

# Basics of quantum mechanics — 61

Newtonian mechanics has two alternative formulations: Lagrangian and Hamiltonian.

Both involve formulation of the kinetic energy ( $T$ ) and the potential energy ( $V$ ) in terms of the:

$\underline{r}_i$  : coordinates of particle  $i$

$\underline{p}_i = m_i \frac{d\underline{r}_i}{dt}$  : linear momentum of particle  $i$

The kinetic energy reads:

$$T = \sum_i \frac{|\underline{p}_i|^2}{2m_i}$$

and the potential energy  $V(\underline{r}_1, \dots, \underline{r}_N)$  is specific to the problem, c. f. page 7 of these notes.

For microscopic systems, it is the Hamiltonian formulation that is found of use as a starting point. The Hamiltonian function reads:

$$H = T + V$$

i.e. the total energy of the system



Experimental observations at the beginning 62  
of the XXth century pointed to the need of  
a description of microscopic systems, different  
from classical mechanics. This was because  
classical mechanics could not explain experimental  
facts, e.g. spectral lines.

Quantum mechanics was developed with this  
purpose. It was worked out in a way to  
give results corresponding to experimental facts.

~~It was not worked out~~ There is no point in  
asking why <sup>in</sup> quantum mechanics ~~works~~ <sup>we do</sup> something  
this or that way. We do it that way because  
this is the way we can match experiment.

It is hard to understand quantum mechanics,  
one rather gets used to working with it.

These notes are going to tell about rules  
(sometimes called postulates) that we follow  
when working with quantum mechanics.

These notes will not explain why the rules are  
such. There will be some hints on why these  
rules are appropriate based on what we expect from  
physical quantities.



Rules (postulates) of quantum mechanics:

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⊖ The notion of a trajectory  $\underline{r}(t)$  is not applicable in quantum mechanics. We instead describe a physical system by a function of  $L_2$ -space (often):

$$\Psi(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N, t)$$

called the wavefunction.

The wavefunction contains all measurable information on the system.

The wavefunction squared has a probability distribution meaning:

$$\underbrace{\Psi^*(\underline{r}_1, \dots, t) \Psi(\underline{r}_1, \dots, t)}_{|\Psi|^2(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N, t)} \underbrace{dv_1 dv_2 \dots dv_N}_{dx_1 dy_1 dz_1}$$

the above is proportional to the probability of finding particle 1 in volume element  $dv_1$  and particle 2 in volume element  $dv_2$  etc. at a given instance of time,  $t$ .

The probability distribution integrated to the entire space for all variables



$$\int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \Psi^* \Psi \, dV_1 \, dV_2 \dots dV_N = N$$

gives the number of particles in the system at any instance of time,  $t$ . With the bra-ket notation introduced in lecture 3:

$$\langle \Psi | \Psi \rangle = N$$

note: the integration involved by  $\langle | \rangle$  is performed for the spatial variables and not for time

⊖ Measurable physical quantities are associated with Hermitian operators defined over  $\mathbb{R}^3$  space. The operators are constructed to fulfill Heisenberg's commutation relation for so-called canonical conjugate pairs, e.g.

$$[\hat{x}, \hat{p}_x] = i\hbar$$

where

$\hat{x}$ : coordinate operator, component  $x$

$\hat{p}_x$ : linear momentum operator,  $-\hbar$

$\hbar = h/2\pi$  : called  $\hbar$ -bar

$h$ : Planck's constant

The step where operators are associated with physical quantities is called quantization.

Usually  $\hat{p}$  and  $\hat{x}$  are quantized and everything is expressed with them (possibly).



A generally used quantization :

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$$\hat{x} = x.$$

$$\hat{y} = y.$$

$$\hat{z} = z.$$

$$\hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}$$

$\hat{p}_y, \hat{p}_z \dots$  analogous

} these operators perform multiplication

HW:

Prove, that  $\hat{p}_x$  as defined above is Hermitian. This relates to the HW on page 37, lecture 2.

