Second quantization

Basics

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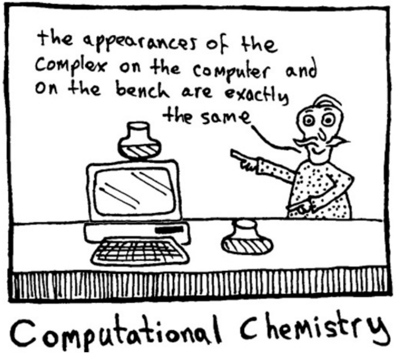
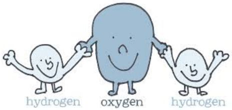
Asking Nature ... and the computer



To learn about the world

- the **experimentalist** asks Nature using his experimental apparatus
- the **theoretician** asks the wave function Ψ
  using mathematical operators $\hat{\Omega}$
- 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 Hamiltonian

$$\hat{H}^{mol} = \hat{T}_N + \hat{T}_e + V_{en} + V_{ee} + V_{nn}$$

  - $\hat{T}_N(\mathbf{R})$ - kinetic energy of nuclei
  - $\hat{T}_e(\mathbf{r})$ - kinetic energy of electrons
  - $V_{en}(\mathbf{r},\mathbf{R})$ - electron-nucleus interaction
  - $V_{ee}(\mathbf{r})$ - electron-electron interaction
  - $V_{nn}(\mathbf{R})$ - nucleus-nucleus interaction

Simplifications

- The Born-Oppenheimer approximation leads to a separation of the
  - electronic problem

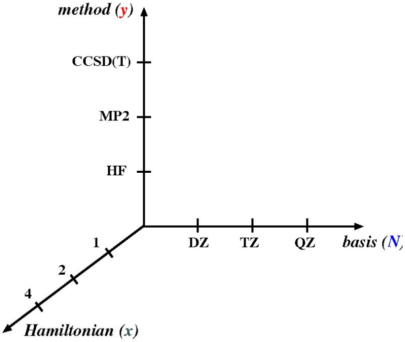
$$H^{el}\Psi^{el}(\mathbf{r};\mathbf{R}) = E^{el}(\mathbf{R})\Psi^{el}(\mathbf{r};\mathbf{R}); \quad H^{el} = \hat{T}_e + V_{en} + V_{ee} + V_{nn}$$

  - ... from the nuclear problem

$$\left[\hat{T}_N + E^{el}(\mathbf{R})\right]\chi(\mathbf{R}) = E^{tot}\chi(\mathbf{R})$$

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

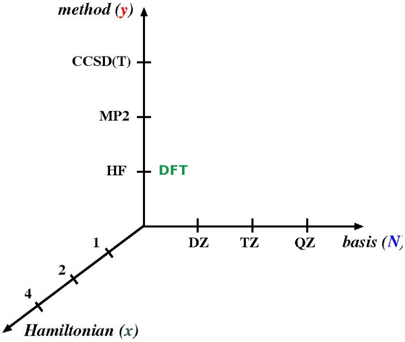
Theoretical model chemistries



$$\text{Electronic Hamiltonian: } \hat{H} = \sum_{i=1}^{N} \hat{h}(i) + \frac{1}{2}\sum_{i\neq j}^{N} \hat{g}(i,j) + V_{nn}$$

Computational cost: xN^{y}

Theoretical model chemistries



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

Computational cost: xN^{y}

The electronic energy

- The electronic wave function

$$\Psi(1, 2, \ldots, N)$$

  is an extraordinarily complicated mathematical beast and generally not available in exact form.

- The expectation value of the electronic Hamiltonian is

$$\mathrm{E} = \left\langle \Psi \left| \hat{\mathrm{H}} \right| \Psi \right\rangle = \sum_{i=1}^{N} \left\langle \Psi \left| \hat{\mathrm{h}}(i) \right| \Psi \right\rangle + \frac{1}{2} \sum_{i \neq j}^{N} \langle \Psi | \hat{\mathrm{g}}(i, j) | \Psi \rangle + \langle \Psi | \mathrm{V}_{nn} | \Psi \rangle$$

- ...and can be simplified.
- The constant term is

$$E_0 = \langle \Psi | \mathrm{V}_{nn} | \Psi \rangle = \mathrm{V}_{nn} \langle \Psi | \Psi \rangle = \mathrm{V}_{nn}$$

  which follows from the normalization of the wave function.

