Physikalische und Theoretische Chemie I&II

Kapitel 10-15 : Teil Theoretische Chemie

Die **Vorlesung** (Schwarz) findet im WS jeweils am Montag von 8-10 h im Raum B-2203 und am Mittwoch von 10-12 h im Raum AR-G113 statt. Beginn dieses Teils der Vorlesung ist aber Freitag, der 10.1.2003. Die **Übungen**, Blätter siehe Homepages der TC, werden ab 17.1.2003 jeweils Freitags von 8-10 h im Raum AR-B2104 abgehalten. Die Zeit, die hier nicht für die Übungsbesprechung benötigt wird, wird für Vertiefungen des Stoffes verwendet. Die **Klausur** findet nach Ende der Vorlesungszeit, nach Vereinbarung, statt.

Die Vorlesung wird in deutsch gehalten, in Anlehnung an Inhalt aus dem PC-Buch von Atkins, Kap. 11-15. Dies Vorlesungsskript, Blätter siehe Homepages der PC bzw. der TC, ist aber in englisch: Sie sollen sich rechtzeitig an die angelsächsischen 'termini technici' gewöhnen. Hier der Inhalt:

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Chapter 10: Mathematical Preliminaries

10.1 Mathematical tools for chemical artisans

A few basic mathematical concepts must be mentioned here (although they are not taught in secondary schools), because they are really needed in science as inevitable tools, also by the modern chemical artisans. (This is not just pure mathematics.)

In science the holistic (ganzheitliche) world is partitioned into parts. Parts interact with each other; parts can change, e.g. because we manipulate them.

Understanding reality in science means two things: 1st, developing an intuitive feeling of the behavior of the parts through nice looking pictures and persuasive sounding words. But 2nd, in the natural sciences this is achieved on a logically coherent and correct basis, i.e. within a formal, e.g. mathematical, theory.

Therefore we need, among others, the following two tools for the physicochemical subjects of this course: 1st, mathematical description of the parts by **vectors,** $|v\rangle$ (in italics)**,** and 2nd, mathematical description of the changing of parts by **operations**, **Op** (bold face).

The objective world is that facet of the world, which is reproducible, and intersubjective (between the colleagues initiated in science). Science is 'elitist' and 'antidemocratic'. In these respects, science (Natur- und Ingenieur-Wissenschaften) is very different from the humanities and arts (sog. Kultur- und Geistes-Wissenschaften).

10.2 Vectors

The position $|r\rangle$ of a point-particle is characterized by 3 Cartesian[1] coordinates. Its state of motion is changed through interaction with a force field, e.g. an electric field, $|F(|r_o\rangle)\rangle$, which has 3 orthogonal components at every point of space. The geometric structure $|s\rangle$ of a rather rigid n-atomic molecule is represented through 3n coordinate values. The positions of its nuclei are quantum mechanically smeared and thermally distributed around their equilibrium values, typically described by 3n - 6 (or –5) vibrational distortion coordinates $|\Delta\rangle$.

The temperature or concentration distribution in a reaction vessel, the electronic charge density distribution in a crystal, the electric field in space, the complex matter field amplitude (so-called state or wave function) of a molecule etc. are described by functions $|f\rangle$ of one, two, three ore more component-functions, each depending on one or three or more variables. Functions can be represented by a Taylor, power, Fourier etc. series with the help of numerable non-finite many Taylor or Fourier etc. coefficients c_i.

$$|r\rangle = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \qquad |F\rangle = \begin{pmatrix} F_x \\ F_y \\ F_z \end{pmatrix} \qquad |s\rangle = \begin{pmatrix} x_1 \\ \vdots \\ z_n \end{pmatrix} \qquad |\Delta\rangle = \begin{pmatrix} \Delta_1 \\ \vdots \\ \Delta_{3n-6} \end{pmatrix} \qquad |f\rangle = \begin{pmatrix} c_0 \\ c_1 \\ \vdots \end{pmatrix}$$

All these different mathematical objects have a few properties in common. For example:

