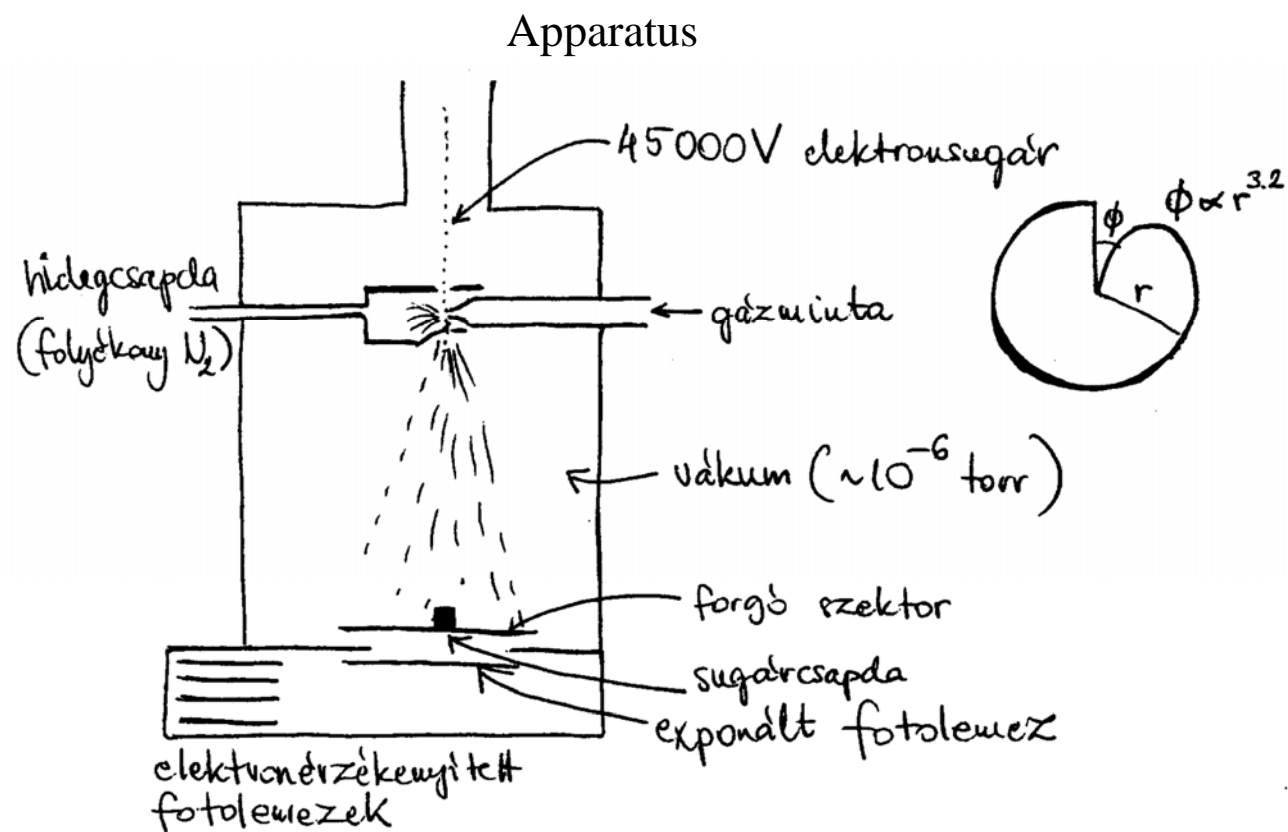# VII. STRUCTURE DETERMINATION USING
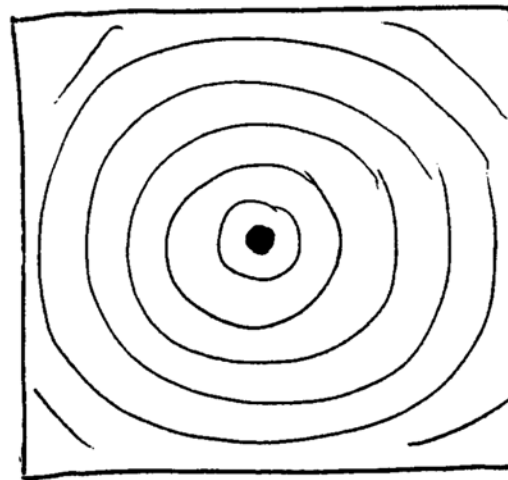# GAS ELECTRON DIFFRACTION (GED)

I. The experiment

Apparatus

Diffraction pattern

The diffractogram consists of diffuse, concentric rings.

