Let's go! U = U(x) only. (but U(x)'s explicit form is not needed) (TDSE) $-\frac{1}{2m} \frac{\partial}{\partial x^2} \Psi(x,t) + U(x) \Psi(x,t) = it \frac{\partial}{\partial t} \Psi(x,t)$ A. Try the method of <u>"Separation of variables"</u> · Important step $Try \overline{\Psi(x,t)} = \Psi(x) \cdot T(t)$ $x \text{ and } t \quad \text{function of } \text{function of }$ • Will come back to better appreciate. lohat it says · Can always try this, Plug I(x,t) = Y(x). T(t) into TDSE but useful or not is another business

2

$$LHS = -\frac{\hbar^{2}}{2m} \frac{\partial^{2}}{\partial x^{2}} \left[\frac{\gamma(\alpha)}{\sqrt{\alpha}} \cdot T(t) \right] + U(\alpha) \left[\frac{\gamma(\alpha)}{\sqrt{\alpha}} \cdot T(t) \right]$$

$$= -\frac{\hbar^{2}}{2m} T(t) \frac{d^{2}}{dx^{2}} \frac{\gamma(\alpha)}{\sqrt{\alpha}} + U(\alpha) \frac{\gamma(\alpha)}{\sqrt{\alpha}} T(t)$$

$$RHS = i\hbar \frac{\partial}{\partial t} \left[\frac{\gamma(\alpha)}{\sqrt{\alpha}} \cdot T(t) \right] = i\hbar \frac{\gamma(\alpha)}{dt} \frac{d}{dt} T(t)$$

$$TDSE \Rightarrow LHS = RHS = -\frac{\hbar^{2}}{2m} T(t) \frac{d^{2}}{dx^{2}} \frac{\gamma(\alpha)}{\sqrt{\alpha}} + U(\alpha) \frac{\gamma(\alpha)}{\sqrt{\alpha}} T(t) = i\hbar \frac{\gamma(\alpha)}{dt} \frac{d}{dt} T(t)$$

$$Givide by \Psi = \psi(\alpha) \cdot T(t) \text{ on both sides :}$$

$$\frac{-\frac{\hbar^{2}}{2m} \frac{1}{\sqrt{\alpha}} \frac{d^{2}}{dx^{2}} \frac{\gamma(\alpha)}{\sqrt{\alpha}} + U(\alpha) = i\hbar \frac{d}{\sqrt{\alpha}} \frac{d}{\sqrt{\alpha}} T(t)}{TEt \frac{d}{\sqrt{\alpha}} \frac{d}{\sqrt{\alpha}} T(t)}$$

$$Find the second seco$$

Now, we judge whether separation of variables is useful or not

$$\begin{array}{c} -\frac{\hbar^{2}}{2m} \frac{1}{\psi(x)} \frac{d^{2}}{dx^{2}} \psi(x) + \psi(x) \quad (=) \quad \text{th} \frac{1}{T(t)} \frac{d}{dt} T(t) \\ \text{Spirit of} \\ \text{Spirito$$

"Want LHS = RHS for all x and all t
"This is possible only if

$$\frac{-\frac{1}{2}}{2m}\frac{1}{\sqrt{2}}\frac{d^{2}}{\sqrt{2}}\frac{1}{\sqrt{2}}(x) + U(x) = \frac{1}{2m}\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\frac{d^{2}}{\sqrt{2}}\frac{1}{\sqrt{2}}(x) + U(x) = \frac{1}{\sqrt{2}}\frac$$

B. Look at "LHS=E" (the spatial equation)



[Remark: TISE is analogous to the normal mode equation in classical wave problems] ⁶

What does $\frac{-t^2}{2m} dx^2 \psi(x) + U(x) \psi(x) = E \psi(x) do?$ " Specify form of $U(x) \Rightarrow a$ differential equation to solve for E and $\frac{y_{\pm}(x)}{2}$ Vé(X) gives the wavefunction Corresponding to energy E " <u>Schrödinger (1926)</u> applied TISE to hydrogen atom, i.e. Found E<0 solutions at discrete values $\frac{-\frac{h^2}{2m}}{2m}\nabla^2\psi(\vec{r}) - \frac{e^2}{4\pi\epsilon_0 r}\psi(\vec{r}) = E\psi(\vec{r})$ -13.6eV

We will do the H-atom problem later in the course

1926.