The electronic energy

One-electron energy

- We can simplify the one-electron energy

$$\begin{aligned} E_1 &= \sum_{i=1}^{N} \left\langle \Psi \left| \hat{\mathrm{h}}(i) \right| \Psi \right\rangle \\ &= \sum_{i=1}^{N} \int \Psi^{\dagger}\left(1,2,\ldots,N\right) \hat{\mathrm{h}}(i) \Psi\left(1,2,\ldots,N\right) \mathrm{d}1\mathrm{d}2\ldots\mathrm{d}N \end{aligned}$$

- ... by noting that since electrons are indistinguishable, *all* one-electron integrals have the same value

$$\left\langle \Psi \left| \hat{\mathrm{h}}(1) \right| \Psi \right\rangle = \left\langle \Psi \left| \hat{\mathrm{h}}(2) \right| \Psi \right\rangle = \ldots = \left\langle \Psi \left| \hat{\mathrm{h}}(N) \right| \Psi \right\rangle$$

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

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

The electronic energy

Two-electron energy

- For the two-electron energy

$$\begin{aligned} E_2 &= \frac{1}{2}\sum_{i\neq j}^{N}\left\langle\Psi\left|\hat{g}(i,j)\right|\Psi\right\rangle \\ &= \frac{1}{2}\sum_{i\neq j}^{N}\int\Psi^{\dagger}\left(1,2,\ldots,N\right)\hat{g}(i,j)\Psi\left(1,2,\ldots,N\right)\mathrm{d}1\mathrm{d}2\ldots\mathrm{d}N \end{aligned}$$

  we can proceed in similar fashion.

- Since electrons are indistinguishable,
  all two-electron integrals have the same value

$$\left\langle\Psi\left|\hat{g}(1,2)\right|\Psi\right\rangle = \left\langle\Psi\left|\hat{g}(1,3)\right|\Psi\right\rangle = \ldots = \left\langle\Psi\left|\hat{g}(N-1,N)\right|\Psi\right\rangle$$

- We can therefore write

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

  where $\frac{1}{2}N\left(N-1\right)$ 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

$$\hat{h}(1) = \hat{h}_0(1) + \hat{v}_{en}(1)$$

- The interaction operators $\hat{v}_{en}(i)$ and $\hat{g}(i,j)$ are multiplicative operators, that is, they do not contain derivatives and can be moved around inside integrals, e.g.

$$\begin{aligned}\left\langle \hat{V}_{eN} \right\rangle &= N \int \Psi^{\dagger}(1,2,\ldots,N)\,\hat{v}_{eN}(1)\Psi(1,2,\ldots,N)\,\mathrm{d}1\mathrm{d}2\ldots\mathrm{d}N \\ &= N \int \hat{v}_{eN}(1)\Psi^{\dagger}(1,2,\ldots,N)\,\Psi(1,2,\ldots,N)\,\mathrm{d}1\mathrm{d}2\ldots\mathrm{d}N \\ &= \int \hat{v}_{eN}(1)n_1(1;1)\mathrm{d}1\end{aligned}$$

- where we have introduced the one-electron density matrix

$$n_1(1;1') = N \int \Psi^{\dagger}(1,2,\ldots,N)\,\Psi(1',2,\ldots,N)\,\mathrm{d}2\ldots\mathrm{d}N$$

The electronic Hamiltonian

2-electron density matrix

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

$$\begin{aligned}\left\langle \hat{T}_e \right\rangle &= N \int \Psi^\dagger(1,2,\ldots,N)\, \hat{h}_0(1) \Psi(1,2,\ldots,N)\, d1d2\ldots dN \\ &= \int \left[\hat{h}_0(1') n(1;1') \right]_{1'\to 1} d1\end{aligned}$$

- The expectation value of the two-electron interaction

$$\begin{aligned}\left\langle \hat{V}_{ee} \right\rangle &= \frac{1}{2} N(N-1) \int \Psi^\dagger(1,2,\ldots,N)\, \hat{g}(1,2) \Psi(1,2,\ldots,N)\, d1d2\ldots dN \\ &= \frac{1}{2} \int \hat{g}(1,2) n_2(1,2;1,2) d1d2\end{aligned}$$

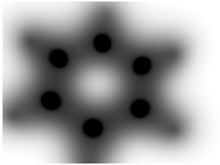
may be expressed in terms of the two-electron density matrix

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

The electronic energy

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

- 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

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

The electronic problem

Separation of variables

- We write the two-electron wave function as

$$\Psi(1,2)=\varphi_a(1)\varphi_b(2)$$

- Insertion into the wave equation gives

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

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

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

The electronic problem

Separation of variables

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

$$\underbrace{\frac{\{h(1)\varphi_a(1)\}}{\varphi_a(1)}}_{\varepsilon_a}+\underbrace{\frac{\{h(2)\varphi_b(2)\}}{\varphi_b(2)}}_{\varepsilon_b}=E$$

- A single wave equation for two electrons

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

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

$$h(1)\varphi_a(1)=\varepsilon_a\varphi_a(1);\quad h(2)\varphi_b(2)=\varepsilon_b\varphi_b(2)$$

- The situation is even simpler ...