HW:

Prove, that  $\hat{p}_x$  and  $\hat{x}$  as defined above fulfill Heisenberg's commutation relation.

Hint: take a function  $f(x)$  and evaluate  $\hat{p}_x \cdot \hat{x} f(x)$ , then  $\hat{x} \cdot \hat{p}_x f(x)$  and compare.

HW:

Prove, that  $[\hat{p}_x, \hat{y}] = 0$

A note on quantization: time is not quantized.

⊖ Measurable values of physical quantities arise as eigenvalues of the corresponding operators. When measuring a physical quantity the wavefunction of the system becomes the eigenfunction of the particular operator at the given instance time,  $t$ .

For example when measuring the linear momentum at time  $t$



$$\hat{P} \Psi(x, t) = \pi \Psi(x, t)$$

↑  
this is  
the value  
we measure;

↖ this is the  
wavefunction of  
the system at  
that particular  
instance of time

(Can only differ by a  
specific amount → hence quantum)

Note: this is why Hermitian operators are used,  
since → eigenvalues are real, c.f. page 43  
↳ the eigenvalue equation is known to  
be solvable in general

Note also: not all quantities are therefore  
measurable at the same instance,  
only those that commute, c.f. page 50  
(since the system has but one  $\Psi$  and it  
has to be a simultaneous eigenvector to  
both operators)

HW: Show, that operators, fulfilling Heisenberg's  
commutation relation can not be measured  
at the same instance of time.

HW: Study the angular momentum operator

$$\underline{\hat{L}} = \underline{\hat{r}} \times \underline{\hat{p}}$$

and show that  $\hat{L}_x$  can not be measured  
simultaneously with  $\hat{L}_y$ .

Hint: evaluate the commutator.

HW: Show, that  $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$  can be  
measured simultaneously with  $\hat{L}_x$ .

Hint: evaluate the commutator.



Terminology: when  $\Psi$  is the eigenfunction 64  
of an operator, then the system  
is said to be in a pure state  
from the point of view of that operator.  
Otherwise the system is termed  
to be in a mixed state from the  
point of view of the operator.

Note: since  $\hat{x}$  and  $\hat{p}_x$  are not simultaneously  
diagonalizable, when the system is in  
pure state from the point of view of  $\hat{p}$   
it is necessarily in mixed state from  
the point of view of  $\hat{x}$  and vice versa

One may ask what can be said of the  
outcome of a measurement of a physical  
quantity when the system is in a mixed  
state. We know that the system is going to  
~~be converted to~~  
~~become~~ a pure state at the instance of the  
measurement, but which pure state?

This question can be answered only in terms  
of probabilities. On average we are going to  
obtain the expectation value of the given  
quantity, taken with the mixed state wavefunction:

$$\langle \Psi | \hat{p} | \Psi \rangle = \langle \hat{p} \rangle \quad \& \text{ (this is obtained on average)}$$



Let us get closer to this average value. 68  
 Use the eigenvalue equation of  $\hat{p}$

$$\hat{p} |\Phi_k\rangle = \pi_k |\Phi_k\rangle$$

and make an expansion of mixed state function  $|\Psi\rangle$  with eigenfunctions  $|\Phi_k\rangle$  used as a basis (ON, since  $\hat{p}$  is Hermitic!)  
 c.f. page 49

$$|\Psi\rangle = \sum_k c_k |\Phi_k\rangle$$

with  $c_k = \langle \Psi | \Phi_k \rangle$  c.f. page 45

Now substitute into the expectation value:

$$\langle \hat{p} \rangle = \sum_{KL} c_k^* \langle \Phi_k | \hat{p} | \Phi_L \rangle c_L = \sum_{KL} c_k^* \underbrace{\langle \Phi_k | \Phi_L \rangle}_{\delta_{KL}} \pi_L c_L =$$

$$= \sum_k |c_k|^2 \pi_k$$

$\uparrow$   
 this gives the probability of measuring  $\pi_k$

We therefore can not tell the outcome of a measurement when the system is in a mixed state, all we can tell is

$\pi_0$  is going to be obtained with probability  $|c_0|^2$   
 $\pi_1$  ———— " ————  $|c_1|^2$   
 and so on



NW: Prove, that the probabilities sum to 1, when the wavefunction is normalized. 69

⊖ The central quantity of quantum mechanics, the wavefunction is obtained from

$$i \hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi \quad (\text{T D S E})$$

termed the time-dependent Schrödinger-equation.

