

CLOSE TO COLLAPSE



MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

Last week: Postulates

- Metal surfaces and operations of STM
- Operators, eigenvalues, eigenfunctions, expectation values; also, in Dirac notation
- Linear operators, Hermitian operators (complete, real)
- Products of operators, and commutators $\hat{C} = [\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$
- Commuting operators and common eigenfunctions
- Four of the five postulates of quantum mechanics
 - I. Wavefunctions
 - II. Operators
 - III. Measurements
 - IV. Expectation values, probabilities $\| \langle \psi_i | \psi \rangle \|^2$

Fourth postulate: expectation values and probabilities

If a series of measurements is made of the dynamical variable A on an ensemble described by Ψ , the average (“expectation”) value is

$$\langle A \rangle = \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

i.e. the probability of obtaining an eigenvalue a_n is

$$P(a_n) = (p_n)^2 = \left| \langle \phi_n | \Psi \rangle \right|^2$$

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Deterministic vs. stochastic

- Classical, macroscopic objects: we have well-defined values for all dynamical variables at every instant (position, momentum, kinetic energy...)
- Quantum objects: we have **well-defined probabilities** of measuring a certain value for a dynamical variable, when a **large number of identical, independent, identically prepared physical systems** are subject to a measurement.

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Quantum double-slit

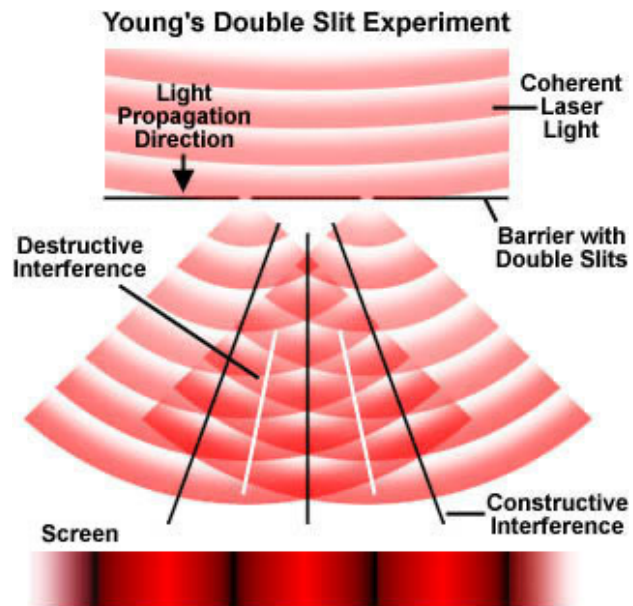
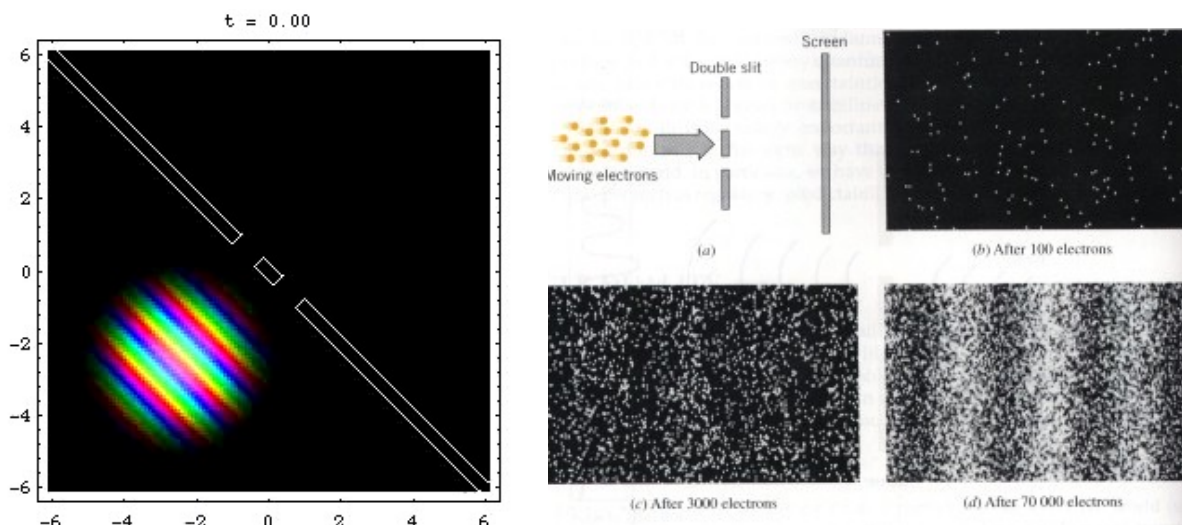