The electronic problem

Indistinguishability

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

$$h(1)\varphi_x(1) = \varepsilon_x\varphi_x(1); \quad x = a, b, c, \ldots$$

- However, the form

$$\Psi(1,2) = \varphi_a(1)\varphi_b(2)$$

  is not an acceptable wave function:
  - electrons are identical particles
  - electrons are fermions:
    the wave function must be antisymmetric under particle exchange
- This leads to the form

$$\Psi(1,2) = \frac{1}{\sqrt{2}}\left\{\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)\right\}$$

The electronic problem

Slater determinants

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

$$\Psi(1,2,\ldots,N) = \frac{1}{\sqrt{N!}}\hat{\mathcal{A}}\varphi_1(1)\varphi_2(2)\ldots\varphi_N(N) = |\varphi_1(1)\varphi_2(2)\ldots\varphi_N(N)|$$

  where $\hat{\mathcal{A}}$ is the **anti-symmetrization operator.**
- The wave function for a system of N interacting electrons is typically expanded in an N-electron basis of **Slater determinants**.
- The fermionic nature of electrons is not built into the electronic Hamiltonian.
- This is achieved with **second quantizatio**n !

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:
  - in the coordinate representation:

$$\mathbf{r} \to \hat{\mathbf{r}} = \mathbf{r}; \quad \mathbf{p} \to \hat{\mathbf{p}} = -i\hbar\frac{\partial}{\partial \mathbf{r}} = -i\hbar\boldsymbol{\nabla}$$

  - in the momentum representation:

$$\mathbf{r} \to \hat{\mathbf{r}} = i\hbar\frac{\partial}{\partial \mathbf{p}}; \quad \mathbf{p} \to \hat{\mathbf{p}} = \mathbf{p}$$

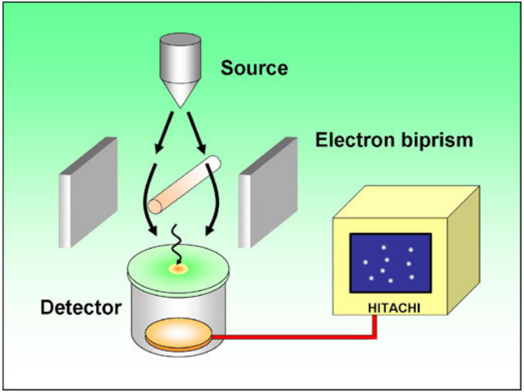
- ...in order to obey the fundamental commutator relation

$$[r_i, p_j] = i\hbar\delta_{ij}$$

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

Intermission: the double slit experiment

Researchers of Hitachi has reproduced the famous double-slit experiment using an electron microscope as electron source, an “electron biprism” as double slit and a very sensitive electron detector.



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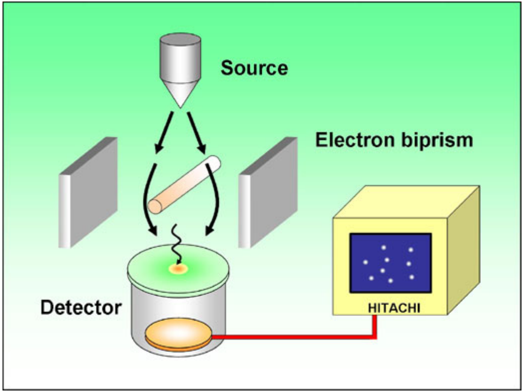

