Module 10a Matrix mechanics

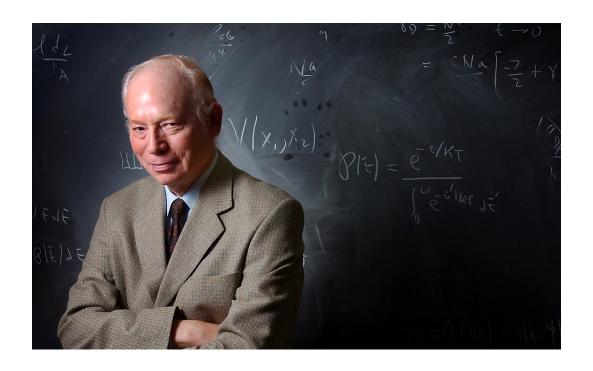
$$pq-qp=rac{h}{2\pi i}1$$

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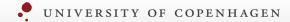




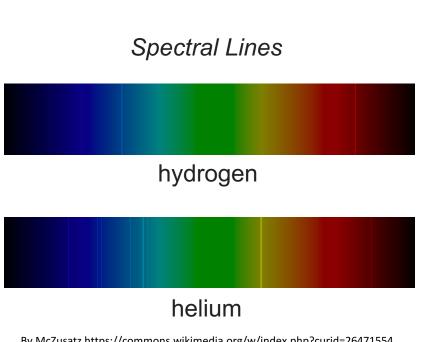
Relax!



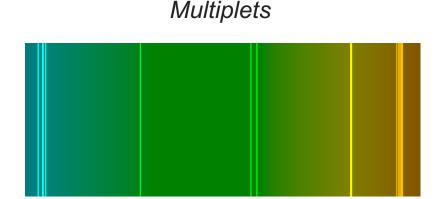
"I have tried several times to read the paper that Heisenberg wrote returning from Helgoland, and, although I think I understand quantum mechanics, I have never understood Heisenberg's motivations for the mathematical steps in his paper." (Steven Weinberg)



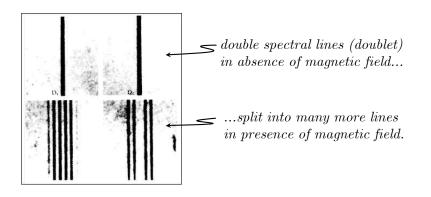
Phenomena: Matter and radiation



By McZusatz https://commons.wikimedia.org/w/index.php?curid=26471554



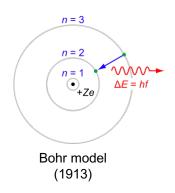
Zeeman effect

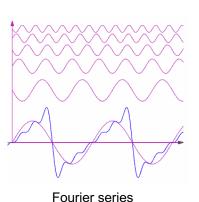






The Correspondence Principle (TCP)





The electron motion is no longer the cause of radiation

Says nothing about the intensity of the radiation

Is it possible to (somehow) relate the electron's motion with radiation?

TCP1: For large n, one should obtain classical (EM) theory

(Bohr 1918)

Now in a stationary state of a periodic system the displacement of the particles in any given direction may always be expressed by means of a Fourier-series as a sum of harmonic vibrations:

$$\xi = \sum C_{\tau} \cos 2\pi (\tau \omega t + c_{\tau}), \tag{14}$$

'Since now on ordinary electrodynamics the intensities of the radiations ... are directly determined from the coefficients C_{τ} in (14), we must therefore expect that for large values of n these coefficients will on the quantum theory determine the probability of spontaneous transition from a given stationary state for which n=n' to a neighbouring state for $n=n''=n'-\tau$.'

TCP2: The transition probabilities (amplitudes) between quantum states correspond to the Fourier coefficients of the electron orbit (for large n)



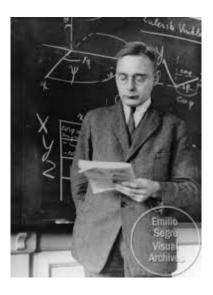
Virtual Oscillators and Dispersion Theory

Virtual Oscillators X Bohr's model (Kramers 1924)

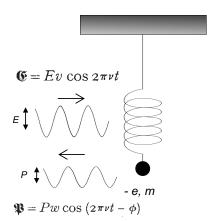
It is well known that a consistent description of the phenomena of dispersion, reflection, and scattering of electromagnetic waves by material media can be given on the fundamental assumption that an atom, when exposed to radiation, becomes a source of secondary spherical wavelets, which are coherent with the incident waves.