The spacings and intensities reflect the structure of the molecule or the mixture if there is more than one type of molecule present.

The rings are superimposed on a background (smooth) that contains no structural information.
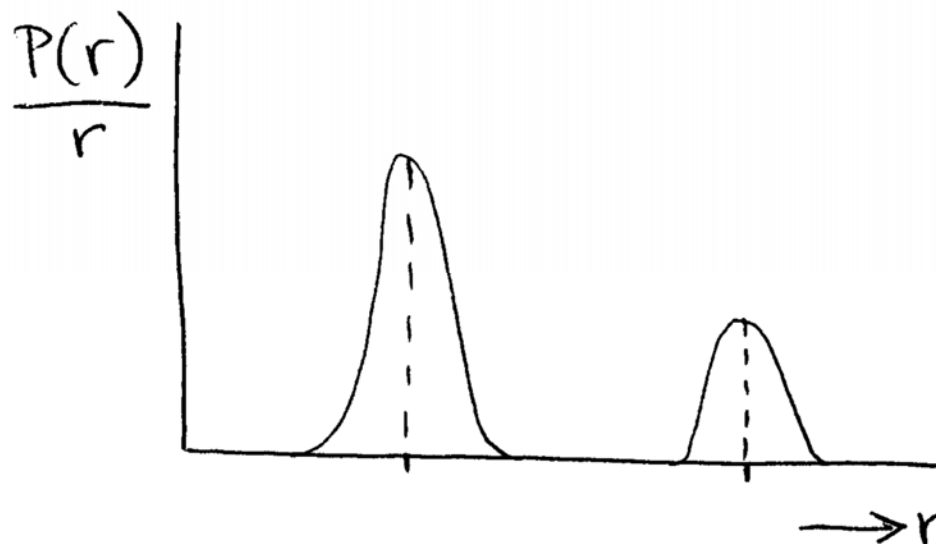
II. Information from GED

Analysis of the diffraction pattern yields information about the scattering power and distribution of matter in space. Primarily this means the average internuclear distances and something about the vibrations of the nuclei. Secondarily, one may learn something about atomic electron distributions.

The typical GED measurement results may be interpreted by a radial distribution function:

(a) peak positions correspond to internuclear distances;

(b) peak widths (HWHM) correspond to mean square amplitudes of vibration;

(c) peak areas are functions of number of distances and atomic numbers of the atomic pairs (if molecule is heated, the peaks get broader but the area remains constant).

$$\frac{P(r)}{r}$$

$$\longrightarrow r$$

III. Advantages of the method

1. Accuracy: in favorable cases atom-atom distances can be measured to ±0,001 Å or less. (There are several types of distances symbolized; for example, r_a, r_g, r_α, r_z, r_0, r_α^0 and r_s.)

2. Speed: For simpler structures one may have the results in a day or so.

3. Structural results for free molecules (interaction-free structures).

4. Very few workers.

IV. Limitations of the method

1. State of matter (must have sufficient vapor pressure).

2. Expense of equipment (time and money).

3. Resolution (data are one-dimensional).

4. Hard to develop novel techniques (mostly left out from the revolution caused by lasers).

V. From plates to data

Idea: to obtain digitalized data for the molecular intensity function in a form such that calculated intensity curves may be easily compared – fitted – to it. Different laboratories prefer different forms. On form:

$$sI_m(s) = k \sum_{i \neq j} A_i(s) A_j(s) r_{ij}^{-1} \cos(\eta_i - \eta_j) \exp(-\ell_{ij}^2 s^2 / 2) \sin[s(r_{ij} - \kappa_{ij} s^2)] \, ,$$

where

$s := (4\pi/\lambda)\sin\Theta \qquad (2\Theta$ is the scattering angle; $\lambda = h / \sqrt{2mE}$)

A_i atomic scattering amplitude for electrons (from tables)
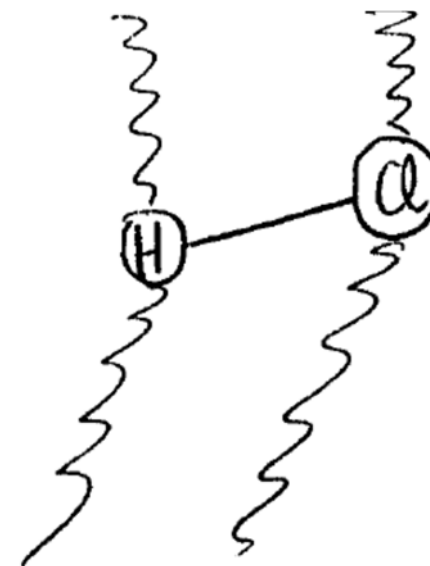
η_i phase shift coefficient

r_{ij} interatomic distance

ℓ_{ij}^2 mean square amplitude of vibration

κ_{ij} anharmonicity constant

- electrons are largely affected by the nucleus

- intensity of scattering depends on Z

- interference pattern gives interatomic distance

- the effect of the electrons in the atoms is important at small angles

$P_{ij}(r)$ for a given pair of atoms could be computed from a

knowledge of the vibrational wavefunctions of the molecule

plus the population of each excited state (Boltzmann factors).