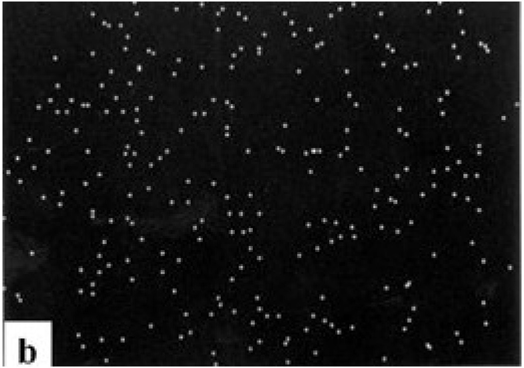

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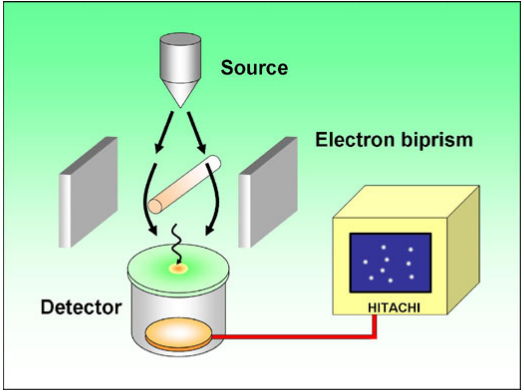

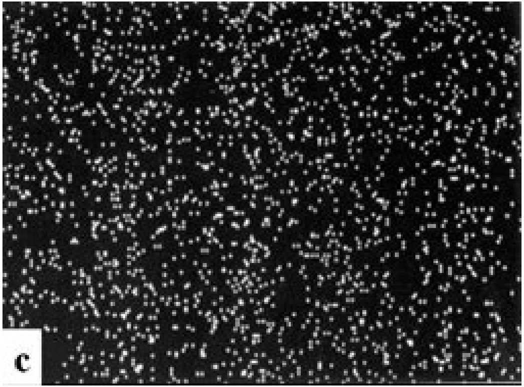

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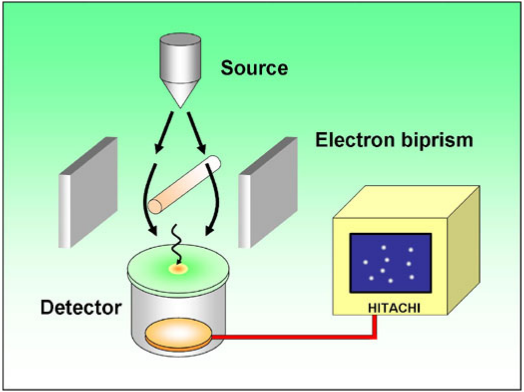

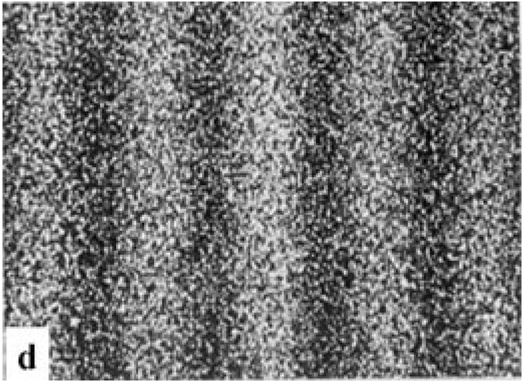

This information is contained in the wave function.

Interpretation of the wave function

- The wave function is interpreted as a probability amplitude.
- For a system of N electrons the quantity

$$\Psi^{\dagger}(1,2,\ldots,N)\,\Psi(1,2,\ldots N)\,d1d2\ldots dN$$

represents the probability of finding of finding the electrons in the infinitesimal volumes $d1$, $d2, \ldots dN$ about the space/spin coordinates 1, 2, $\ldots$ N

- This leads to the normalization condition

$$\int \Psi^{\dagger}(1,2,\ldots,N)\,\Psi(1,2,\ldots N)\,d1d2\ldots dN = 1$$

Second quantization

- The electron density can be obtained from the quantity

$$\rho(1) = N \int \Psi^{\dagger}(1,2,\ldots,N)\,\Psi(1,2,\ldots N)\,d2\ldots dN$$

- The electron density integrates to the number of electrons

$$\int \rho(1)\,d1 = N.$$

- We now introduce an **operator**

$$\hat{N} = \int \hat{\psi}^{\dagger}(1)\,\hat{\psi}(1)\,d1$$

- ... in terms of operators $\hat{\psi}^{\dagger}(1)$ and $\hat{\psi}(2)$, 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.

