

Creation and Annihilation operators

References and Acknowledgements

*The material discussed here follows
the textbook below*

- ▶ [Methods of Electronic structure calculations: From molecules to solids](#), M. Springborg (Chapter 12)

The Hückel method

- We will discuss the so called second quantization
- The Hückel model was developed to study the electronic orbitals and their energies for the π electrons in organic molecules.
- The method is based on defining an effective Hamiltonian:

$$\hat{H}_{\text{Hückel}} = \sum_{i=1}^N \hat{h}_{\text{eff}}(i)$$

- **This operator contains only single particle operators** \hat{h}_{eff} and it is assumed that the exact solutions to the single-particle equations

$$\hat{h}_{\text{eff}}\phi_i = \varepsilon_i\phi_i$$

can be written exactly as a finite linear combinations of the π functions on the different atoms

$$\phi_i = \sum_{j=1}^M \chi_j c_{ji}$$

Here χ_j is the π function of the j^{th} atom and we have a total of M atoms. We assume that $\{\chi_j\}$ constitutes a complete set for the problem of interest.

Projection operators

- Assume that we have a complete set of functions $\{\chi_k\}$. We assume that the functions are orthonormal. Any function can be expanded as

$$g(\vec{r}) = \sum_{j=1}^M \chi_j(\vec{r}) d_j, \quad |g\rangle = \sum_{j=1}^M d_j |\chi_j\rangle.$$

- From this, we can derive:

$$\langle \chi_l | g \rangle = \sum_{k=1}^M d_j \langle \chi_l | \chi_k \rangle = d_l$$

- Or equivalently

$$|g\rangle = \sum_{k=1}^M d_k |\chi_k\rangle = \sum_{k=1}^M |\chi_k\rangle \langle \chi_k | g \rangle = \left[\sum_{k=1}^M |\chi_k\rangle \langle \chi_k| \right] |g\rangle = 1 \cdot |g\rangle$$

Projection operators

- The sum of the projection operators, $\hat{P}_k = |\chi_k\rangle\langle\chi_k|$, is the identity

$$1 = \sum_{k=1}^M \hat{P}_k.$$

- We shall now use the projection operators in obtaining an expression for the Hückel Hamiltonian operator \hat{h}_{eff} .
- The expression that will be derived is that of the so-called **second quantized form**.

The Hückel method

- The Hückel method amounts to solving the single-particle equations,

$$\hat{h}_{\text{eff}}|\phi_i\rangle = \varepsilon_i|\phi_i\rangle$$

- We rewrite the left-hand side and use the projection operators,

$$\begin{aligned}\hat{h}_{\text{eff}}|\phi_i\rangle &= 1 \cdot \hat{h}_{\text{eff}} \cdot 1 \cdot |\phi_i\rangle \\ &= \sum_{k=1}^M \hat{P}_k \cdot \hat{h}_{\text{eff}} \cdot \sum_{l=1}^M \hat{P}_l \cdot |\phi_i\rangle \\ &= \sum_{k=1}^M |\chi_k\rangle\langle\chi_k| \cdot \hat{h}_{\text{eff}} \cdot \sum_{l=1}^M |\chi_l\rangle\langle\chi_l| \cdot |\phi_i\rangle \\ &= \sum_{k=1}^M |\chi_k\rangle\langle\chi_k| \hat{h}_{\text{eff}} \sum_{l=1}^M |\chi_l\rangle\langle\chi_l|\phi_i\rangle \\ &= \sum_{k,l=1}^M |\chi_k\rangle\langle\chi_k| \hat{h}_{\text{eff}} |\chi_l\rangle\langle\chi_l|\phi_i\rangle \\ &= \sum_{k,l=1}^M |\chi_k\rangle h_{kl} \langle\chi_l|\phi_i\rangle,\end{aligned}$$

where the matrix elements

$$h_{kl} = \langle\chi_k|\hat{h}_{\text{eff}}|\chi_l\rangle$$

The Hückel method

- We can rewrite as

$$\begin{aligned}\hat{h}_{\text{eff}}|\phi_i\rangle &= [\hat{h}_{\text{eff}}]|\phi_i\rangle \\ &= \left[\sum_{k,l=1}^M |\chi_k\rangle h_{kl} \langle \chi_l| \right] |\phi_i\rangle \\ &= \left[\sum_{k,l=1}^M h_{kl} |\chi_k\rangle \langle \chi_l| \right] |\phi_i\rangle\end{aligned}$$

- We have not made any assumptions about the function, ϕ_i so the Eq. above is generally valid. This means that

$$\hat{h}_{\text{eff}} = \sum_{k,l=1}^M h_{kl} |\chi_k\rangle \langle \chi_l|$$

- We introduce the operators,

$$\begin{aligned}\hat{a}_k^\dagger &= |\chi_k\rangle \\ \hat{a}_k &= \langle \chi_k|\end{aligned}$$

<--- Creation operator

<--- Annihilation operator

Creation and annihilation operators

➤ Then

$$\hat{h}_{\text{eff}} = \sum_{k,l=1}^M h_{kl} \hat{a}_k^\dagger \hat{a}_l$$

➤ The operators \hat{a}_k^\dagger and \hat{a}_k are the so called creation and annihilation operators.