The intensity striking the plate contains:

(a) molecular-structure sensitive (atom-atom distances and vibrational amplitudes) scattering;

(b) background scattering from the sample ("atomic" scattering);

(c) extraneous scattering from the apparatus, all modified by the rotating sector as well as by some geometric factor.

Putting this into an equation:

$$I_p = I_T \cdot \alpha(s) \cdot G(2\Theta) = \left(\frac{I_m(s)}{s^4} + \frac{I_{atomic}}{s^4} + I_{app} \right) \cdot \alpha(s) \cdot G(2\Theta),$$

where

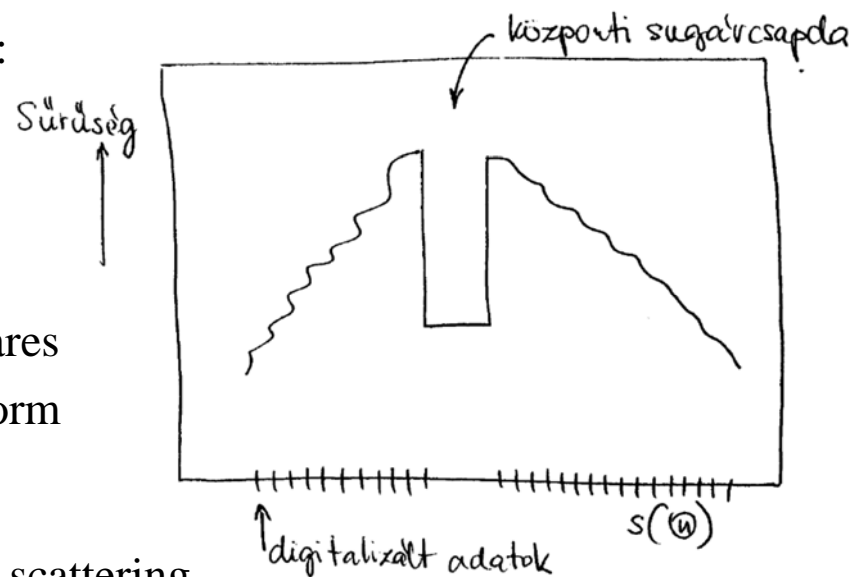$\alpha(s)$ sector functions $G(2\Theta)$ geometric factor

I_{atomic} sample background I_{app} apparatus background scattering

Make a microdensitometer scan of the plate:

Background removal is done by a least-squares
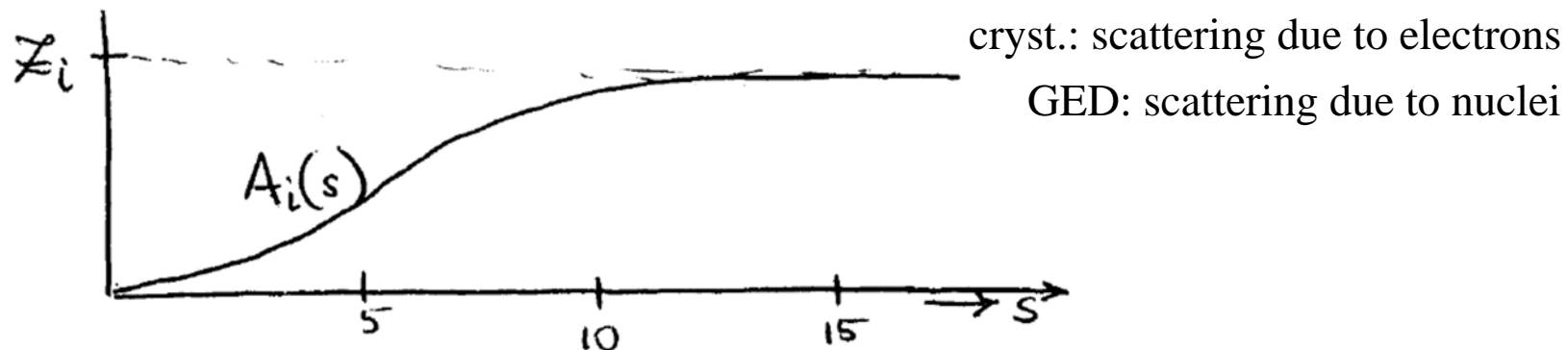fitting procedure, which operates with the form