$\hat{H}$  above is the quantized Hamiltonian function, written with  $\hat{p}$  and  $\hat{r}$  c.f. page 61.

NW: Show, that the (TDSE) conserves particle number over time

Hint: evaluate  $\frac{d}{dt} \langle \Psi | \Psi \rangle = \langle \frac{\partial \Psi}{\partial t} | \Psi \rangle + \langle \Psi | \frac{\partial \Psi}{\partial t} \rangle$

then use (TDSE) to substitute  $\frac{\partial \Psi}{\partial t}$  then

use  $\hat{H}^\dagger = \hat{H}$  and the properties of scalar product. Of course we would like to see zero by the end.

Let us now solve (TDSE)! We use the technique of separation, c.f. page 8

$$\Psi(\underline{r}, t) = \Phi(\underline{r}) f(t)$$

and substitute into the (TDSE)

$$i \hbar \frac{df}{dt} \Phi = \hat{H} \Phi f$$



rearranging and introducing  $E$  as constant, we find the two equations

a)  $\frac{d f(t)}{dt} = -\frac{i}{\hbar} E f(t)$

b)  $\hat{H} \Phi(x) = E \Phi(x)$

(SE)

The solution of a) reads  $f(t) = f(0) \exp(-\frac{i}{\hbar} E t)$

We can recognize b) as the eigenvalue equation of  $\hat{H}$ .

Terminology: b) is called the time independent Schrödinger-equation

We know, that b) in fact has multiple solutions:

$$\hat{H} \Phi_k(x) = E_k \Phi_k(x)$$

with these the separated solution of the (TDSE) can be written as

$$\Psi(x, t) = \sum_k c_k \Phi_k(x) \exp(-\frac{i}{\hbar} E_k t) \quad (\text{8})$$

NW: Prove, that the  $\Psi(x, t)$  above indeed fulfills the (TDSE) on page 69

Terminology: when all but one  $c_k$  is zero in (8)

e.g.  $c_0 = 1, c_1 = c_2 = \dots = 0$  then

$$\Psi(x, t) = \Phi_0 \exp(-\frac{i}{\hbar} E_0 t) \quad (\text{9})$$

such a solution is called a stationary solution.



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**NW:** Show, that the probability distribution of a stationary solution is independent on time (hence the terminology)

Hint: calculate the partial derivative

$$\frac{\partial}{\partial t} \Psi^*(\underline{r}, t) \Psi(\underline{r}, t) \text{ using } (\text{A})$$

Let us now study the change <sup>over time</sup> of the expectation value of a physical quantity, characterized by operator  $\hat{A}$ :

$$\frac{d}{dt} \langle \hat{A} \rangle = \underbrace{\left\langle \frac{\partial}{\partial t} \Psi \right| \hat{A} | \Psi \rangle}_{-\frac{i}{\hbar} \hat{H} \Psi} + \langle \Psi | \underbrace{\left( \frac{\partial}{\partial t} \hat{A} \right)}_{-\frac{i}{\hbar} \hat{H} \Psi} | \Psi \rangle + \langle \Psi | \hat{A} | \underbrace{\frac{\partial}{\partial t} \Psi}_{-\frac{i}{\hbar} \hat{H} \Psi} \rangle$$

$$= \frac{i}{\hbar} \langle \Psi | \underbrace{\hat{H} \hat{A}}_{\hat{H}} | \Psi \rangle + \langle \Psi | \left( \frac{\partial}{\partial t} \hat{A} \right) | \Psi \rangle - \frac{i}{\hbar} \langle \Psi | \hat{A} \hat{H} | \Psi \rangle =$$

$$= \langle \Psi | \left( \frac{\partial}{\partial t} \hat{A} \right) | \Psi \rangle - \frac{i}{\hbar} \langle \Psi | [\hat{A}, \hat{H}] | \Psi \rangle$$

From this we can deduce that for an operator that fulfills

$$\frac{\partial \hat{A}}{\partial t} = 0 \quad (0)$$

$$\text{and } [\hat{A}, \hat{H}] = 0 \quad (000)$$

the expectation value does not change over time. Such quantities are called constants of motion.