Field operators

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

$$\begin{aligned}
\left[\hat{\psi}^{\dagger}(1), \hat{\psi}^{\dagger}(2)\right]_{+} &= \hat{\psi}^{\dagger}(1)\hat{\psi}^{\dagger}(2) + \hat{\psi}^{\dagger}(2)\hat{\psi}^{\dagger}(1) &= 0 \\
\left[\hat{\psi}(1), \hat{\psi}(2)\right]_{+} &= \hat{\psi}(1)\hat{\psi}(2) + \hat{\psi}(2)\hat{\psi}(1) &= 0 \\
\left[\hat{\psi}(1), \hat{\psi}^{\dagger}(2)\right]_{+} &= \hat{\psi}(1)\hat{\psi}^{\dagger}(2) + \hat{\psi}^{\dagger}(2)\hat{\psi}(1) &= \delta(1-2)
\end{aligned}$$

- Bosons obey corresponding commutator relations.

Expansion of field operators

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

$$\int \varphi_p^\dagger(1)\varphi_q(1)d1 = \langle \varphi_p | \varphi_q \rangle = S_{pq} = \delta_{pq}$$

- We now expand the field operators in this basis

$$\hat{\psi}(1) = \sum_q \varphi_q(1)\hat{a}_q; \quad \hat{\psi}^\dagger(1) = \sum_q \varphi_q^\dagger(1)\hat{a}_q^\dagger$$

- We find the expansion coefficients $\hat{a}_p$ and $\hat{a}_p^\dagger$ by

$$\hat{a}_p = \int \varphi_p^\dagger(1)\hat{\psi}(1)d1; \quad \hat{a}_p^\dagger = \int \hat{\psi}^\dagger(1)\varphi_p(1)d1$$

Expansion of field operators

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

$$\hat{\psi}(1) = \sum_q \varphi_q(1)\hat{a}_p \rightarrow |\hat{\psi}\rangle = \sum_q |\varphi_q\rangle\hat{a}_p$$

- … such that

$$\langle\varphi_p|\hat{\psi}\rangle = \sum_q \langle\varphi_p|\varphi_q\rangle\,\hat{a}_q = \sum_q \delta_{pq}\hat{a}_q = \hat{a}_p$$

- The expansion coefficients $\hat{a}_p$ and $\hat{a}_p^\dagger$ are operators as well:
  - $\hat{a}_p$ is denoted an annihilation operator
  - $\hat{a}_p^\dagger$ is denoted a creation operator and is the conjugate of $\hat{a}_p$
  - which means that $\left(\hat{a}_p^\dagger\right)^\dagger = \hat{a}_p$

Annihilation and creation operators

- The algebra of the annihilation and creation operators follows from the algebra of the field operators. We have

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

- .. from which we deduce

$$\left[\hat{a}_p, \hat{a}_q^\dagger\right]_+ = \left[\int \varphi_p^\dagger(1)\hat{\psi}(1)d1, \int \hat{\psi}^\dagger(2)\varphi_q(2)d2\right]_+$$

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

$$\begin{aligned}
\left[\hat{a}_p, \hat{a}_q^\dagger\right]_+ &= \int\int \varphi_p^\dagger(1)\varphi_q(2)\left[\hat{\psi}(1), \hat{\psi}^\dagger(2)\right]_+ d1d2 \\
&= \int\int \varphi_p^\dagger(1)\varphi_q(2)\delta(1-2)d1d2 \\
&= \int \varphi_p^\dagger(1)\varphi_q(1)d1 = \delta_{pq}
\end{aligned}$$

Algebra of annihilation and creation operators

- We just found that (using an orthonormal basis)

$$\left[\hat{\psi}(1),\hat{\psi}^\dagger(2)\right]_+ = \delta(1-2) \quad\Rightarrow\quad \left[\hat{a}_p,\hat{a}_q^\dagger\right]_+ = \delta_{pq}$$

- In a similar manner we find that

$$\begin{aligned}\left[\hat{\psi}^\dagger(1),\hat{\psi}^\dagger(2)\right]_+ &= 0 \;\Rightarrow\; \left[\hat{a}_p^\dagger,\hat{a}_q^\dagger\right]_+ = 0\\ \left[\hat{\psi}(1),\hat{\psi}(2)\right]_+ &= 0 \;\Rightarrow\; \left[\hat{a}_p,\hat{a}_q\right]_+ = 0\end{aligned}$$

Occupation-number vectors

- Let us consider a simple example:
  We have 4 orbitals $\{\varphi_1, \varphi_2, \varphi_3, \varphi_4\}$ (M=4).
- With two electrons (N=2) we can build $\begin{pmatrix} 4 \\ 2 \end{pmatrix} = 6$ determinants. One example is

$$\Phi(1,2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \varphi_1(1) & \varphi_3(1) \\ \varphi_1(2) & \varphi_3(2) \end{vmatrix}$$