Figure 4 Intensity Distribution of Fringes

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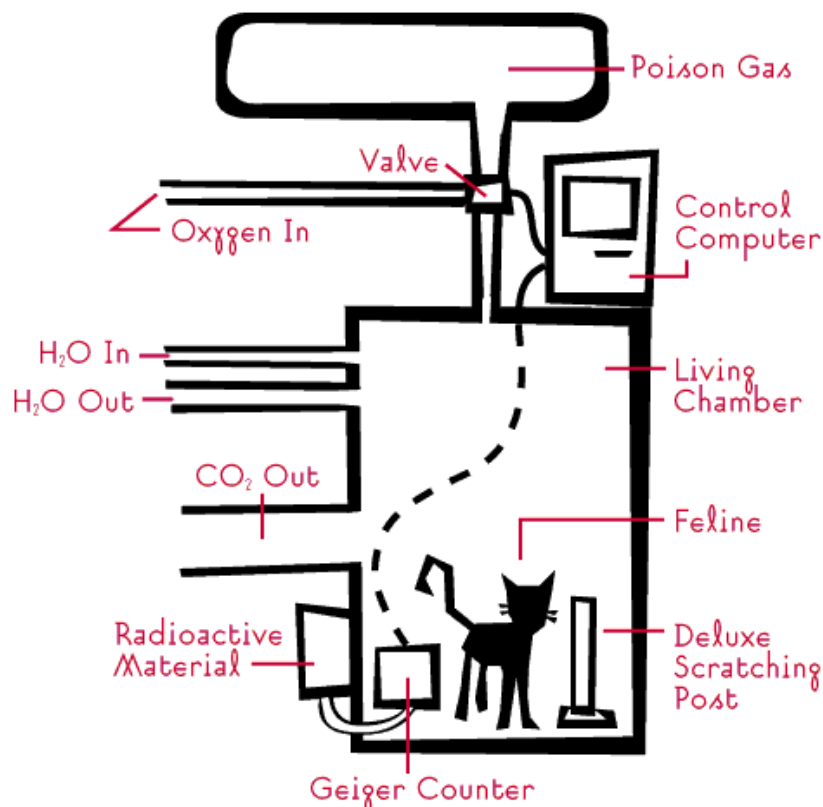
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Fifth postulate: collapse

- If the measurement of the physical quantity A gives the result a_n , the wavefunction of the system immediately after the measurement is the eigenvector $|\varphi_n\rangle$

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When scientists turn bad...



Cat wavefunction

$$|\Psi_{cat}(t)\rangle = |\Psi_{alive}\rangle \left(\exp\left(-\frac{t}{\tau}\right) \right)^{\frac{1}{2}} + |\Psi_{dead}\rangle \left(1 - \exp\left(-\frac{t}{\tau}\right) \right)^{\frac{1}{2}}$$

- There is not a value of the observable until it's measured (a conceptually different “statistics” from thermodynamics)

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NEWS • 18 SEPTEMBER 2018

Reimagining of Schrödinger's cat breaks quantum mechanics – and stumps physicists

In a multi-'cat' experiment, the textbook interpretation of quantum theory seems to lead to contradictory pictures of reality, physicists claim.

[Davide Castelvecchi](#)

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Top Three List

- **Albert Einstein:** *“Gott wurfelt nicht!” [God does not play dice!]*
- **Werner Heisenberg** *“I myself . . . only came to believe in the uncertainty relations after many pangs of conscience. . .”*
- **Erwin Schrödinger:** *“Had I known that we were not going to get rid of this damned quantum jumping, I never would have involved myself in this business!”*

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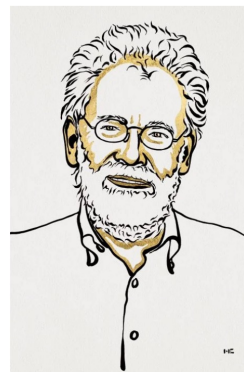
The Nobel Prize in Physics 2022



III. Niklas Elmehed © Nobel Prize Outreach
Alain Aspect
Prize share: 1/3



III. Niklas Elmehed © Nobel Prize Outreach
John F. Clauser
Prize share: 1/3



III. Niklas Elmehed © Nobel Prize Outreach
Anton Zeilinger
Prize share: 1/3

The Nobel Prize in Physics 2022 was awarded jointly to Alain Aspect, John F. Clauser and Anton Zeilinger "for experiments with entangled photons, establishing the violation of Bell inequalities and pioneering quantum information science"