In Bohr's theory of spectra, the picture of electrons which are elastically bound inside the atom is abandoned, and for it is substituted a picture according to which an atom exhibiting an absorption line of frequency v is capable of performing under the influence of the illumination a transition from the state under consideration to a stationary state the energy content of which is $h\nu$ greater.

On Bohr's principle of correspondence, the possibility for such transitions is considered as being directly connected with the periodicity properties of the motion of the atom, in such a way that every possible transition between two stationary states is conjugated with a certain harmonic oscillating component in the motion.



Goal: Determine the lines' *amplitudes* (transition probabilities)



Classical, does not obey TCP

$$P=E\sum_i f_irac{e^2}{m} \; rac{1}{4\pi^2(v_i^2-v^2)}$$
 - v_i and v_j are the absorption and emission frequencies

In agreement with TCP

$$P = E \frac{e^2}{4\pi^2 m} \left(\sum \frac{f_i}{v_i^2 - v^2} - \sum \frac{f_j}{v_j^2 - v^2} \right)$$

Kramers dispersion formula

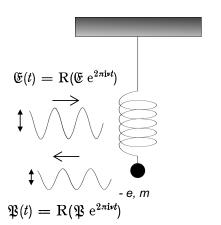
- f_i and f_i are the absorption and emission coefficients, which are proportional to the Einstein (1917) coefficients



Virtual Oscillators and Dispersion Theory

Kramers & Heisenberg (Jan 1925)

When an atom is exposed to external monochromatic radiation of frequency v, it not only emits secondary monochromatic spherical waves of frequency v which are coherent with the incident radiation; but the correspondence principle also demands, in general, that spherical waves of other frequencies are emitted as well. These frequencies are all of the form $|v\pm v^*|$, where hv^* denotes the energy difference of the atom in the state under consideration and some other state.



 $\mathfrak{P}(t) = \mathbb{R}\{\mathfrak{P} e^{2\pi i \nu t} + \sum_{k} \mathfrak{P}_{k} e^{2\pi i (\nu + \nu_{k})t} + \sum_{l} \mathfrak{P}_{l} e^{2\pi i (\nu - \nu_{l})t}\}$ Expressed in words, the result can be stated as follows: Under the influence of irradiation with monochromatic light, an atom not only emits coherent spherical waves of the same frequency as that of the incident light: it also emits systems of incoherent spherical waves, whose frequencies can be represented as combinations of the incident frequency with other frequencies that correspond to possible transitions to other stationary states.



The Study of Multiplets



der Mehrfachlinien und ihrer Zeemankomponenten.

Von A. Sommerfeld und W. Heisenberg in München.

Mit zwei Abbildungen. (Eingegangen am 26. August 1922.)

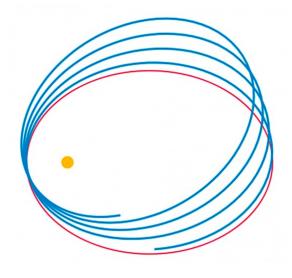
Das Korrespondenzprinzip gestattet, wie bekannt, aus dem kinematischen Charakter der Atombahnen auf die Intensität der Spektrallinien zu schließen, die dem Wechsel der Atombahnen entspringen. Der kinematische Charakter einer Atombahn ist qualitativ bekannt, wenn die sie charakterisierenden Quantenzahlen festgestellt sind. Die letztere Aufgabe darf heutzutage für große Gruppen von Spektrallinien als gelöst gelten, nicht nur für Einfachlinien, sondern auch für Mehrfachlinien (Dubletts, Tripletts, allgemein "Multipletts") und ihre magnetischen Aufspaltungen (die anomalen Zeemankomponenten).