Erwin Schrodinger (1887 – 1961) 1933 Nobel Prize (shared Prize with Dirac)

Wrote 2 papers in Annalen der Physik in 1926 (27 Jan 1926 & 23 Feb 1926)

ANNALEN DER PHYSIK. VIERTE FOLGE. BAND 79.

1. Quantisierung als Eigenwertproblem; 2 von E. Schrödinger.

(Zweite Mitteilung.) 1)

23 February 1926 [39 pages]

§ 1. Die Hamiltonsche Analogie swischen Mechanik und Optik.

Bevor wir daran gehen, das Eigenwertproblem der Quantentheorie für weitere spezielle Systeme zu behandeln, wollen wir den allgemeinen Zusammenhang näher beleuchten, welcher zwischen der Hamiltonschen partiellen Differentialgleichung (H. P.) eines mechanischen Problems und der "zugehörigen" Wellengleichung, d. i. im Falle des Keplerproblems der Gleichung (5) der ersten Mitteilung, besteht. Wir hatten diesen Zusammenhang vorläufig nur kurz seiner äußeren analytischen Struktur nach beschrieben durch die an sich unverständliche Transformation (2) und den ebenso unverständlichen Übergang von der Nullsetzung eines Ausdrucks zu der Forderung, daß das Raumintegral des nämlichen Ausdruckes stationär sein soll.²)

Der innere Zusammenhang der Hamiltonschen Theorie mit dem Vorgang der Wellenausbreitung ist nichts weniger als neu. Er war Hamilton selbst nicht nur wohlbekannt, sondern bildete für ihn den Ausgangspunkt seiner Theorie der Mechanik, die aus seiner Optik inhomogener Medien hervorgewachsen ist.³) Das Hamiltonsche Variationsprinzip kann

2) Dieser Rechenvorgang wird in der vorliegenden Mitteilung nicht weiter verfolgt. Er sollte nur zur vorläufigen raschen Orientierung über den äußerlichen Zusammenhang zwischen der Wellengleichung und der H. P. dienen. ψ steht nicht wirklich zur Wirkungsfunktion einer bestimmten Bewegung in der von der Gleichung (2) der ersten Mitteilung behaupteten Beziehung. — Hingegen ist der Zusammenhang der Wellengleichung und der Variationsaufgabe selbstverständlich höchst real: der Integrand des stationären Integrals ist die Lagrange-Funktion für den Wellenvorgang.

3) Vgl. z. B. E. T. Whittaker, Analytische Dynamik (Deutsche Ausgabe bei Springer 1924). Kap. 11. S. 806ff.

Annalen der Physik. IV. Folge. 79.

¹⁾ Siehe diese Annalen 79. S. 361. 1926. Es ist zum Verständnis nicht unbedingt nötig, die erste Mitteilung vor der zweiten zu lesen.

After 22 pages, there came the Time-independent Schrodinger Equation (TISE)

(18'') div grad
$$\psi + \frac{8\pi^{*}}{h^{2}} (E - V) \psi = 0$$

Schrodinger then applied his method to 1D harmonic oscillator (page 26)

(22)
$$\frac{d^2 \psi}{d q^2} + \frac{8 \pi^2}{h^2} (E - 2 \pi^2 \nu_0^2 q^2) \psi = 0$$

[Why? Recall implications of *Planck's formula* and *Einstein's model of solids*] Schrodinger solved (22) skillfully (we will do it later) and obtained

(25')
$$E_n = \frac{2n+1}{2}h\nu_0$$
; $n = 0, 1, 2, 3, \dots$
 $\delta_n = 0, 1, 2, 3, \dots$ as implied by thermal radiation
and heat capacities of solids
(26') $\mu_n = 2\pi h\nu_0 + \frac{1}{2}h\nu_0$ and heat capacities of solids

(26')
$$\psi_n(q) = e^{-\frac{2\pi^* \nu_0 q^2}{\hbar}} H_n\left(2\pi q \sqrt{\frac{\nu_0}{\hbar}}\right)$$

Schrodinger then moved on to work out

- the rigid Rotator problem in 2D and 3D
- the 3D oscillator problem

Schrodinger (27 January 1926) in Annalen der Physik (16 pages)

3. Quantisierung als Eigenwertproblem; von E. Schrödinger.

(Erste Mitteilung.)