NW: Show, that the energy is a constant of motion!

Hint: check whether the two assumptions

( $\frac{\partial \hat{H}}{\partial t} = 0$ ) and ( $[\hat{H}, \hat{H}] = 0$ ) at the bottom of page 41

hold for the  $\hat{H}$  corresponding to  $\hat{H}$  on page 61

Recall:  $[\hat{A}, \hat{H}] = 0$  means, that  $\hat{A}$  and  $\hat{H}$  are simultaneously diagonalizable,

c.f. page 50. Hence we can find simultaneous eigenvectors to  $\hat{A}$  and  $\hat{H}$ .

The above adds to this the fact, that such an eigenvector remains eigenvector to both  $\hat{A}$  and  $\hat{H}$  over time,

where  $\frac{\partial \hat{A}}{\partial t} = 0$  also holds.

This is exploited in practice by finding operators

$\hat{A}$  fulfilling ( $\frac{\partial \hat{A}}{\partial t} = 0$ ) and ( $[\hat{A}, \hat{H}] = 0$ ) on page 41. Such

operators  $\hat{A}$  are typically symmetry operators. You

are going to see quite a bit of this in advanced physical chemistry.

Such operators  $\hat{A}$  are usually easier to diagonalize

than  $\hat{H}$ . Moreover, there is a lot of degeneracy

usually affecting the eigenvalues of such  $\hat{A}$ .

(The set of eigenvalues is called the spectrum of  $\hat{A}$ .)



Suppose, that  $\hat{A}$  has the eigenvalues, 73  
 eigenvector pairs:

$$\lambda_1, \lambda_1, \dots, \lambda_1, \lambda_2, \lambda_2, \dots, \lambda_2, \lambda_3, \dots$$

$$\underbrace{(|v_1\rangle, |v_2\rangle, \dots, |v_n\rangle)}_{\text{degenerate}}, \underbrace{(|v_{n+1}\rangle, |v_{n+2}\rangle, \dots, |v_{n+m}\rangle, |v_{n+m+1}\rangle, \dots)}_{\text{non-degenerate}}$$

giving rise to the matrix representation of  $\hat{H}$   
 on the basis of  $\{|v_i\rangle\}_{i=1}^{\dots}$

$$\begin{pmatrix} (U_1) & & & \\ & \emptyset & & \\ & & (U_2) & \\ & & & \emptyset \\ & & & & (U_3) \end{pmatrix}$$

This means, that  $\underline{\underline{H}}$  exhibits blocks that can be  
 nondiagonal only in the subspace corresponding to  
 degenerate blocks of  $\hat{A}$ , c.f. page 52.

As a result, the diagonalization problem of  $\hat{H}$  is  
 reduced to these blocks only. Note, that ~~the~~ these  
 blocks are still of infinite dimension in general.

But it helps to categorize the diagonalization  
 problem of  $\hat{H}$  according to the degenerate eigen-  
 values of  $\hat{A}$ . The eigenvalues are labeled by  
 integers and it is these integers, that are  
 called quantum numbers.