- or, in short-hand notation

$$\Phi(1,2) = |\varphi_1\varphi_3|$$

- We can map this into an **occupation-number vector** (ONV)

$$\Phi_k(1,2) = |\varphi_1\varphi_3| \quad \rightarrow \quad |\mathbf{k}\rangle = |k_1, k_2, k_3, k_4\rangle = |1,0,1,0\rangle$$

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

Occupation-number vectors

Vacuum state and annihilation

- Another example is

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

- A special occupation-number vector is the **vacuum state**

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

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

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

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

Occupation-number vectors

Creation operators

- Creation operators increase occupation numbers by one

$$\begin{aligned}
\hat{a}_1^\dagger \left|vac\right\rangle &= \left|1,0,0,0\right\rangle \\
\hat{a}_2^\dagger \left|vac\right\rangle &= \left|0,1,0,0\right\rangle \\
\hat{a}_3^\dagger \left|vac\right\rangle &= \left|0,0,1,0\right\rangle \\
\hat{a}_4^\dagger \left|vac\right\rangle &= \left|0,0,0,1\right\rangle
\end{aligned}$$

- ..but, since they refer to fermions,
  occupation numbers can not be greater than one

$$\hat{a}_1^\dagger \left|1,0,0,0\right\rangle = \hat{a}_1^\dagger \hat{a}_1^\dagger \left|vac\right\rangle = 0$$

- This follows directly from the special case

$$\left[\hat{a}_p^\dagger, \hat{a}_p^\dagger\right]_+ = \hat{a}_p^\dagger \hat{a}_p^\dagger + \hat{a}_p^\dagger \hat{a}_p^\dagger = 2\hat{a}_p^\dagger \hat{a}_p^\dagger = 0$$

Occupation-number vectors

More creation

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

$$\hat{a}_1^\dagger |0,1,0,0\rangle = |1,1,0,0\rangle = \hat{a}_1^\dagger \hat{a}_2^\dagger |vac\rangle$$

- Using the algebra of creation operators we find

$$\hat{a}_2^\dagger |1,0,0,0\rangle = \hat{a}_2^\dagger \hat{a}_1^\dagger |vac\rangle = -\hat{a}_1^\dagger \hat{a}_2^\dagger |vac\rangle = -|1,1,0,0\rangle$$

- ..showing how the fermion antisymmetry is built into the operators.

Fock space

..or occupation-number space

- Occupation number vectors (ONVs) have the general form

$$|\mathbf{k}\rangle = |k_1, k_2, \ldots, k_M\rangle\,; \quad k_p = 0 \,\text{or}\, 1$$

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

- Any ONV can be generated from the vacuum state

$$|\mathbf{k}\rangle = \prod_{p=1}^{M} \left(\hat{a}_p^\dagger\right)^{k_p} |vac\rangle$$

- An inner-product in Fock space is defined by

$$\langle \mathbf{k}|\mathbf{m}\rangle = \delta_{\mathbf{k},\mathbf{m}} = \prod_{p=1}^{M} \delta_{k_p,m_p}$$

and is one if all occupation numbers are identical, zero otherwise.

- A special case

$$\langle vac|vac\rangle = 1$$

Fock space

..or occupation-number space

- The dual vector $\langle \mathbf{k}|$ is obtained by conjugation, e.g. starting from

$$|\mathbf{k}\rangle = |1,0,1,1\rangle = \hat{a}_1^\dagger \hat{a}_3^\dagger \hat{a}_4^\dagger \, |vac\rangle$$

- ... we have

$$\langle \mathbf{k}| = \langle 1,0,1,1| = \langle vac| \left(\hat{a}_1^\dagger \hat{a}_3^\dagger \hat{a}_4^\dagger \right)^\dagger = \langle vac| \, \hat{a}_4 \hat{a}_3 \hat{a}_1$$

  - notice the change of operator order under conjugation
  - annihilation operators become creators when operating to the left
  - the dual vacuum state can therefore be defined by