§ 1. In dieser Mitteilung möchte ich zunächst an dem einfachsten Fall des (nichtrelativistischen und ungestörten) Wasserstoffatoms zeigen, daß die übliche Quantisierungsvorschrift sich durch eine andere Forderung ersetzen läßt, in der kein Wort von "ganzen Zahlen" mehr vorkommt. Vielmehr ergibt sich die Ganzzahligkeit auf dieselbe natürliche Art, wie etwa die Ganzzahligkeit der Knotenzahl einer schwingenden Saite. Die neue Auffassung ist verallgemeinerungsfähig und rührt, wie ich glaube, sehr tief an das wahre Wesen der Quantenvorschriften.

Worked on the Hydrogen atom problem (allowed energies are known from spectrum and Bohr's model (1913))

$$\Delta \psi + \frac{2m}{K^2} \left(E + \frac{e^2}{r} \right) \psi = 0$$

After 10 pages of calculations, Schrodinger obtained E<0 solutions for hydrogen with energies given by

$$-E_{l} = \frac{me^{4}}{2K^{2}l^{2}}$$

In modern form, *l* is the quantum number *n K* is $(\frac{h}{2\pi})$

and the Hydrogen atom wavefunctions

Since the hydrogen atom allowed energies $-\frac{13.6}{n^2}$ (eV) were known (Balmer, Lyman series) at that time, Schrodinger showed explicitly that by solving his equation and requiring well-behaving wavefunctions, *E* in his equation gives the system's (H-atom) allowed energies.

In September 1926, Schrodinger wrote a long paper introducing his theory in English in the *Physical Review* (published by the American Physical Society)

Second Series

December, 1926

Vol. 28, No. 6

THE

PHYSICAL REVIEW

AN UNDULATORY THEORY OF THE MECHANICS OF ATOMS AND MOLECULES

By E. Schrödinger

Abstract

The paper gives an account of the author's work on a new form of quantum theory. §1. The Hamiltonian analogy between mechanics and optics. §2. The analogy is to be extended to include real "physical" or "undulatory" mechanics instead of mere geometrical mechanics. §3. The significance of wave-length; macro-mechanical and micro-mechanical problems. §4. The wave-equation and its application to the hydrogen atom. §5. The intrinsic reason for the appearance of discrete characteristic frequencies. §6. Other problems; intensity of emitted light. §7. The wave-equation derived from a Hamiltonian variationprinciple; generalization to an arbitrary conservative system. §8. The wavefunction physically means and determines a continuous distribution of electricity in space, the fluctuations of which determine the radiation by the laws of ordinary electrodynamics. §9. Non-conservative systems. Theory of dispersion and scattering and of the "transitions" between the "stationary states." §10. The question of relativity and the action of a magnetic field. Incompleteness of that part of the theory.

E. Schrodinger, Physical Review 28 (1926) 1049 <u>https://journals.aps.org/pr/abstract/10.1103/PhysRev.28.1049</u> (accessible from CUHK sites or VPN)

• Key Points
Solving TISE gives the (many) allowed energies of a quantum system
and the wavefunction
$$Y_E(x)$$
 corresponding to a state of definite energy E.

Key Points from Schrodinger's early applications (important concepts):

- TISE is an equation to solve for the wavefunction Ψ and E
- Not all values of ${\it E}$ are allowed, only certain values of ${\it E}$ give well-behaved Ψ
- A well-behaved (QM allowed) Ψ has an accompanying allowed E
- The allowed E values are the allowed values of energy of the system

The separation constant *E* happens to give the allowed values of a quantum mechanical problem as specified by U(x)

C. Look at "RHS = E" (the temporal (time) equation)

gives it d T(t) = E T(t) Governs the time (temporal) part, i.e. how RHS = Ea state of definite energy E $\frac{dT(t)}{dt} = \frac{E}{it}T(t) = -\frac{iE}{t}T(t)$ evolves in ' Asking: "Find T(t) that "d" it once gives itself with a prefactor" $T(t) = e^{-iEt}$ (could have a constant factor in front) By inspection, Physical Meaning * <u>A state</u> of <u>definite energy</u> <u>E</u> (obtained by solving TISE), thus with wavefunction $Y_E(x)$, evolves in time as $Y'_E(x) e^{-i\frac{E}{E}}$

Important QM concept!