# Basics of quantum chemistry - 74

Quantum chemistry discusses atoms, molecules based on quantum mechanics.

generally used system of units: atomic units

units are:  $\hbar, m_e, e, 4\pi\epsilon_0$  c.f. SzO2, 1.1.

atomic unit of length:  $a_0 = 4\pi\epsilon_0 \frac{\hbar^2}{m_e e^2} \approx 0,53 \text{ \AA}$

atomic unit of energy:  $E_h = \frac{e^2}{4\pi\epsilon_0 a_0} \approx 414 \cdot 10^{-18} \text{ J}$   
Bohr-radius  
hartree

Since in quantum mechanics the Hamiltonian plays a key role in determining  $\Psi$ , we write

$\hat{H}$  for a system of  $N$  electrons and  $M$  nuclei

with atomic numbers  $Z_A$ :

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \hat{\nabla}_i^2 - \frac{1}{2} \sum_{A=1}^M \frac{\hat{\nabla}_A^2}{M_A} - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_{i < j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{A < B}^M \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}$$

↑ kinetic energy of electrons  
 ↑ kinetic energy of nuclei  
 ↑ potential energy of electron-nucleus attraction  
 $\mathbf{r}_i$ : position of electron  
 $\mathbf{R}_A$ : position of nucleus  
 ↑ potential energy of electron-electron repulsion  
 ↑ potential energy of nucleus-nucleus repulsion



All we have to do in quantum chemistry is ~~75~~  
 to solve the eigenvalue problem of this  $\hat{H}$ , c.f.  
 page ~~70~~. Unfortunately this is far too difficult to  
 do except for very special cases. We therefore  
 make approximations. One very general approxi-  
 mation, c.f. SZO 2.1.2 is the Born-Oppenheimer  
 approximation (Bo):

$$\Psi(\underline{r}_1, \dots, \underline{r}_N, R_1, \dots, R_M) \approx \Phi_{\text{nuc}}(R_1, \dots, R_M) \Phi_{\text{elec}}(\underline{r}_1, \dots, \underline{r}_N, R_1, \dots, R_M)$$

$\uparrow$  exact wavefunction                       $\uparrow$  approximate form

If you substitute the above form of  $\Psi$  in the  
 (SE) of page ~~70~~ you will find that it does NOT  
 fulfill it. Hence this is not a correct separation  
 step, only approximative. Also note, that

$$\Phi_{\text{elec}}(\underbrace{\underline{r}_1, \dots, \underline{r}_N}_{\text{variables}}, \underbrace{R_1, \dots, R_M}_{\text{parameters, i.e. integration implied by bracket does not involve these}})$$

The outcome of this approximate separation are  
 two eigenvalue equations:

a)  $\hat{H}_{\text{elec}} \Phi_{\text{elec}} = \epsilon_{\text{elec}} \Phi_{\text{elec}}$

b)  $\hat{H}_{\text{nuc}} \Phi_{\text{nuc}} = \epsilon \Phi_{\text{nuc}}$



where

$$\hat{H}_{\text{elec}} = -\frac{1}{2} \sum_i \hat{\nabla}_i^2 - \sum_i \sum_A \frac{z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\hat{H}_{\text{nuc}} = -\frac{1}{2} \sum_A \frac{\hat{\nabla}_A^2}{M_A} + \underbrace{\sum_{A < B} \frac{z_A z_B}{|\mathbf{R}_A - \mathbf{R}_B|}}_{\mathcal{E}_{\text{tot}}} + \mathcal{E}_{\text{elec}}$$

The eigenvalue equation a) on page 75 is

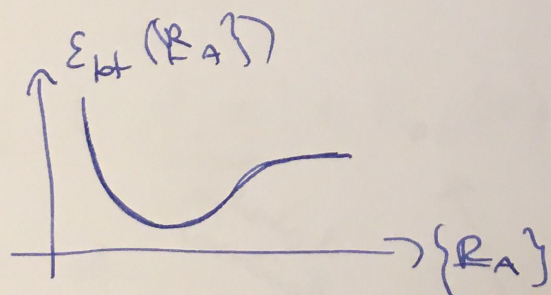
termed the electronic structure problem. The

equation b) is termed the nuclear problem.