$$s^4 I_T = I_m(s) + I_{atomic} + s^4 I_{app},$$

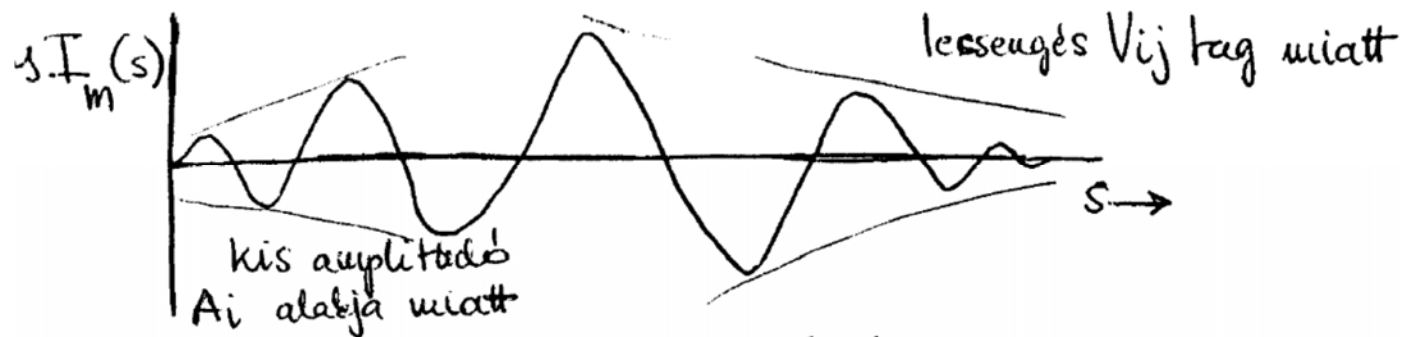where I_{atomic} is a sum of elastic and inelastic scattering.

VI. Some remarks about intensity curves

A) $\quad sI_m(s) = k\sum\limits_{i\neq j} A_i(s)A_j(s)\,r_{ij}^{-1}\cos(\eta_i - \eta_j)V_{ij}(s)\sin[s(r_{ij} - \kappa_{ij}s^2)]$

is the so-called variable coefficient intensity curve. Reason: A_i, available from tables and characteristic of nucleus i, is a rapidly varying function of s:

cryst.: scattering due to electrons

GED: scattering due to nuclei

Consequently, the appearance of $sI_m(s)$ for a diatomic molecule is
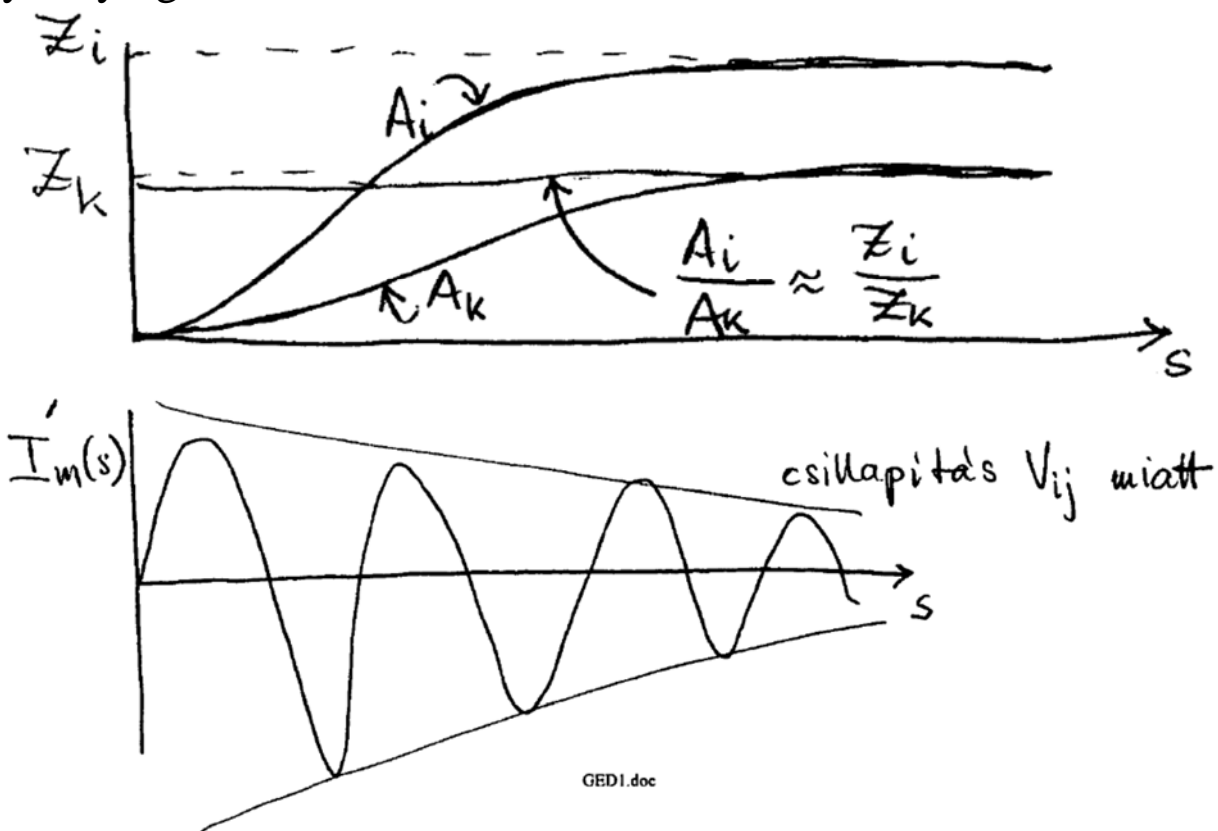
$$I'_{\mathrm{m}}(s) = sI_{\mathrm{m}}(s)\{Z_k Z_l A_k^{-1} A_l^{-1}\} =$$