More explicit meaning. "Recall TISE $-\frac{\hbar^2}{2m} dx^2 + U(x) \psi(x) = E\psi(x)$ allows many solutions $E_{i} \leftrightarrow \Psi_{E_{i}}(x)$ evolves in time as $\Psi_{E_{i}}(x) \stackrel{-iE_{i}t}{t}$ E2 <> VE2(X) evolves in time as VEX C-IEt $E_n \leftrightarrow \psi_{E_n}(x)$ evolves in time as $\psi_{E_n}(x) e^{-i\frac{E_n}{E_n}t}$ obtained by solving TISE They are states of definite energy each with its own time part, as a result of TDSE and U = U(x) only

D. Putting Things together : Back to Time-dependent Schrödinger Equation " Consider a linear combination of $\psi_{E_n}^{(u)} e^{-i E_n t}$, i.e. $\overline{\Psi}(\mathbf{x},t) = \alpha_1 \sqrt{e^{-i \frac{\epsilon}{2}t}} + \alpha_2 \sqrt{e^{-i \frac{\epsilon}{2}t}} + \cdots + \alpha_n \sqrt{e^{-i \frac{\epsilon}{2}t}} + \cdots$ = $\sum_{n=1}^{\infty} a_n \psi_{E_n} e^{-i E_n t}$ (assuming TISE allows infinitely many solutions) -Important QM concept Such a combination is a solution to the time-dependent Schrödinger Equation

Here is the proof

 $\frac{-\hbar^2}{2m}\frac{\partial}{\partial x^2}\overline{\Psi}(x,t) + U(x)\overline{\Psi}(x,t) = -448 \text{ of TDSE}$ $= -\frac{t^2}{2m} \frac{\partial^2}{\partial x^2} \left(\sum_{n=1}^{\infty} a_n \sqrt{\frac{1}{En}} e^{-iEnt/n} \right) + U(x) \sum_{n=1}^{\infty} a_n \sqrt{\frac{1}{En}} e^{-iEnt/n}$ $= \sum_{n=1}^{\infty} a_n e^{-i \frac{\pi}{2} t} \left(\frac{1}{2m} \right) \frac{d^2 v}{dx^2 t} E_n(x) + \sum_{n=1}^{\infty} a_n e^{-i \frac{\pi}{2} t} U(x) \frac{1}{t} \frac{1}{E_n}(x)$ $= \sum_{n=1}^{\infty} a_n e^{-i \frac{Ent}{En}} \left[\frac{-t^2}{2m} \int_{X^2}^{d^2} \frac{\gamma_E(\omega)}{F_n(\omega)} + U(x) \frac{\gamma_E(x)}{F_n(x)} \right]$ = $\sum_{n=1}^{\infty} a_n E_n Y_E \otimes e^{-i E_n t}$ $TDEE_{th} \frac{1}{2t} \Psi(xt) = ih \frac{1}{2t} \sum_{n=1}^{\infty} a_n \psi_{E_n}(x) e^{-iE_n t} = ih \sum_{n=1}^{\infty} a_n \psi_{E_n}(x) \frac{1}{2t} e^{-iE_n t}$ $= \sum_{n=1}^{\infty} a_n E_n \Psi_E(x) e^{-i \frac{E_n t}{R}} = 1HS$. The combination I(x,t) = 2 an VEW C in satisfies TDSE. Done!

Reminder: The result is more important than the proof!

A quick application: Time evolution of a "specific form"

4

Given a system, i.e.
$$U(x) \ \sigma x \ U(\overline{r})$$

Let's say the state of the system at some time (called) $t=0$ is:
 $\overline{\Psi}(x,t=0) = \overline{\Psi}(x,0) = a, \ \psi_{E_{x}}(x) + a_{z} \ \psi_{E_{x}}(x) + \cdots + a_{n} \ \psi_{E_{n}}(x) + \cdots = (*)$
Question: Let $\overline{\Psi}(x,t=0)$ evolve in time (don't do anything in between),
what is $\overline{\Psi}(x,t=0)$ evolve in time (don't do anything in between),
what is $\overline{\Psi}(x,t=0)$.
Reasoning: $\psi_{E_{n}}(x)$ is a solution to TISE, thus a state of energy E_{n} , it evolves
as $\psi_{E_{n}}(x) e^{-i\underline{E}\underline{t}}$. Therefore, each term evolves with its non time part.
Answer:
 $\overline{\Psi}(x,t) = a, \ \psi_{E_{n}}(x) e^{-i\underline{E}\underline{t}} + a_{z} \ \psi_{E_{n}}(x) e^{-i\underline{E}\underline{t}} + \cdots + a_{n} \ \psi_{E_{n}}(x) e^{-i\underline{E}\underline{t}} + \cdots = (+)$

+Meaning: Don't make any measurement, because measurements play a special vole in QM and they change the state.