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

The number operator

- Notice that in Fock space there is no restriction on particle number N, except $N \leq M$.
- We now return to the operator

$$\hat{N} = \int \hat{\psi}^{\dagger}(1)\,\hat{\psi}(1)\,d1$$

- Expanding the field operators in some orthonormal orbital basis $\{\varphi_p(1)\}_{p=1}^{M}$ we obtain

$$\hat{N} = \int \hat{\psi}^{\dagger}(1)\hat{\psi}(1)d1 = \sum_{pq}\left\{\int \varphi_p^{\dagger}(1)\varphi_q(1)d1\right\}\hat{a}_p^{\dagger}\hat{a}_q = \sum_{pq}\delta_{pq}\hat{a}_p^{\dagger}\hat{a}_q = \sum_{p}\hat{a}_p^{\dagger}\hat{a}_p$$

- ... which defines the **number operator** $\hat{N}$. For instance

$$\hat{N}\,|1,0,1,1\rangle = 3\,|1,0,1,1\rangle$$

- 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

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

The number operator

and commutator algebra

- Suppose that

$$\hat{N}\left|\mathbf{k}\right\rangle = N\left|\mathbf{k}\right\rangle$$

- What about $\hat{N}a_p^\dagger\left|\mathbf{k}\right\rangle$?
- We can rewrite this as

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

- We need to solve the commutator

$$\left[\hat{N}, \hat{a}_p^\dagger\right] = \sum_q \left[\hat{a}_q^\dagger\hat{a}_q, \hat{a}_p^\dagger\right]$$

- We may use a commutator rule such as

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

The number operator

and commutator algebra

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

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

- We therefore rather form the rule

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

- ... which gives

$$\left[\hat{N}, \hat{a}_p^\dagger\right] = \sum_q \left[\hat{a}_q^\dagger \hat{a}_q, \hat{a}_p^\dagger\right] = \sum_q \left(\hat{a}_q^\dagger \underbrace{\left[\hat{a}_q, \hat{a}_p^\dagger\right]_+}_{=\delta_{pq}} - \underbrace{\left[\hat{a}_q^\dagger, \hat{a}_p^\dagger\right]_+}_{=0} \hat{a}_q \right) = \hat{a}_p^\dagger$$

- Our final result is thereby

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

The number operator

and commutator algebra

- What about $\hat{N}a_p\left|\mathbf{k}\right\rangle$?
- We can write this as

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

- We can proceed as before, but instead we note that
  - $\left[\hat{A}, \hat{B}\right]^\dagger = \left(\hat{A}\hat{B} - \hat{B}\hat{A}\right)^\dagger = \hat{B}^\dagger\hat{A}^\dagger - \hat{A}^\dagger\hat{B}^\dagger = -\left[\hat{A}^\dagger, \hat{B}^\dagger\right]$
  - $\hat{N}^\dagger = \sum_p \left(\hat{a}_p^\dagger\hat{a}_p\right)^\dagger = \hat{N}$ (hermitian operator)
- ... so that

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

Counting electron pairs

- Let us have a look at the second quantization operator

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

- Operator algebra

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

- ...shows that it counts electron pairs

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

What does the second-quantized electronic Hamiltonian look like?

- The first-quantized form

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

- The second-quantized form

$$\hat{H} = \int \hat{\psi}^{\dagger}(1)\hat{h}(1)\hat{\psi}(1)\mathrm{d}1 + \frac{1}{2}\int \hat{\psi}^{\dagger}(1)\hat{\psi}^{\dagger}(2)\hat{g}(1,2)\hat{\psi}(2)\hat{\psi}(1)\mathrm{d}1\mathrm{d}2 + V_{NN}$$

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

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

What does the second-quantized electronic Hamiltonian look like?

- The one-electron part

$$
\begin{aligned}
\hat{H}_1 &= \int \hat{\psi}^\dagger(1)\hat{h}(1)\hat{\psi}(1)\mathrm{d}1 \\
&= \sum_p \sum_q \left\{ \int \varphi_p^\dagger(1) h(1) \varphi_q(1)\mathrm{d}1 \right\} \hat{a}_p^\dagger \hat{a}_q = \sum_{p,q} h_{pq} \hat{a}_p^\dagger \hat{a}_q
\end{aligned}
$$

- Proceeding in the same way with the two-electron part we obtain

$$
\begin{aligned}
\hat{H}_2 &= \frac{1}{2} \int \hat{\psi}^\dagger(1)\hat{\psi}^\dagger(2)\hat{g}(1,2)\hat{\psi}(2)\hat{\psi}(1)\mathrm{d}1\mathrm{d}2 \\
&= \frac{1}{2} \sum_{pq,rs} V_{pq,rs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r
\end{aligned}
$$