B)

$$k\sum_{i \neq j} \frac{A_i A_j}{A_k A_l} Z_k Z_l \, r_{ij}^{-1} \cos(\eta_i - \eta_j) V_{ij}(s) \sin[s(r_{ij} - \kappa_{ij} s^2)]$$

is the so-called constant coefficient intensity curve. Reason: $(A_i A_j / A_k A_l) Z_k Z_l$ are very slowly varying functions of s:

$$\frac{A_i}{A_k} \approx \frac{Z_i}{Z_k}$$

csillapítás V_{ij} miatt

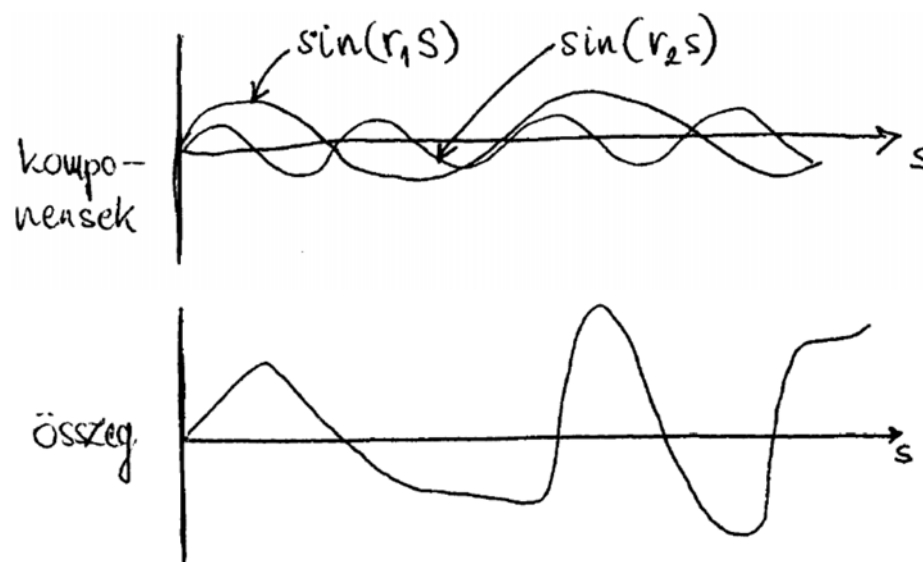GED1.doc

VII. Structure refinement

A) The method of trial and error

The trial structure is an approximate structure which serves as the basis for refinement. Some features of the structure may often be deduced directly from the intensity curve, others from the radial distribution calculation described later. Chemical intuition/rules as well as even approximate quantum chemical computations should provide help.