Die Bewegung des Serienelektrons betrachten wir in erster Näherung als eben. In die Bahnebene legen wir die rechtwinkligen Koordinatenachsen ξ , η . Wäre die Bahn rein periodisch, z. B. elliptisch, so hätten wir bei komplexer Zusammenfassung von ξ und η :

$$\xi + i\eta = \sum_{s=-\infty}^{s=+\infty} a_s e^{is \, 0_n t}. \tag{1}$$

Die ganze Zahl s vertritt korrespondenzmäßig die Quantensprünge Δn . Die Koeffizienten a_s der Fourierreihe sind komplexe Konstante.







The Study of Multiplets

Beziehung zwischen inneren Quantenzahlen und Intensitäten von Mehrfachlinien.

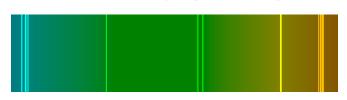
Von H. C. Burger und H. B. Dorgelo in Utrecht.

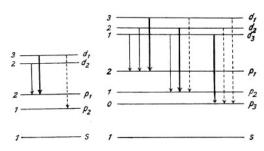
(Mitteilung aus dem Physikalischen Institut der Universität Utrecht.)
(Eingegangen am 8. März 1924.)

Im folgenden werden wir uns vom Atom keine modellmäßige Vorstellung bilden, und nur annehmen, daß bei einem Übergang des Atoms von einem energiereicheren zu einem energieärmeren Zustand der Energieüberschuß gemäß der Bohrschen Frequenzbedingung als monochromatische Strahlung emittiert wird. Die Intensität einer Spektrallinie ist also proportional dem Produkt aus der Konzentration des Atoms im Anfangszustand und der Wahrscheinlichkeit des Sprunges vom Anfangs- zum Endzustand.

$ \begin{array}{c} 2 k + 1 \\ 6 k - 3 \\ 2 k - 1 \\ 6 k - 3 \\ 2 k - 3 \end{array} $	$ \begin{array}{c} 1 \\ \hline (6 k - 3) (6 k + 3) \\ 11 \\ \hline (6 k - 3) (6 k + 3) \\ 12 k^2 - 12 k - 9 \end{array} $	$ \begin{array}{r} 11 \\ \hline (6 k - 3) (6 k + 3) \\ 12 k^2 - 14 \\ \hline (6 k - 3) (6 k + 3) \end{array} $	$ \frac{12 k^2 + 12 k - 9}{(6 k - 3) (6 k + 3)} $
$\frac{6k-3}{}$	$ \begin{array}{c c} \hline (6 k - 3) (6 k + 3) \\ \hline 2 k - 1 \\ 6 k + 3 \end{array} $	$ \frac{2 k + 1}{6 k + 3} $	$ \frac{2 k + 3}{6 k + 3} $

Intensity schemes (in terms of quantum numbers)





$1 p_1 \left(\frac{5}{2} \right)$	1	18	100
1 $p_2\!\left(\!rac{3}{2} ight)$	19	5 4	0
1 $p_3\Bigl(rac{1}{2}\Bigr)$	25	0	0
	$2 d_3\left(rac{3}{2} ight)$	$2 d_2\left(rac{5}{2} ight)$	$2 d_1\left(\frac{7}{2}\right)$

- Utrecht "sum rules": The sum of the intensities are the in the same ratio as the quantum numbers of their final states
- Sommerfeld's attack on TCP
- Heisenberg: "Sharpening" of TCP



Models vs lawful regularities



Sommerfeld

"Thus it is, that at the moment we are at a loss with the *modell-mässigen* meaning of the line multiplicities of the non-hydrogenic elements... All the more valuable are all the lawful regularities [Gesetzmässigkeiten] that present themselves empirically..."

"I found it particularly beautiful in the presentation of the complex structure that you have left all *modellmässig* considerations to one side. The model idea now finds itself in a difficult, fundamental crisis... One now has the impression with all models, that we speak there a language that is not sufficiently adequate for the simplicity and beauty of the quantum world."