Since  $\mathcal{E}_{\text{elec}}$  depends on  $\{\mathbf{R}_A\}$  as parameters,

$\mathcal{E}_{\text{tot}}$  also depends on  $\{\mathbf{R}_A\}$ . This gives rise to

the notion of the potential energy surface (PES):



The simplest electronic structure problem is the hydrogen atom problem, specified by the electronic Hamiltonian (we will omit 'elec' in the following)

$$\hat{H} = -\frac{1}{2} \hat{\nabla}^2 - \frac{1}{r}$$

where  $r$  is the distance from the origin.



This is one famous example that can be solved analytically (not easily), c.f. G 20.3.1, 20.3.2

The solution is helped by finding

$$[\hat{l}_z, \hat{H}] = 0$$

$$[\hat{l}^2, \hat{H}] = 0$$

where  $\hat{l}$  is the angular momentum operator.

Eigenvalue problem of  $\hat{l}_z$  gives rise to quantum number 'm'. Eigenvalue problem of  $\hat{l}^2$

gives rise to quantum number 'l'. And finally eigenvalue problem of  $\hat{H}$  ~~separates~~ gives rise to

quantum number 'n'. The solution reads:

$$\psi_{nlm}(r, \vartheta, \varphi) = R_{nl}(r) Y_l^{(m)}(\vartheta, \varphi)$$

↑  
orbitals of the hydrogen atom

↑ spherical coordinates

↑ radial function  $l < n$

↑ spherical harmonic functions  $-l \leq m \leq l$

$$E_n = -\frac{1}{2} \cdot \frac{1}{n^2}, \quad n = 1, \dots$$

↑  
orbital energy; note that E not depends on l and m implies degeneracy in the spectrum



Stepping to many-electron systems we have to make further approximations.

These approximations must respect a property stemming from the fermionic property of electrons, and that is antisymmetry:

$$\Psi_{\text{elec}}(x_1, \dots, x_i, \dots, x_j, \dots, x_N) = -\Psi_{\text{elec}}(x_1, \dots, x_j, \dots, x_i, \dots, x_N)$$

we will omit this further on

note the change in the index and in the sign

Terminology: the above antisymmetry is often called the Pauli exclusion principle

What is  $x_i$ ? Combined spatial and spin coordinate

$$x_i(r_i, \omega_i) \text{ spin-coordinate}$$

What is the spin-coordinate? It is the quantum mechanical way of describing the intrinsic angular momentum that electrons possess.

You will see more on this in advanced physical chemistry. For now it suffices that we have to work with  $x_i$  instead of simply  $r_i$ .



Note:  $\hat{H}$  as we wrote on page ~~74~~ does not ~~79~~ affect the spin-coordinate. Hence in this description the spin does not affect energetics. Spins affect energetics when  $\hat{H}$  involves magnetic interactions, for example, c.f. Zeeman-effect or NMR or hyperfine coupling.

A generally used approximation scheme for many-electron systems is the Hartree-Fock approximation. This starts by a separation-type idea

$$\Psi(x_1, \dots, x_N, \underbrace{R_1, \dots, R_N}_{\substack{\text{we are} \\ \text{not going} \\ \text{to indicate} \\ \text{these further} \\ \text{parameters}}}) \stackrel{?}{\cong} \psi_1(x_1) \psi_2(x_2) \dots \psi_N(x_N)$$

The above form is obviously wrong since it does not fulfill  $(\otimes)$  on page ~~78~~. Let us set this antisymmetric then!

$$\Psi_{\text{Slater}} \sim \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) & \dots & \psi_N(x_1) \\ \psi_1(x_2) & \psi_2(x_2) & & \psi_N(x_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(x_N) & \psi_2(x_N) & & \psi_N(x_N) \end{vmatrix} \quad \begin{array}{l} \text{This is} \\ \text{called} \\ \text{a} \\ \text{Slater -} \\ \text{determinant.} \end{array}$$

This is basically the product form upgraded to fulfill antisymmetry.