Example: YX_2 molecule, with two different nucleus-nucleus distance

$$I'(s) \approx 2\frac{Z_X Z_Y}{r_1}V_{XY}\sin sr_1 + \frac{Z_X^2}{r_2}V_{XX}\sin sr_2$$

This is a sum of two sine waves:

B) The radial distribution (RD) method

Obviously, the trial-and-error method will be hopeless for complicated molecules. The RD method depends on the Fourier Integral Theorem:

$$F(x) = \frac{1}{\sqrt{2\pi}} \int_0^\infty G(y)\sin xy\, dy$$

$$G(y) = \frac{1}{\sqrt{2\pi}} \int_0^\infty F(x)\sin xy\, dx$$

This is a pair of Fourier transforms. Let's identify $y \to s$ and $x \to r$, *i.e.*, transform from "s space" to "r space":

$$F(r) = \frac{1}{\sqrt{2\pi}} \int_0^\infty I'(s)\sin rs\, ds$$
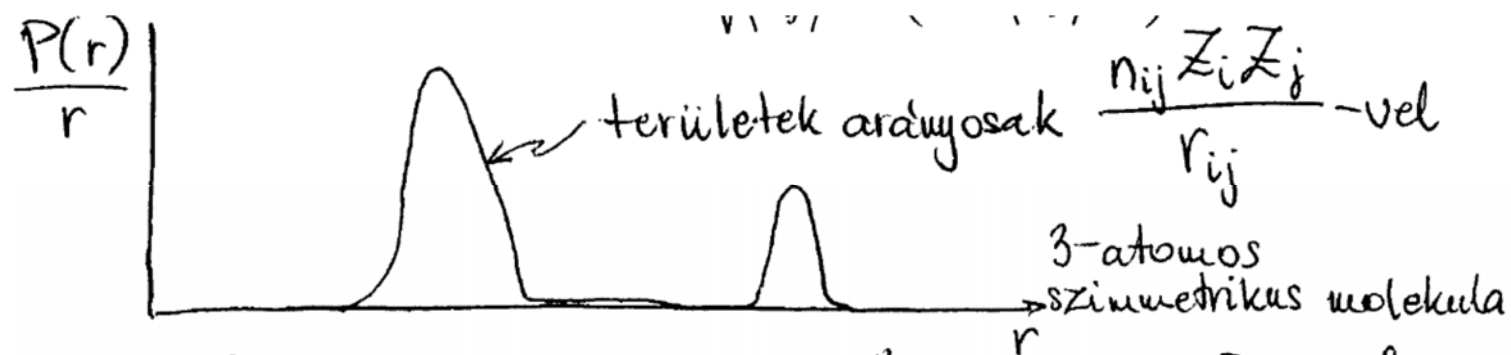
$$I'(s) = \frac{1}{\sqrt{2\pi}} \int_0^\infty \frac{P(r)}{r}\sin rs\, dr,$$

$P(r)$ is the probability of finding two atoms a distance r apart.
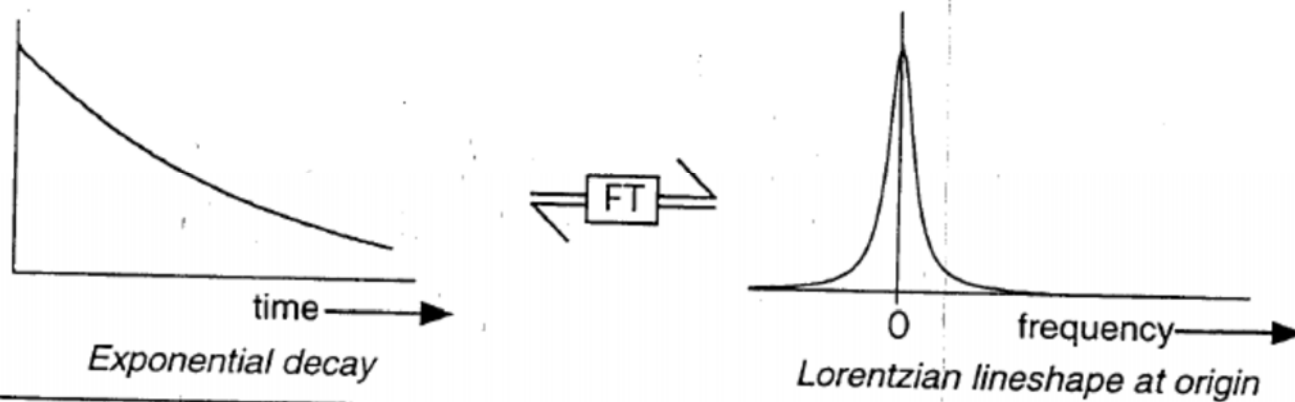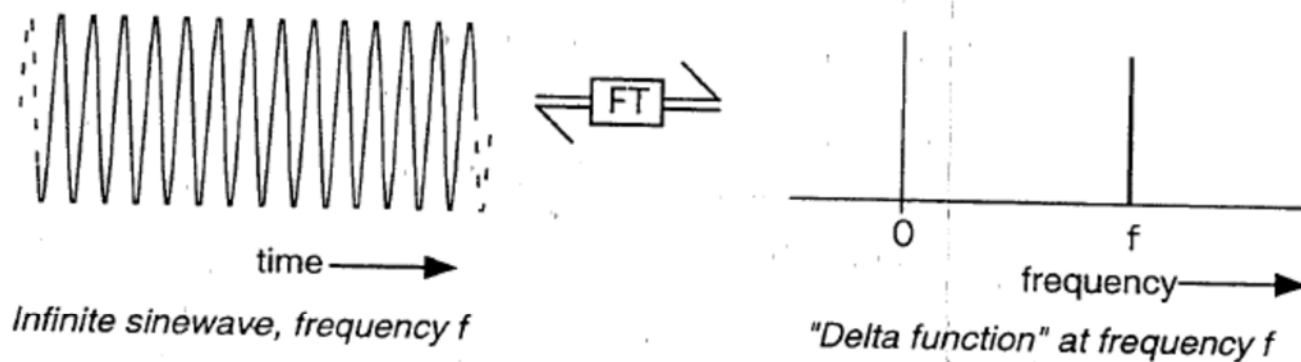
With the help of the Fourier transform