One can add two of them in any order and obtain a new object of the same kind, they form a closed set:

$$|v_1\rangle + |v_2\rangle = |v_2\rangle + |v_1\rangle = |v_3\rangle \quad .$$

[1] **Descartes**, 1596-1650, France – Germany – Sweden : analytical geometry, geometric optics, Discours de la Méthode pour bien conduire la raison

The order does not matter: this is called commutative or Abelian (abelsch). One can "linearly combine" vectors with complex numbers, and these "**linear combinations**" follow some rules of 'primary school mathematics':

$$c_1 \cdot |v_1\rangle + c_2 \cdot |v_2\rangle = |v_4\rangle \quad ;$$

$$c \cdot (|v_1\rangle + |v_2\rangle) = c \cdot |v_1\rangle + c \cdot |v_2\rangle \quad , \quad 0 \cdot |v_1\rangle = |0\rangle \quad , \quad 1 \cdot |v_1\rangle = |v_1\rangle \quad .$$

Any object, which obeys the set of rules of mathematical vectors, is called a physical realization of a **vector** $|v\rangle$, such as a force $|F\rangle$, a structure $|s\rangle$, a function $|f\rangle$. A vector can by symbolized by an arrow. All linear combinations of a basic set of vectors ("**a basis**") are said to "span a **vector space**". There are vector spaces of **dimension** 1 (such as a line), of dimension 2 (such as a plane), of dimension 3 (such as "real space" or "momentum space" or "reciprocal or quantum number space"), of dimension 6 (e.g. phase space of a point particle), or of ∞ dimensions (such as the space of differentiable functions), etc.

10.3 Scalar products

If vectorial objects can be combined in pairs to yield a complex number, $|v_1\rangle,|v_2\rangle \rightarrow c_{12}$, we have a vector space with a measure or gauge. In typical cases such a vector space is called a "**Hilbert space**".[2] Some rules for "**scalar products**" are

$$(|v_1\rangle)^+ \cdot (|v_2\rangle) = \langle v_1|v_2\rangle = \langle v_2|v_1\rangle^* = c \quad \text{and} \quad \langle v_1|v_1\rangle \geq 0 \quad ,$$

$$\langle v_3|c_1 \cdot v_1 + c_2 \cdot v_2\rangle = \langle v_3|v_1\rangle \cdot c_1 + \langle v_3|v_2\rangle \cdot c_2 \quad .$$

The rules for scalar products are as in 'primary and secondary school mathematics', accordingly:

$$\langle v_1|v_1\rangle = \text{real} \quad , \quad \langle c_2 \cdot v_2|v_1\rangle = c_2^* \cdot \langle v_2|v_1\rangle \quad .$$

If $\langle v_1|v_2\rangle = 0$, the two vectors are said to be "**orthogonal**" (or one vector vanishes).

Note: In real life, we obtain, through counting, for measures of reality always integer numbers (times 10^{-n} units). The mathematics of integer numbers is very tricky. To make life 'easily understandable' we introduce the complex numbers. Their mathematics is especially general and applicable, and they give a deep insight into the laws of the objective world.

For $\langle v_1|v_2\rangle = L^2$, the vector is said to be "normalized to L", L is its "**length**".

Admissible definitions of scalar products are

$$\langle v_1|v_2\rangle = \sum_i c_{i1}^* \cdot c_{i2} \quad \text{or} \quad \langle f_1|f_2\rangle = \int_{\text{left}}^{\text{right}} dx \cdot f_1^*(x) \cdot f_2(x) \quad .$$

$|v\rangle$ is called an ordinary or "ket" vector. $|v\rangle^{*T} = |v\rangle^+ = \langle v|$ is called a "complex conjugated and transposed" or "adjoint" or "bra" vector. Then, a scalar product is a bra-ket. This is the **Dirac** type of writing. The scalar product is the product of two matrices, a row matrix and a column matrix. You need 'not learn more than matrix multiplication'.