9

E. General Initial Value Problems in Quantum Mechanics

* Need a system, i.e. need to know
$$U(x)^{\dagger} or U(\overline{r})$$

Question: The state of the system at $t=0$ is given to be some form
Called $\overline{\Phi}(x,t=0) = \overline{\Phi}(x)$. What is the state $\overline{\Phi}(x,t)$ at time t ?

Putting the results together, we have the following 3-step recipe

⁺ If U = U(x,t), the problem is harder. The recipe here does not work for U(x,t). However, the time-evolution is still governed by TDSE.

Step 1: Solve the time-independent Schrodinger Equation

Remark: This is why we will work out many TISE problems in 1D, 2D, 3D

Step 2: Expand given initial wavefunction in terms of states of definite energies

Step 2: Take the given $\overline{\Phi}(x,t=0) = \overline{\Phi}(x)$, write it as $\Phi(\mathbf{X}) = a_1 \psi_{E_1}(\mathbf{X}) + a_2 \psi_{E_2}(\mathbf{X}) + \cdots + a_n \psi_{E_n}(\mathbf{X}) + \cdots = \sum a_n \psi_{E_n}(\mathbf{X})$ ■ $\Phi(x)$ is given, $Y_{E_n}(x)$ are known after Step 1 " Need a set {a, az, ..., an, ...} = {any of coefficients to make "LHS = RHS" " All an can be found by doing integrals (c.f. Fourier analysis) " At end of Step 2, we have $\frac{\overline{\Phi}(x,t=0)}{2} = \sum_{n=1}^{\infty} Q_n V_{E_n}(x) \qquad \text{`Expand } \overline{\Phi}(x,t=0) \text{ in terms of } \\
\frac{\overline{2}}{2} = \sum_{n=1}^{\infty} \overline{\frac{1}{2}} = \sum_{n=1}^{\infty} \overline{\frac{1}{2}} = \sum_{n=1}^{\infty} \overline{\frac{1}{2}} + \sum_{n=1}^{\infty} \overline{\frac{1}{2}} = \sum_{n=1}^{\infty} \overline{\frac{1}{2}} + \sum_{n=1}^{\infty} \overline$

Remark: See Sample Question SQ10 for an example

Step 3: Let each definite energy state evolve with its own time part

Step 3: Get D(x,t) by letting each YEn (x) evolve with its own time part $\overline{\Phi}(x,t=0) = \sum_{n=1}^{\infty} a_n \gamma_{E_n}(x)$ after Step 1 and Step 3 $\Phi(\mathbf{x},t) = a_1 \psi_{E_1} e^{i \frac{1}{2}t} + a_2 \psi_{E_2} e^{i \frac{1}{2}t} + \dots + a_n \psi_{E_n} e^{-i \frac{1}{2}t} + \dots$ $\begin{aligned}
\overline{\Psi}(\mathbf{x},t) &= \sum_{n=1}^{\infty} a_n \gamma_{E_n} (\mathbf{x}) C^{-i} \frac{E_n t}{h} \quad \text{En are obtained in Step 1} \\
(Answer)
\end{aligned}$ Step1 Why? Time-evolution in QM is governed by TDSE and $\underline{\Psi}(x,t)$ satisfies TDSE

Initial-value problems are a big part of QM, Steps 1,2,3 solve the problems for U = V(x) or $U(\overline{r})$ [U with no explicit time in it]

All Done (without knowing the explicit form of U(x))!

Remark: For those who have studied the classical wave equation (e.g. a string fixed at its two ends), the steps in solving initial value problems starting from TDSE are exactly the same as those starting from the classical wave equation. See Problem Set 1.

Check Point/Summary " How does "separation of variables" work? From TDSE TISE L how? ■ What does TISE do? Solving TISE, what does it mean? Solving for what? How does a state of definite energy evolve in time? How does a state $\overline{\Psi}(x,t=0) = \alpha_1 \Psi_{E_1}(x) + \alpha_2 \Psi_{E_2}(x) + \cdots + \alpha_n \Psi_{E_n}(x) + \cdots + \alpha_$

* For a system defined by U(x) or U(\vec{r}), what are the steps for solving the initial value problem that $\Psi(x,t=o) = \Psi(x,o) = \Psi(x)$?

" Write down TDSE and TISE for standard problems

Think through these check-point questions and write down your answers quietly while explaining the ideas to yourself is an effective way to check on your understanding.