acting on an object representing an N -electron system.

- In order to represent electrons (fermions) field operators must obey the following **anti-commutation** relations

$$\left[\hat{\psi}^\dagger(1), \hat{\psi}^\dagger(2) \right]_+ = \hat{\psi}^\dagger(1)\hat{\psi}^\dagger(2) + \hat{\psi}^\dagger(2)\hat{\psi}^\dagger(1) = 0$$

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- Bosons obey corresponding **commutator** relations.

Expansion of field operators

- Suppose that we have some orthonormal orbital basis $\{\varphi_p(\mathbf{1})\}_{p=1}^M$

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- This is perhaps easier seen using bracket notation, for instance

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- Remembering that the integral signs are like summation signs we obtain

$$\begin{aligned} \left[\hat{a}_p, \hat{a}_q^\dagger \right]_+ &= \int \int \varphi_p^\dagger(1) \varphi_q(2) \left[\hat{\psi}(1), \hat{\psi}^\dagger(2) \right]_+ d1 d2 \\ &= \int \int \varphi_p^\dagger(1) \varphi_q(2) \delta(1 - 2) d1 d2 \\ &= \int \varphi_p^\dagger(1) \varphi_q(1) d1 = \delta_{pq} \end{aligned}$$

Algebra of annihilation and creation operators

- We just found that (using an orthonormal basis)

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- In a similar manner we find that

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- ... where *occupation numbers* k_p are either 0 or 1,
since electrons are fermions.

Occupation-number vectors

Vacuum state and annihilation

- Another example is

$$\Phi_m(1, 2, 3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \varphi_4(1) \\ \varphi_1(2) & \varphi_2(2) & \varphi_4(2) \\ \varphi_1(3) & \varphi_2(3) & \varphi_4(3) \end{vmatrix} = |\varphi_1\varphi_2\varphi_4\rangle \rightarrow |\mathbf{m}\rangle = |1, 1, 0, 1\rangle$$

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- Annihilation operators reduce occupation numbers by one and therefore all give zero when acting on $|\text{vac}\rangle$

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

Occupation-number vectors

Vacuum state and annihilation

- Another example is

$$\Phi_m(1, 2, 3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \varphi_4(1) \\ \varphi_1(2) & \varphi_2(2) & \varphi_4(2) \\ \varphi_1(3) & \varphi_2(3) & \varphi_4(3) \end{vmatrix} = |\varphi_1\varphi_2\varphi_4\rangle \rightarrow |\mathbf{m}\rangle = |1, 1, 0, 1\rangle$$

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- This even serves as a definition of the vacuum state.

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Creation operators

- Creation operators increase occupation numbers by one

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- This follows directly from the special case

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Occupation-number vectors

More creation

- We can build ONVs corresponding to $N = 2$

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Fock space

..or occupation-number space

- Occupation number vectors (ONVs) have the general form

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and reside in a Fock space of dimension 2^M .

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- A special case

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- ▶ the dual vacuum state can therefore be defined by

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The number operator

- Notice that in Fock space there is no restriction on particle number N , except $N \leq M$.

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- The occupation number vectors are eigenvectors of the number operator.

Counting electrons

- The field operators do not relate to specific electrons; rather, they sample contributions to the **electron quantum field** in space



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- Quantum field theory explains why electrons are the same everywhere: they all belong to the same field !

The number operator

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- We may use a commutator rule such as

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

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- The algebra of creation and annihilation operators is, however, expressed in terms of anti-commutators

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- Our final result is thereby

$$\hat{N}\hat{a}_p^\dagger |\mathbf{k}\rangle = \left(\hat{a}_p^\dagger \hat{N} + [\hat{N}, \hat{a}_p^\dagger] \right) |\mathbf{k}\rangle = \hat{a}_p^\dagger (\hat{N} + 1) |\mathbf{k}\rangle = (N + 1) \hat{a}_p^\dagger |\mathbf{k}\rangle$$

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Counting electron pairs

- Let us have a look at the second quantization operator

$$\begin{aligned}\hat{N}_{pair} &= \frac{1}{2} \int \hat{\psi}^\dagger(1)\hat{\psi}^\dagger(2)\hat{\psi}(2)\hat{\psi}(1)d1d2 \\ &= \frac{1}{2} \sum_{pqrs} \left\{ \int \varphi_p^\dagger(1)\varphi_q^\dagger(2)\varphi_r(2)\varphi_s(1)d1d2 \right\} \hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_r\hat{a}_s \\ &= \frac{1}{2} \sum_{pqrs} \left\{ \int \varphi_p^\dagger(1)\varphi_s(1)d1 \int \varphi_q^\dagger(2)\varphi_r(2)d2 \right\} \hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_r\hat{a}_s \\ &= \frac{1}{2} \sum_{pqrs} \{\delta_{ps}\delta_{qr}\} \hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_r\hat{a}_s = \frac{1}{2} \sum_{pq} \hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_q\hat{a}_p\end{aligned}$$

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$$\begin{aligned}\hat{N}_{pair} &= \frac{1}{2} \int \hat{\psi}^\dagger(1)\hat{\psi}^\dagger(2)\hat{\psi}(2)\hat{\psi}(1)d1d2 \\ &= \frac{1}{2} \sum_{pqrs} \left\{ \int \varphi_p^\dagger(1)\varphi_q^\dagger(2)\varphi_r(2)\varphi_s(1)d1d2 \right\} \hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_r\hat{a}_s \\ &= \frac{1}{2} \sum_{pqrs} \left\{ \int \varphi_p^\dagger(1)\varphi_s(1)d1 \int \varphi_q^\dagger(2)\varphi_r(2)d2 \right\} \hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_r\hat{a}_s \\ &= \frac{1}{2} \sum_{pqrs} \{\delta_{ps}\delta_{qr}\} \hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_r\hat{a}_s = \frac{1}{2} \sum_{pq} \hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_q\hat{a}_p\end{aligned}$$

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$$\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_q\hat{a}_p = -\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_p\hat{a}_q = -\hat{a}_p^\dagger \left(\delta_{pq} - \hat{a}_p\hat{a}_q^\dagger \right) \hat{a}_q = \hat{a}_p^\dagger\hat{a}_p\hat{a}_q^\dagger\hat{a}_q - \delta_{pq}\hat{a}_p^\dagger\hat{a}_q$$

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- ...shows that it counts electron pairs

$$\hat{N}_{pair} = \frac{1}{2} \hat{N} (\hat{N} - 1)$$

What does the second-quantized electronic Hamiltonian look like?

- The first-quantized form

$$\hat{H} = \sum_{i=1}^N \hat{h}(i) + \frac{1}{2} \sum_{i \neq j}^N \hat{g}(i, j) + V_{NN}$$

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(notice the order of electron coordinates in the two-electron operator)

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- This gives a formula for finding the second-quantized form of any one- and two-electron operator.

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- **Data reduction:** $\mathbf{C} : \begin{pmatrix} M \\ N \end{pmatrix} \rightarrow \mathbf{D}/\mathbf{d} : M^2/M^4 \quad !!!$

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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.

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(data compression)