(and assuming a Gaussian peak distribution $P_{ij}(r) = \dfrac{1}{\sqrt{2\pi \ell_{ij}^2}} \exp\left(\dfrac{-(r_e - r_{ij})^2}{2\langle \ell_{ij}^2 \rangle} \right)$):
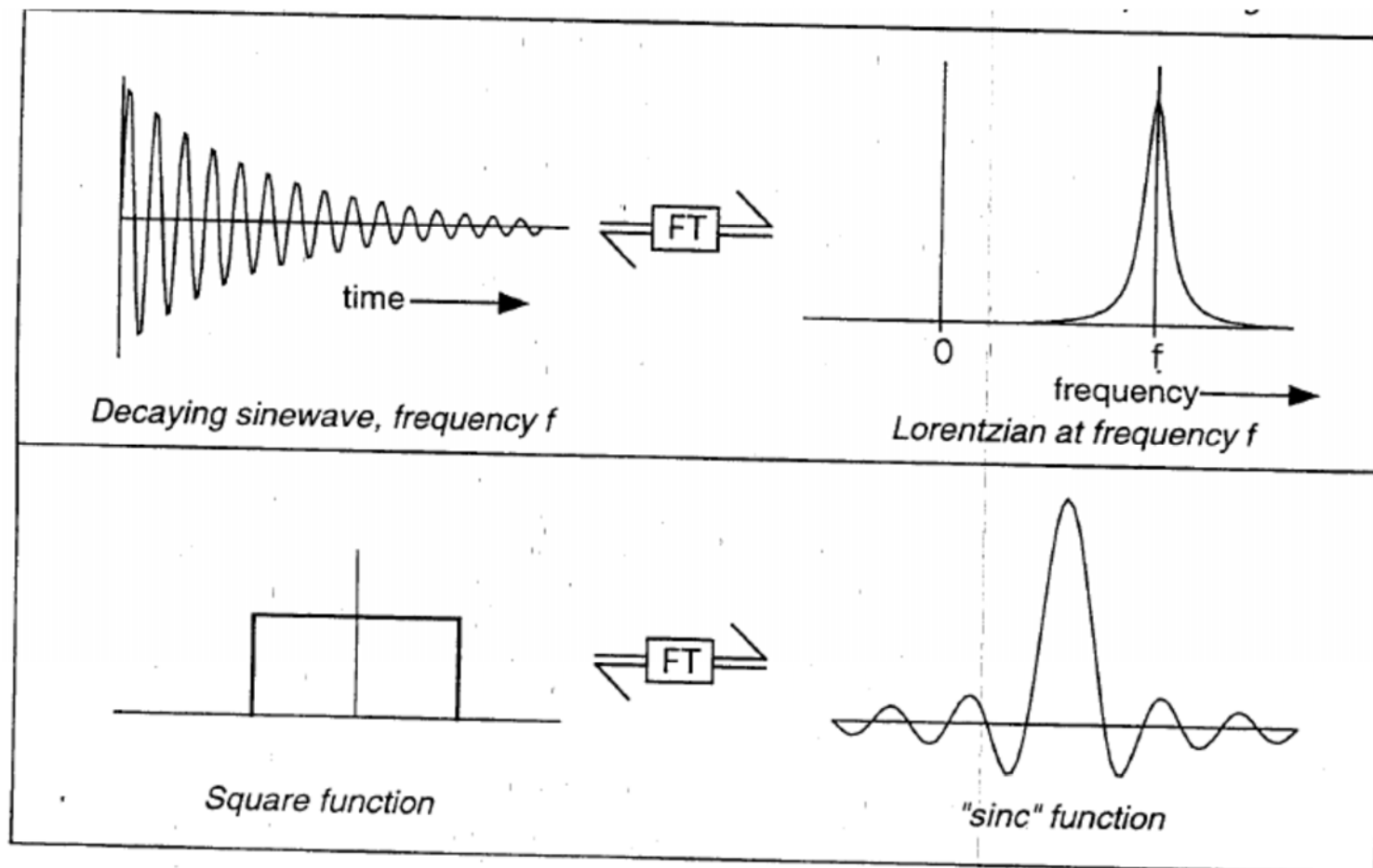
$$\frac{P(r)}{r} = \frac{1}{\sqrt{2\pi}} \sum \frac{n_{ij} Z_i Z_j}{r_{ij}} \frac{1}{\sqrt{\langle \ell_{ij}^2 \rangle}} \exp\left(\frac{-(r_{ij} - r_{ij}^e)^2}{2\langle \ell_{ij}^2 \rangle} \right)$$