➤ Let us consider a general function that can be expanded as

$$|g\rangle = \sum_{j=1}^M d_j |\chi_j\rangle$$

➤ We consider:

$$\begin{aligned} \hat{a}_k^\dagger \hat{a}_l |g\rangle &= \hat{a}_k^\dagger \hat{a}_l \sum_{j=1}^M d_j |\chi_j\rangle \\ &= |\chi_k\rangle \langle \chi_l | \sum_{j=1}^M d_j |\chi_j\rangle \\ &= \sum_{j=1}^M d_j |\chi_k\rangle \langle \chi_l | \chi_j\rangle \\ &= d_l |\chi_k\rangle. \end{aligned}$$

Creation and annihilation operators

$$|g\rangle = \sum_{j=1}^M d_j |\chi_j\rangle \quad \hat{a}_k^\dagger \hat{a}_l |g\rangle = d_l |\chi_k\rangle$$

- Thus electrons that belonged to atom l are transferred to atom k , or, alternatively, we annihilate the electrons on the l^{th} atom and create them on the k^{th} atom.

$$\hat{h}_{\text{eff}} = \sum_{k,l=1}^M h_{kl} \hat{a}_k^\dagger \hat{a}_l.$$

- **The Hückel Hamiltonian operator (in second quantization form) contains a linear combination of pairs of creation and annihilation operators for the individual atomic orbitals multiplied by the matrix element for the two atomic orbitals.**

$$\hat{h}_{\text{eff}} = \sum_{k,l=1}^{N_b} h_{kl} \hat{a}_k^\dagger \hat{a}_l.$$

- The basic assumption is that the atomic orbitals form a *complete* set of *orthonormal* functions. For the extended Hückel model the single-particle Hamiltonian operator takes exactly the same form as in Eq. above, except that M is to be replaced by the number of (orthonormal) basis functions.

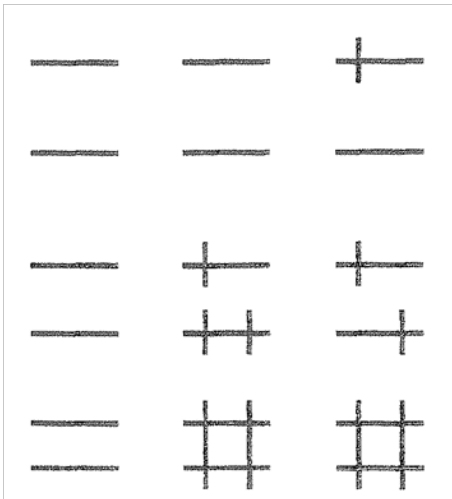
Creation and annihilation operators

- Also the PPP and the other semi-empirical methods can be defined with the help of annihilation and creation operators. They contain terms of the form

$$h_{klmn} \hat{a}_k^\dagger \hat{a}_l^\dagger \hat{a}_m \hat{a}_n.$$

Electronic excitations

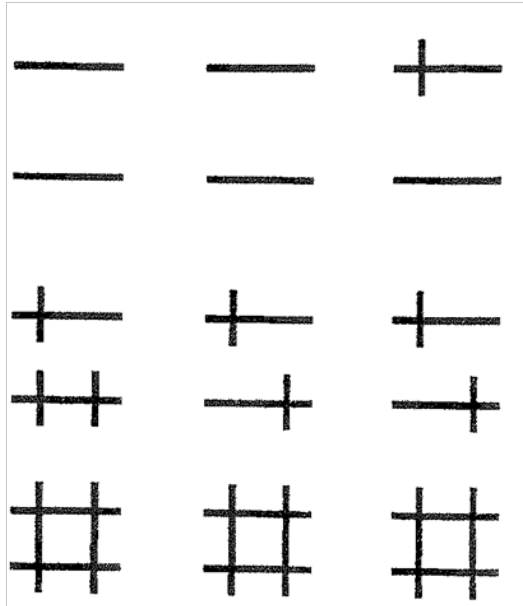
- Annihilation and creation operators are useful when studying electronic configurations extracted from the Hartree-Fock approximation. They are also important when discussing correlation effects.
- A Hartree-Fock(-Roothaan) calculation yields orbitals as in the fig. below. A set of orbitals are obtained without their occupancies (left) but one will choose the orbitals (middle) to be occupied when interested in the ground state.
- One may also consider an excited state obtained by transferring an electron from an energetically lower (occupied) orbital to an energetically higher (vacant) orbital (figure on the right).