Pauli



Perturbation Theory and the Anharmonic Oscillator

Heisenberg to Pauli (Sep 1922)

Die Gleichung des Oszillators sei (δ sehr klein)

$$\ddot{x} + \omega^2 x + \delta x^2 = 0.$$

Wir versuchen

$$x = ae^{i\omega t} + a_2e^{2i\omega t} + a_3e^{3i\omega t} + \dots$$

Es ergibt sich

$$a_2 = \left(\frac{\delta \cdot a}{\omega^2}\right) a \cdot \frac{1}{3}$$
 $a_3 = \left(\frac{\delta a}{\omega^2}\right)^2 \cdot a \cdot \frac{1}{12}$

$$a_4 = \left(\frac{\delta a}{\omega^2}\right)^3 \cdot a \cdot \frac{1}{54}$$
 u.s.w. allgemein

$$a_n = \left(\frac{\delta a}{\omega^2}\right)^{n-1} \cdot a \cdot z$$
, wo z eine reine Zahl ist.

- Recursion relations determine the Fourier coefficients
- But how to determine the first term (a)?

Ji ghi firmy do Orgillusoro

fri (d fift klain)

$$\ddot{x} + \omega^2 t + d \dot{x}^2 = d$$
.

Air orthogon

 $t = ae^{i\omega t} + a_2 e^{2i\omega t} + a_3 e^{3i\omega t} + \cdots$
 $fragist frif$
 $a_2 = (\frac{da}{\omega^2})a \cdot \frac{1}{3}; a_3 = (\frac{da}{\omega^2})^2 a \cdot \frac{1}{12};$
 $a_4 = (\frac{da}{\omega^2})^3 a \cdot \frac{1}{54} \text{ in fig. allyumin}$
 $a_n = (\frac{da}{\omega^2})^n \cdot a \cdot 2, \text{ yr 2 min prime}$

Juft iff.

http://www.heisenberg-gesellschaft.de/

Source: Van der Wærden (1967)





Perturbation Theory and the Anharmonic Oscillator

Your question: Why is $x(t)^2$ of such great importance?

Heisenberg's interview with Thomas Kuhn

Well, the point was that from this moment I actually did work on quantum mechanics straight away, because when I had studied the classical intensities of the Kepler ellipse, I very soon found out that it was too complicated to guess the intensities. And then I found—that was the point—that if I knew the Fourier series of, say, a coordinate x, I wanted also to know the Fourier series of x^2 . And so I studied more generally the question of the connection between the Fourier series of x and that of x^2 , or that of x and y and that of x times y. And that was, of course, already practically matrix mechanics. Then I went from the hydrogen back to a problem where I could do the thing by just multiplying in a simple way so that besides x, I only needed x^2 and x^3 and not





Perturbation Theory and the Anharmonic Oscillator

Heisenberg's interview with Thomas Kuhn

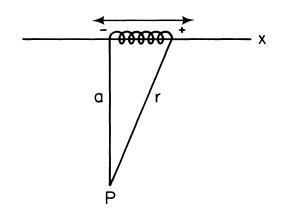
more. The simplest example was the anharmonic oscillator and thereby I came to the anharmonic oscillator in quantum mechanics. You will find in the first paper on the anharmonic oscillator in quantum mechanics also a statement that it was (at fault) if one knew x also to know x^2 or x times y and that kind of thing. So that was really the point. But the point came out from my attempts to work straight on the hydrogen atom and since these attempts had failed, I went to the more general question of what I could do about multiplication of these Fourier series.⁵⁶



Perturbation Theory and the Anharmonic Oscillator

The "turning point"
Heisenberg to Kronig (June 1925)

Force (K) at P



$$K = -e^2/a^2 + e^2/(a^2 + x^2) = (e^2/a^2)[-1 + 1/(1 + x^2/a^2)]$$

$$1/(1+x^2/a^2) = b_0 + b_1 \cos \omega t + b_2 \cos 2\omega t + \dots$$

$$1/(1+x^2/a^2) = 1 - x^2/a^2 + x^4/a^4 - x^6/a^6 + \dots$$

$$b_1 = -\frac{2(a_0a_1 + \frac{1}{2}a_1a_2 + ...)}{a^2}$$
 Classically

Quantum theoretically

Anharmonic oscillator

$$\ddot{x} + \omega^2 x + \lambda x^2 = 0$$

$$b_1(n, n-1) = -\frac{1}{a^2} [a_0(n) a_1(n, n-1) + a_1(n, n-1) a_0(n-1) + \ldots].$$