The two functions $f_1 = e^{-x^2}$ and $f_2 = x \cdot e^{-x^2}$, which are "gerade" and "ungerade" = "symmetric" and "antisymmetric" with respect to "inversion at the origin", are orthogonal:

$$\text{if} \quad \langle f_1|f_2\rangle = \int_{-\infty}^{+\infty} dx \cdot g \cdot u \equiv 0 \quad , \quad "f_1 \perp f_2" \quad .$$

[2] **David Hilbert**, 1862-1943, Königsberg – Göttingen : algebraic interrelations, number theory, axiomatic geometry and mathematics, functional analysis

10.4 Operators

$|f_1\rangle \xrightarrow{\text{Op}} |f_2\rangle$ is written as $\mathbf{Op} \circ |f_1\rangle = |f_2\rangle$ or $\mathbf{Op}\ f_1(x) = f_2(x)$.

The simplest kind of operators "act" on linear combinations of vectors as in 'primary school mathematics'. These **linear Operators** are defined by

$$\mathbf{L} \circ (c_1 \cdot |f_1\rangle + c_2 \cdot |f_2\rangle) = |\mathbf{L} \circ f_1\rangle \cdot c_1 + |\mathbf{L} \circ f_2\rangle \cdot c_2 \quad .$$

Examples of linear operators : **f(x)·** , $\mathbf{D_x = d/dx}$, **rotation** ; counterexamples : √ , **f(x)+**

The most important operator in science is the "time evolution operator", which "propagates" the state function according to **causality**. Kant[3] realized that causality is the precondition for the possibility of experience and of science. The most basic equation of causality is the Schrödinger equation.

Another important type of operators are the "**Hermitean operators**" [4] :

$$\langle f_1|\mathbf{H} \circ f_2\rangle = \langle \mathbf{H} \circ f_1|f_2\rangle \quad \text{or} \quad \int_a^b dx \cdot f_1^* \cdot (\mathbf{H} \circ f_2) = \int_a^b dx \cdot (\mathbf{H}^* \circ f_1^*) \cdot f_2 \quad , \quad \text{for } \textit{any } f_1, f_2 \text{ !}$$

Examples of Hermitean operators : real **h(x)·**, imaginary differentiation **i·d/dx** ; counterexamples: **h(x)+** , **d/dx** (note: Hermiticity depends on the boundaries).

The **eigen-values and eigen-functions/vectors** of operators are λ_n, g_n with

$$\mathbf{Op} \circ g_n = g_n \cdot \lambda_n \quad .$$

Example: mirror reflection has $\lambda = -1$ for g = vertical line, and $\lambda = +1$ for g = mirror plane

Hermitean, linear operators have the following properties

1) Eigenvalues are real, $\lambda_n = \lambda_n^*$
2) Eigen-functions/vectors are renormalizible: that is, for any complex number c_n :
   if $\mathbf{Op} \circ (g_n) = (g_n) \cdot \lambda_n$, then also $\mathbf{Op} \circ (c_n \cdot g_n) = (c_n \cdot g_n) \cdot \lambda_n$ (eigen-spaces)
3) Different eigenfunctions of the same eigenvalue can be arbitrarily linear combined:
   if also $\mathbf{Op} \circ (g_m) = (g_m) \cdot \lambda_n$, then also $\mathbf{Op} \circ (c_n g_n + c_m g_m) = (c_n g_n + c_m g_m) \cdot \lambda_n$
4) Eigenfunctions for different eigenvalues are automatically orthogonal.
5) Different eigenfunctions for the same eigenvalue can be chosen linear combined so as to form a set of orthogonal basic eigenfunctions

The eigenfunctions to a given eigenvalue span a one, or a two, or a three, … dimensional eigen-Hilbert-sub-space; the eigenvalue is then called singly, doubly, triply, … degenerate.