Orbitals as obtained from a Hartree-Fock calculation. The left part shows the orbitals without their occupancies, whereas in the middle we have the occupancies for the ground state. The right part shows those of an excited state

Electronic excitations

- The last process consists effectively of an annihilation of an electron in one of the energetically lower orbitals, and a subsequent creation of the electron in one of the energetically higher orbitals.



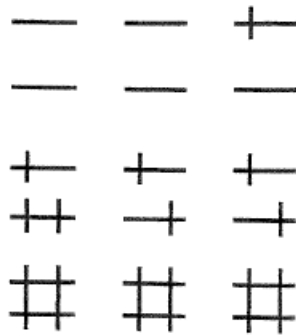
The process of generating the right diagram from the middle one. The middle figure corresponds to the situation where one electron has been annihilated

- This process is introduced only as a convenient mathematical model. We will assume that we have ordered the orbitals according to increasing orbital energies,

$$\varepsilon_1 \leq \varepsilon_2 \cdots \leq \varepsilon_N \cdots \leq \varepsilon_{N_b}$$

N_b is the number of basis functions in the calculation and the number of orbitals that can be calculated.

Electronic excitations



- The configuration of the left side of the Fig. is given by the Slater determinant

$$\Phi_0 = |\phi_1, \phi_2, \dots, \phi_N|.$$

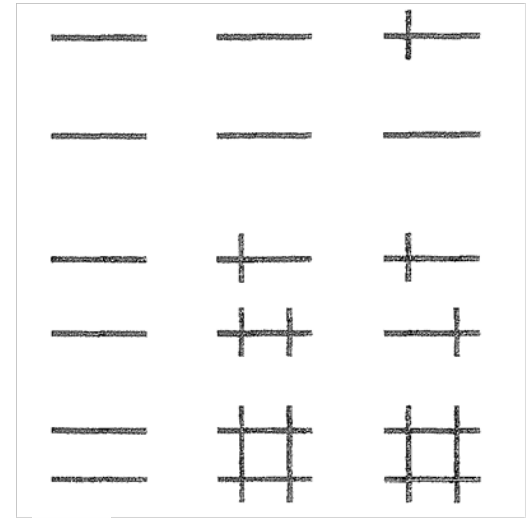
- Assuming that the configuration of the middle part of Fig. corresponds to that of the left part except that the electron of the n^{th} orbital has been removed, we can write this as

$$\begin{aligned}\hat{a}_n \Phi_0 &= \hat{a}_n |\phi_1, \phi_2, \dots, \phi_N| \\ &= \hat{a}_n |\phi_1, \phi_2, \dots, \phi_{n-1}, \phi_n, \phi_{n+1}, \dots, \phi_N| \\ &= |\phi_1, \phi_2, \dots, \phi_{n-1}, \phi_{n+1}, \dots, \phi_N|.\end{aligned}$$

Electronic excitations

- Here, the operator \hat{a}_n , removes the electron of the n^{th} orbital.
- Similarly, we will assume that the excited electron of the right configuration occupies the v^{th} orbital ($v > N$). This configuration is written as

$$\begin{aligned}
 & |\phi_1, \phi_2, \dots, \phi_{n-1}, \phi_{n+1}, \dots, \phi_N, \phi_v| \\
 &= \hat{a}_v^\dagger |\phi_1, \phi_2, \dots, \phi_{n-1}, \phi_{n+1}, \dots, \phi_N| \\
 &= \hat{a}_v^\dagger \hat{a}_n |\phi_1, \phi_2, \dots, \phi_{n-1}, \phi_n, \phi_{n+1}, \dots, \phi_N| \\
 &= \hat{a}_v^\dagger \hat{a}_n |\phi_1, \phi_2, \dots, \phi_N| \\
 &= \hat{a}_v^\dagger \hat{a}_n \Phi_0 \\
 &\equiv \Phi_n^v,
 \end{aligned}$$



\hat{a}_v^\dagger creates an electron in the v^{th} orbital. The lower index implies that the orbital ϕ_n , has been emptied, whereas the upper index implies that the orbital ϕ_v has been occupied instead.

Electronic excitations

- Here we have introduced creation and annihilation operators as a convenient tool for describing excited configurations in terms of the ground-state configuration.
- Note that this is used here as a notation of mathematical operations not related directly with any physical model.
- The creation and annihilation operators occur here always in pairs.
- When more than one electron is excited, we will use the following notation:

$$\Phi_{k,l,m,\dots}^{\kappa,\lambda,\mu,\dots} = \hat{a}_{\kappa}^{\dagger} \hat{a}_k \hat{a}_{\lambda}^{\dagger} \hat{a}_l \hat{a}_{\mu}^{\dagger} \hat{a}_m \dots \Phi_0$$