$$x = a_0 + a_1 \cos \omega t + a_2 \cos 2\omega t + \dots$$

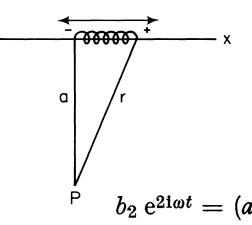
$$x^2 = (a_0^2 + a_1^2/2) + 2(a_0a_1 + a_1a_2)\cos \omega t + \dots$$

Source: Mackinnon (1977)



Perturbation Theory and the Anharmonic Oscillator

The "turning point"
Heisenberg to Kronig (June 1925)



Can there be an atomic interpretation?

x = displacement from an equilibrium position the electron might have, i.e., from a stable orbit.

x's represent transitions from a stable orbit *n*.

$$x(n,t) = \sum_{n=0}^{\infty} a_n e^{ni\omega t} \qquad 1/(1+x^2/a^2) = \sum_{m=0}^{\infty} b_m e^{mi\omega t}$$

$$b_2 e^{2i\omega t} = (a_1 e^{i\omega t})^2 \longrightarrow b_2(n, n-2) = a_1(n, n-1) a_1(n-1, n-2)$$

What is the precise physical interpretation to be accorded a term like $(a_1e^{i\omega t})^2$ in equation (14)? In the virtual oscillator model the term $b_2e^{2i\omega t}$ could represent a transition from state n to state n-2. Correspondingly, the right-hand side of equation (14) should represent an ordered sum of the virtual transitions leading from state n to state n-2 through an intermediate jump of 1, 2, or more steps.

Source: Mackinnon (1977)





Über quantentheoretische Umdeutung kinematischer und mechanischer Beziehungen.

Main points

Von W. Heisenberg in Göttingen. (Eingegangen am 29. Juli 1925.)

- Classical Mechanics is not valid in the atomic range (e.g. Bohr's frequency).
- We need a new (Quantum) Mechanics, which replaces differential quotients by difference quotients (Correspondence Principle).
- The theory should contain only quantities that are in principle observables (namely, transition frequencies and probabilities, i.e., amplitudes)
- The solution is a reinterpretation of our kinematics: instead of x(t) we should consider the set of all possible transitions from a given state n

$$\chi(t) \longrightarrow \mathfrak{A}(n, n-\alpha)e^{i\omega(n, n-\alpha)t}$$



Über quantentheoretische Umdeutung kinematischer und mechanischer Beziehungen.

Von W. Heisenberg in Göttingen.

(Eingegangen am 29. Juli 1925.)

Heuristics: Translations

Classical



Quantum-theoretical

Energy and frequency
$$v(n,\,lpha)=lpha v(n)=lpha\,rac{1}{h}\,rac{\mathrm{d} W}{\mathrm{d} n}$$

$$v(n, n - \alpha) = \frac{1}{h} \{W(n) - W(n - \alpha)\}$$

Adding frequencies
$$v(n,\alpha)+v(n,\beta)=v(n,\alpha+\beta)$$

$$v(n, n-\alpha) + v(n-\alpha, n-\alpha-\beta) = v(n, n-\alpha-\beta)$$

$$v(n-\beta, n-\alpha-\beta)+v(n, n-\beta)=v(n, n-\alpha-\beta)$$

Crucial question: What about the amplitudes?

Amplitudes

 $\operatorname{Re}\{\mathfrak{A}_{\alpha}(n) e^{i\omega(n)\alpha t}\}$

 $\operatorname{Re}\{\mathfrak{A}(n, n - \alpha) e^{i\omega(n, n-\alpha)t}\}$



Über quantentheoretische Umdeutung kinematischer und mechanischer Beziehungen.

Von W. Heisenberg in Göttingen.

(Eingegangen am 29. Juli 1925.)