The Slater determinant is also called the antisymmetric product just for this reason. 80

$\Psi_{\text{Slater}}$  is a trial function that we substitute into the variation principle, c.f. page 54 (⊕)

$$\delta \frac{\langle \Psi_{\text{Slater}} | \hat{H} | \Psi_{\text{Slater}} \rangle}{\langle \Psi_{\text{Slater}} | \Psi_{\text{Slater}} \rangle} = 0$$

There is a rather complicated derivation here that we omit. Let us see directly the outcome.

$$\hat{f}(i) \psi(x_i) = \epsilon \psi(x_i) \quad (\diamond \diamond)$$

with 
$$\hat{f}(i) = -\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_j^{\text{occ}} \int \psi_j^*(x_j) \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \psi_j(x_j) d\mathbf{v}_j d\omega_j$$

This is the so-called Fock-operator.

$$- \sum_j^{\text{occ}} \int \psi_j^*(x_j) \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \hat{P}_{ij} \psi_j(x_j) d\mathbf{v}_j d\omega_j$$

This operator permutes  $x_j$  and  $x_i$ , acting to the right.

Equation ( $\diamond \diamond$ ) is an eigenvalue equation of the Fock-operator, also termed Fockian. It determines  $\psi$ , called molecular orbitals (MO) and  $\epsilon$  called orbital energies.



Did we gain anything? ~~Yes~~ We started from an eigenvalue equation and landed on another eigenvalue equation. Note, however, that our starting equation involved the many-electron function,  $\Psi_{\text{Slater}}$ , our resulting equation involves the one-electronic function,  $\psi(x_i)$ , the MO. This is much more easy to solve by numerical means simply because <sup>of</sup> the reduced number of variables. In other words we did separate. Again, only approximatively, since  $\Psi_{\text{Slater}}$  can not fulfill the SE of  $\hat{H}_{\text{elec}}$  written on page 76.

What can we tell of the solution implied by  $(\diamond\diamond)^2$ ?

- ⊖ There are multiple MOs and orbital energies. These are generally arranged in increasing energy order, and the bottommost  $N$  are filled into  $\Psi_{\text{Slater}}$ . This is called the Aufbau principle. The upper side 'occ' in  $\hat{f}(i)$  refers to this. MOs filled into  $\Psi_{\text{Slater}}$  are called 'occupied' those fulfilling  $(\diamond\diamond)$  but not making it into  $\Psi_{\text{Slater}}$  are called 'virtual'.



⊖ Since the determinant is invariant to making linear combination of its columns, the occupied orbitals can be mixed by a unitary transformation (to conserve orthonormality). This is the way of generating so-called localized MO's. The MO's fulfilling (⊗) are called canonical MO's. Their special property is the associated orbital energy. Localized MO's do not possess orbital energy.

⊖ There is a price to pay in this approximation, and this is the rather complicated nature of the Fock-operator. The third and fourth term of the Fockian describes inter-electron interaction in a so-called mean-field manner.

Note also, that  $f(i)$  depends on its own solution, since it involves  $\psi_j$ !

Hence the eigenvalue equation of (⊗) can only be solved in an iterative manner, to achieve self-consistency.

The ~~approx~~ technique is often termed for this reason the self-consistent-field technique.







What AO's are used?

One could think of hydrogen-atom eigenfunctions, c.f. page 44, they are unfortunately impractical because of the exponential decay of the radial part

$$R_{nl} \sim e^{-\alpha_n r}$$

In practice so-called gauss-type orbitals (GTO) are used as AO's that decay as  $e^{-\zeta r^2}$

The LCAO-MO method arrives to the matrix eigenvalue problem of  $\hat{F}$  represented in the basis of  $\{\chi_\mu\}$  c.f. again pages 56-58. Elements of matrix  $\underline{F}$  are obtained as

$$F_{\mu\nu} = \langle \chi_\mu | \hat{F} | \chi_\nu \rangle$$

Note, that AO's are generally not orthonormal, this is why their overlap matrix  $\underline{S}$  usually appears

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle \neq \delta_{\mu\nu}$$

In doing, note that the MO concept originates in the Hartree-Fock approximation. It is however very useful and applied in approximations stepping beyond Hartree-Fock quite extensively.