- Dirac notation: $V_{pq,rs} = \langle \varphi_p \varphi_q | \varphi_r \varphi_s \rangle = \int \varphi_p^\dagger(1) \varphi_q^\dagger(2) \hat{g}(1,2) \varphi_r(1) \varphi_s(2)\mathrm{d}1\mathrm{d}2$
- Mulliken notation: $g_{pq,rs} = (\varphi_p \varphi_q | \varphi_r \varphi_s) = \int \varphi_p^\dagger(1) \varphi_r^\dagger(2) \hat{g}(1,2) \varphi_q(1) \varphi_s(2)\mathrm{d}1\mathrm{d}2$

What does the second-quantized electronic Hamiltonian look like?

- The final form is

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

- This is a very convenient operator form:
  - The fermion antisymmetry is built into the operator
  - The operator is expressed in terms of one- and two-electron integrals, which are the basic ingredients of quantum chemistry codes
  - The form is universal; there is no reference to the number of electrons !
- ..but note that it is a *projected* operator:
  - it “lives” in the space defined by the orbital set $\{\varphi_p\}_{p=1}^{M}$.

The electronic energy in second quantization

- The electronic Hamiltonian is

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

- The wave function is now expressed as a linear combination of occupation number vectors (limited to occupation N)

$$|0\rangle = \sum_k C_k \, |\mathbf{k}\rangle$$

- The energy is given as the expectation value

$$E = \left\langle 0 \middle| \hat{H} \middle| 0 \right\rangle = \sum_{pq} h_{pq} D_{pq} + \frac{1}{2} \sum_{pq,rs} V_{pq,rs} d_{pq,rs} + V_{NN}$$

  - Matrix elements h_{pq} and $V_{pq,rs}$ depends on the operator, but are independent of wave function
  - **Orbital density matrices** D_{pq} and $d_{pq,rs}$ are independent of operator, but depend on wave function

Orbital density matrices

- **One-electron orbital density matrix**

$$D_{pq} = \left\langle 0 \left| \hat{a}_p^\dagger \hat{a}_q \right| 0 \right\rangle$$

  - dimension: M^2
  - contains all information needed to calculate expectation values of one-electron operators
  - diagonalization gives natural orbitals

- **Two-electron orbital density matrix**

$$d_{pq,rs} = \left\langle 0 \left| \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \right| 0 \right\rangle$$

  - dimension: M^4
  - contains all information needed to calculate expectation values of two-electron operators

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

Summary

- 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**

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

  and reflects the fermionic nature of electrons.

Summary

- **One-electron operators** are translated into their second quantized form by

$$\sum_{i=1}^{N}\hat{f}(i) \quad\rightarrow\quad \int \psi^{\dagger}(1)f(1)\psi(1)\mathrm{d}1 = \sum_{pq}\left\langle \varphi_p\left|\hat{f}\right|\varphi_q\right\rangle \hat{a}_p^{\dagger}\hat{a}_q$$

- **Two-electron operators** are translated into their second quantized form by

$$\begin{aligned}\frac{1}{2}\sum_{i=1}^{N} g(i,j) \quad &\rightarrow \quad \frac{1}{2}\int \hat{\psi}^{\dagger}(1)\hat{\psi}^{\dagger}(2)\hat{g}(1,2)\hat{\psi}(2)\hat{\psi}(1)\mathrm{d}1\mathrm{d}2\\ &= \quad \frac{1}{2}\sum_{pq,rs}\langle\varphi_p\varphi_q\left|\hat{g}\right|\varphi_r\varphi_s\rangle \hat{a}_p^{\dagger}\hat{a}_q^{\dagger}\hat{a}_s\hat{a}_r\end{aligned}$$

- Nice features is that:
  - **Antisymmetry** is automatically built into the operators
  - They are **expressed in terms of integrals**, building blocks of quantum chemistry codes

Summary

- The **second-quantized electronic Hamiltonian** is expressed as

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

- The **electronic energy** becomes

$$E = \left\langle 0 \middle| \hat{H} \middle| 0 \right\rangle = \sum_{pq} h_{pq} D_{pq} + \frac{1}{2} \sum_{pq,rs} V_{pq,rs} d_{pq,rs} + V_{nn}$$

- which nicely separates
  - **operator content**,
    in terms of integrals h_{pq} and $V_{pq,rs}$, and
  - **wave function content**,
    in terms of orbital density matrices D_{pq} and $d_{pq,rs}$
    (data compression)