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[3] **Immanuel Cant**, 1724-1804, Königsberg : rational philosophy, Kant-Laplace cosmology, critique of naive rationalism (Descartes[1], Leibniz 1646-1716, C. Wolff 1679-1754 – [Karl Popper, 1902-1994] – and of English empirism (Bacon 1561-1626, Hobbes 1588-1679, Locke 1632-1704, Hume 1711-1776)
Man can understand through concepts, categories, such as 'conserved substances' ('erhaltene Substanzen') and 'causal laws' ('Kausalgesetze') – the forms of perception (Formen der Anschauung) are space and time. By analyzing the preconditions of experience (Bedingungen der Möglichkeit von Erfahrung) one can know something about the real world surrounding us before any experience *a priori.* However, through experience one can – with less security – know *a posteriori* something about the specific details of **Time** (linear, directed, finite, etc. ?) and **Matter** (mass = energy, bipolar electricity, tripolar color charge, boson number, etc.). In the course of time, matter changes some parameters (of 3-dimensional **Space** and of further dimensions) according to the **Causal Law** (Newtonian-Hamiltonian or Schrödinger-Dirac type etc.; forces are gravitational, electromagnetic, 'weak' or 'strong')

[4] **Hermite**, 1822-1901, France : mathematician

10.5 Representations

Given a complete set of bases $\{|b_i\rangle\}$ or $\{|b_j'\rangle\}$, then the object (abstract vector $|v\rangle$) can be "represented" by a **representation-vector** in this basis :

$$|v\rangle = \sum_i |b_i\rangle c_i = \sum_j |b_j'\rangle c_j' \cong \begin{pmatrix} c_1 \\ \vdots \end{pmatrix}_{\{|b_i\rangle\}} \cong \begin{pmatrix} c_1' \\ \vdots \end{pmatrix}_{\{|b_j'\rangle\}} \quad \text{where } c_i = \langle b_i|v\rangle \quad , \quad c_j' = \langle b_j'|v\rangle \quad .$$

A linear operator can be "represented" by a **representation-matrix** in this basis :

$$\mathbf{H} \cong \begin{pmatrix} H_{11}H_{12}\dots \\ H_{21}H_{22}\dots \\ \vdots \end{pmatrix}_{\{|b_i\rangle\}} \quad \text{with } H_{ji} = \langle b_j|\mathbf{H}\circ b_i\rangle \quad . \text{ The column vector } \begin{pmatrix} H_{1i} \\ \vdots \end{pmatrix} \text{ is } \mathbf{H}\circ|b_i\rangle \, .$$

The multiplication rule for matrices is defined so that there is a direct correspondence to consecutive linear operations, $\mathbf{H}\circ\mathbf{G} = \mathbf{K} \rightarrow [H_{ik}]\cdot[G_{kj}] = [K_{ij}]$.

A Hermitean operator is represented by a "self-adjoint", i.e. transposed-complex-conjugate (complex-symmetric) matrix, $H_{ji} = H_{ij}^{*}$.

The **trace** (**spur**) of a matrix, $\mathrm{tr}(H_{ij}) = \mathrm{sp}(H_{ij}) = \sum_i H_{ii}$ is characteristic for the operator: it is the same, independent of the chosen orthornormal basis : $\mathrm{sp}(H_{ij}) = \mathrm{sp}(H_{ij}') =$ "**character**" .

10.6 Symmetry

A **transformation T** is the transition from one set of variables to another equivalent set. Examples:

$$(x, y, z) \rightarrow (r, \vartheta, \varphi) \quad \text{or} \quad (x\,;\,y) \rightarrow (\cos\alpha \cdot x + \sin\alpha\,;\, -\sin\alpha \cdot x + \cos\alpha \cdot y) \quad \text{or}$$

$$(x_1, y_1, x_2, y_2) \rightarrow (x_2, y_2, x_1, y_1) \quad \text{or} \quad (x, y, z) \rightarrow (-x, -y, -z) \quad .$$

These transformations are named 'cartesian to polar', 'planar rotation', 'permutation', 'three dimensional inversion'. If the form of an operator is invariant upon a coordinate transformation, i.e.

if $\mathbf{T}(x' \leftarrow x) \circ \mathbf{H}(x) \circ \mathbf{T}(x \leftarrow x') = \mathbf{H}'(x') = \mathbf{H}(x')$, i.e. $\mathbf{T}^{-1}\mathbf{H}\mathbf{T} = \mathbf{H}$ or $\mathbf{H}\mathbf{T} = \mathbf{T}\mathbf{H}$,

then **T** is called a "**symmetry**" (transformation) of **H .**

A symmetry **S** leaves the basic operator-equation of the system invariant.