Heuristics: Translations

Classical



Quantum-theoretical

Fourier series

$$x(n, t) = \sum_{-\infty}^{+\infty} \mathfrak{A}_{\alpha}(n) e^{i\omega(n)\alpha t}$$

A similar combination of the corresponding quantum-theoretical quantities seems to be impossible in a unique manner and therefore not meaningful, in view of the equal weight of the variables n and $n-\alpha$. However, one may readily regard the ensemble of quantities $\mathfrak{A}(n, n-\alpha)e^{i\omega(n, n-\alpha)t}$ as a representation of the quantity x(t) and then attempt to answer the above question: how is the quantity $x(t)^2$ to be represented?

 $x(t)^2$

$$x(t)^2 = \sum_{-\infty}^{+\infty} \mathfrak{B}_{\beta}(n) e^{i\omega(n)\beta t}$$

In quantum theory, it seems that the simplest and most natural assumption would be to replace equations (3) and (4) by:

$$\mathfrak{B}(n,n-\beta)e^{\mathrm{i}\omega(n,n-\beta)t} = \sum_{-\infty}^{+\infty} \mathfrak{A}(n,n-\alpha)\mathfrak{A}(n-\alpha,n-\beta)e^{\mathrm{i}\omega(n,n-\beta)t}$$

$$x(t)y(t) \qquad \mathfrak{C}_{\beta}(n) = \sum_{\alpha}^{+\infty} \mathfrak{A}_{\alpha}(n) \mathfrak{B}_{\beta-\alpha}(n)$$

$$\mathfrak{C}_{\beta}(n) = \sum_{-\infty}^{+\infty} \mathfrak{A}_{\alpha}(n) \mathfrak{B}_{\beta-\alpha}(n) \qquad \mathfrak{C}(n, n-\beta) = \sum_{-\infty}^{+\infty} \mathfrak{A}(n, n-\alpha) \mathfrak{B}(n-\alpha, n-\beta)$$

Whereas in classical theory x(t)y(t) is always equal to y(t)x(t), this is not necessarily the case in quantum theory.



Über quantentheoretische Umdeutung kinematischer und mechanischer Beziehungen.

Von W. Heisenberg in Göttingen.

(Eingegangen am 29. Juli 1925.)

Heuristics: Translations

The "old" quantum condition



n could be continuous

 $\oint p \, \mathrm{d}q = \oint m\dot{x} \, \mathrm{d}x = J(=nh)$

$$x = \sum_{-\infty}^{+\infty} a_{\alpha}(n) e^{i\alpha\omega_n t}$$

$$m\dot{x} = m \sum_{-\infty}^{+\infty} a_{\alpha}(n) i\alpha \omega_n e^{i\alpha \omega_n t}$$

$$\oint m\dot{x} \, dx = \oint m\dot{x}^2 \, dt = 2\pi m \sum_{-\infty}^{+\infty} a_{\alpha}(n) a_{-\alpha}(n) \alpha^2 \omega_n$$

$$\oint m\dot{x}^2 dt = 2\pi m \sum_{-\infty}^{+\infty} |a_{\alpha}(n)|^2 \alpha^2 \omega_n$$

In the earlier theory this phase integral was usually set equal to an integer multiple of h, i.e., equal to nh, but such a condition does not fit naturally into the dynamical calculation. It appears, even when regarded from the point of view adopted hitherto, arbitrary in the sense of the correspondence principle,

$$\frac{\mathrm{d}}{\mathrm{d}n}(nh) = \frac{\mathrm{d}}{\mathrm{d}n} \oint m\dot{x}^2 \,\mathrm{d}t \qquad h = 2\pi m \sum_{-\infty}^{+\infty} \alpha \frac{\mathrm{d}}{\mathrm{d}n} (\alpha \omega_n \cdot |a_{\alpha}|^2)$$

We have to admit that only equation (15) has a simple quantum-theoretical reformulation which is related to *Kramers*' dispersion theory: 1

$$h = 4\pi m \sum_{n=0}^{\infty} \{|a(n, n+\alpha)|^2 \omega(n, n+\alpha) - |a(n, n-\alpha)|^2 \omega(n, n-\alpha)\}. \quad (16)$$



Matrix Mechanics (Born & Jordan)

Heisenberg's mathematics is matrix analysis

The mathematical basis of Heisenberg's treatment is the law of multiplication of quantum-theoretical quantities, which he derived from an ingenious consideration of correspondence arguments. The development of his formalism, which we give here, is based upon the fact that this rule of multiplication is none other than the well-known mathematical rule of matrix multiplication. The infinite square array (with discrete or continuous indices) which appears at the start of the next section, termed a matrix, is a representation of a physical quantity which is given in classical theory as a function of time. The mathematical method of treatment inherent in the new quantum mechanics is thereby characterized through the employment of matrix analysis in place of the usual number analysis.