területek arányosak $\dfrac{n_{ij} Z_i Z_j}{r_{ij}}$ -vel

3-atomos szimmetrikus molekula

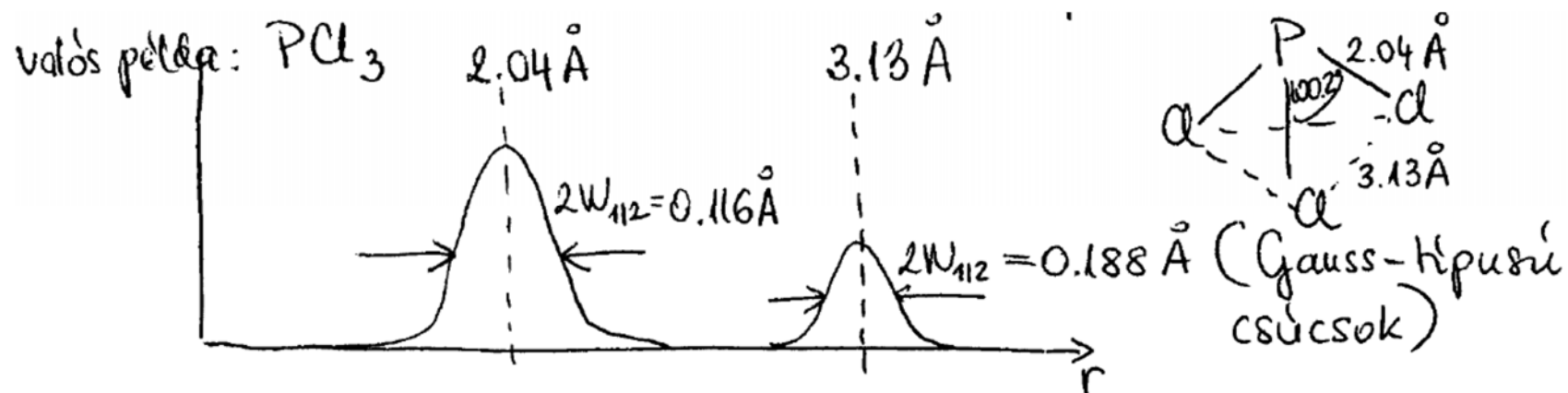## Box 2.3: Fourier Transform Pairs

Fourier transformation is a mathematical process (here represented by FT) which interconverts two functions. Below are Fourier pairs which are important in NMR.

time ———▶

Infinite sinewave, frequency f

FT

0   f

frequency ———▶

"Delta function" at frequency f

time ———▶

Exponential decay

FT

0   frequency ———▶

Lorentzian lineshape at origin

Decaying sinewave, frequency f → FT → Lorentzian at frequency f

Square function → FT → "sinc" function

Real example, PCl$_3$:

valós példa: PCl$_3$ 2.04 Å   3.13 Å $2W_{112}=0.116$Å $2W_{112}=0.188$ Å (Gauss-tipusú csúcsok)

P 2.04 Å, 100°, 3.13Å

During the structure refinement the method of weighted linear least squares is employed. The refinement is stopped when the theoretical and the experimental intensity curves deviate from each other less than a prescribed limit. It often happens that the GED intensity curve does not contain sufficient information to decide between several structural possibilities.

NB: distances defined by MW spectroscopy and GED are not the same, the differences are small but significant.