The space of degenerate eigen-functions/vectors is also invariant under symmetry. Namely

$$\mathbf{H}\circ g = g \cdot \lambda \rightarrow (\mathbf{S}^{-1}\mathbf{H}\mathbf{S})g = g\lambda \rightarrow \mathbf{H}\circ(\mathbf{S}g) = (\mathbf{S}g)\cdot\lambda$$

that is, **S**g is a vector in the same eigen-subspace.

But an individual eigen-function/vector, i.e. the mathematical function describing an individual state of the system, is transformed by a symmetry into a linear combination of degenerate eigenfunctions

$$\mathbf{H}\circ g_{nm} = g_{nm}\cdot\lambda_n \;, \quad \mathbf{S}^{-1}\circ\mathbf{H}\circ\mathbf{S} = \mathbf{H} \;, \quad \mathbf{S}\circ g_{nm} = \sum_{m'} g_{nm'}\cdot S_{m'm}$$

$S_{m'm}$ is called the symmetry operator **representation matrix** (Matrix-Darstellung). The characters of the symmetry representation matrices are specific (characteristic) for the type n of the eigenspace. The type is called the '**species**' ('**Rasse**') or 'symmetry type' or 'irreducible representation' ('irreduzible Darstellung').

10.7 Atomic Units

The standard international system has four electro-mechanical units: 1 m, 1 kg, 1 s, 1 C.

By setting a natural constant in a basic law of nature ≡ 1, one of the common units is replaced by a product of the remaining other units.

Atomic, molecular and solid state theoreticians set: $4\pi\varepsilon_o = h/2\pi = m_e = e \equiv 1$ au . Then the SI units disappear. Every atomic unit is 1 au = 1 .

Then many basic equations become simpler ; but dimensional cross-checking is no longer possible. This is no draw-back for those who do not create calculational mistakes.

Length: **1 au = 1 Bohr** [5] = 1 $a_o = 4\pi\varepsilon_o\hbar^2/m_e e^2$ = 52.9 pm ≈ **1/2 Å**
(O – H ≈ 2 Bohr , C – C ≈ 3 Bohr)

Mass: 1 au = 1 $m_e = 0.911 \cdot 10^{-30}$ kg
1 chemical M.U. = 1823 au
Hydrogen: 1.008 M.U. ~ 1837 au = (1836 + 1) au ; μ(C-C) ≈ 11 kau

Time: **1 au** = time needed for a classical electron to move by 1 rad on the nonexistent Bohr orbit = 0.0242 fs ≈ **fs/40**

Velocity: **1 au** = α · c = **c/137** = 2188 km/s (order of electronic v is Z)

Angular Momentum: **1 au = 1 ħ** = h/2π = $10.55 \cdot 10^{-35}$ Js

Charge: **1 au = 1 e = 1 F/N_A** = $16 \cdot 10^{-20}$ C

Dielectric constant: **1 au = $4\pi\varepsilon_o$**

Energy: **1 au = 1 Hartree** [6] **= 2 · IP(H) = 27.2117 eV**
1 eV = $16 \cdot 10^{-20}$ J = **96.5 kJ/mol ~ 8065 cm^{-1} ~ 11605 K**
(order of chem. bond energies: 1-10 eV; order of vib. quanta: 10± kJ/mol)

Dipol moment: **1 au** = 1 e Bohr = **2.54 Debye** = $8.5 \cdot 10^{-30}$ Cm ; typical order up to Debyes

Force constant: **1 au = 15.57 N/cm** (typical order: 1 – 10 N/cm)

(see also the inner cover of Atkins or some other book of physical chemistry, remember 1-2 digits !)

[5] **Bohr**, 1885-1962, Kopenhagen : classical atomic model, physical explanation of the chemical periodic system, basic concepts and interpretations of quantum theory, theory of the nucleus, helped in the nuclear bomb project, teacher of Heisenberg with whom he had disagreed in some political issue

[6] **Hartree**, 1897-1958, Cambridge : together with his father the first extensive atomic SCF calculations