Matrix Mechanics (Born & Jordan)

Recipes (Tomonaga)

Recipe (I): Consider that each quantity is a matrix and that, when the quantity is real-number-like, the matrix is hermitian.

Recipe (II): Assume that the (n, n') element of the matrix of a physical quantity oscillates, as a function of time, as $\exp(2\pi i v_{nn'}t)$.

Recipe (III): For the frequencies there is the combination law

$$v_{nn'} + v_{n'n''} = v_{nn''}$$
 $v_{nn} = 0$, and $v_{nn'} = -v_{n'n}$

Recipe (IV): The time derivative of a physical quantity should be defined by the matrix whose elements are the time derivatives of the corresponding elements of the matrix representing the original quantity.

$$x = \begin{bmatrix} x_{11} & x_{12} & x_{13} \dots \\ x_{21} & x_{22} & x_{23} \dots \\ x_{31} & x_{32} & x_{33} \dots \end{bmatrix} \quad v = \begin{bmatrix} \dot{x}_{11} & \dot{x}_{12} & \dot{x}_{13} \dots \\ \dot{x}_{21} & \dot{x}_{22} & \dot{x}_{23} \dots \\ \dot{x}_{31} & \dot{x}_{32} & \dot{x}_{22} \dots \end{bmatrix} \quad v = 2\pi i \begin{bmatrix} 0 & v_{12}x_{12} & v_{13}x_{13} \dots \\ v_{21}x_{21} & 0 & v_{23}x_{23} \dots \\ v_{31}x_{31} & v_{32}x_{32} & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix} \quad (\dot{A})_{nn'} = 2\pi i v_{nn'} A_{nn'}$$



Matrix Mechanics (Born & Jordan)

Recipes (Tomonaga)

Recipe (V): $(A + B)_{nn'} = A_{nn'} + B_{nn'}$

Recipe (VI): $(AB)_{nn'} = \sum_{n''} A_{nn''} B_{n''n'}$

Recipe (VII): Using the definition of time derivative, sum, and product as given above, insert the coordinates and their time derivatives into the equation of motion characteristic of the given dynamical system.

Newton's 2nd law

Hamilton's equations

Hamiltonian (energy)

$$\ddot{x} + f(x) = 0$$

$$\ddot{x} + f(x) = 0$$
 $\dot{q} = \frac{\partial H}{\partial p}$ $\dot{p} = -\frac{\partial H}{\partial q}$ $H = \frac{1}{2m}p^2 + U(q)$

$$H=\frac{1}{2m}\,p^2+U(q)$$

Recipe (VIII): Assume that the momentum p, conjugate to the coordinate q, satisfies the relationship,

$$pq - qp = \frac{h}{2\pi i} 1$$

Therefore, we arrive at the conclusion that the matrix H must be a diagonal matrix; i.e.,

$$H_{nn'} = W_n \delta_{nn'}$$
,

Your Questions

- What does Heisenberg mean by the revolution of the electron? Quantum jump?
- What difficulties are there when you have a hydrogen atom in a crossed field?
- What is the Einstein-Bohr frequency condition?
- I am not familiar with Kramers work, what is his dispersion theory?
- Why does Heisenberg has such an interest the quantum-theoretical x(t)^2 at the beginning of the paper? Is this already intended to the amplitude square as probability?
- When did the bra ket notation started in matrix mechanics/QM?
- What exactly are the variables n and alpha and what is the difference between them?
- Why is x(t)^2 of such great importance?
- The field strengths he describes in the beginning: Where do they come from and what exactly do they represent with respect to the moving electron?