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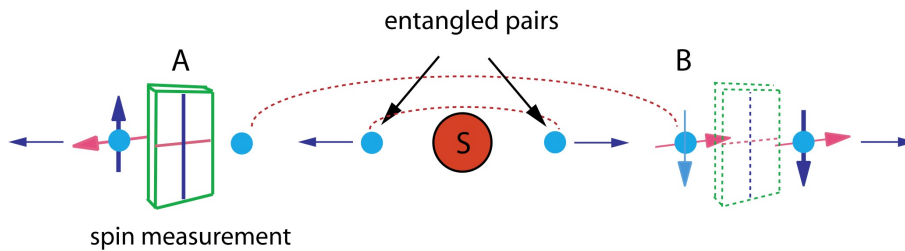
Can Quantum-Mechanical Description of Physical Reality Be Considered Complete?

A. EINSTEIN, B. PODOLSKY AND N. ROSEN, *Institute for Advanced Study, Princeton, New Jersey*

(Received March 25, 1935)

In a complete theory there is an element corresponding to each element of reality. A sufficient condition for the reality of a physical quantity is the possibility of predicting it with certainty, without disturbing the system. In quantum mechanics in the case of two physical quantities described by non-commuting operators, the knowledge of one precludes the knowledge of the other. Then either (1) the description of reality given by the wave function in

quantum mechanics is not complete or (2) these two quantities cannot have simultaneous reality. Consideration of the problem of making predictions concerning a system on the basis of measurements made on another system that had previously interacted with it leads to the result that if (1) is false then (2) is also false. One is thus led to conclude that the description of reality as given by a wave function is not complete.



<https://www.nobelprize.org/uploads/2022/10/advanced-physicsprize2022.pdf>

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Uncertainties, and Heisenberg's Indetermination Principle

$$(\Delta A)^2 = \langle (A - \langle A \rangle)^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2$$

$$\Delta A \Delta B \geq \frac{1}{2} |\langle [A, B] \rangle|$$

POSITION \rightarrow x \rightarrow NON-COMMUTING \rightarrow EASY TO PROVE

$$\left[x, -i\hbar \frac{d}{dx} \right] = i\hbar$$

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Linewidth Broadening

PHYSICAL REVIEW A 62 063404

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

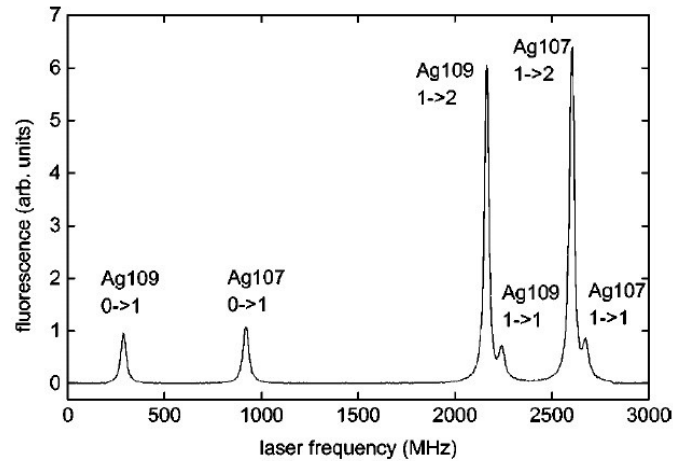


FIG. 2. The $^2S_{1/2}-^2P_{3/2}$ spectrum, obtained with a frequency-doubled diode laser aligned perpendicular to the thermal atomic beam.

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Good Quantum Numbers

$$\frac{d\langle A \rangle}{dt} = \frac{d\langle \Psi | \hat{A} | \Psi \rangle}{dt} = \frac{1}{i\hbar} \langle [\hat{A}, \hat{H}] \rangle$$

↑
T.R. M.R.
SCHIL. P.R.

↑
If \hat{A} commutes with the Hamiltonian, and it does not depend on time, its expectation value does not change with time (it's a constant of motion – if we are in an eigenstate, that quantum number will remain constant)

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Variational Principle

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

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Variational Principle

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$E[\Psi] \geq E_0$$

If $E[\Psi] = E_0$ then Ψ is the ground state wavefunction, and viceversa...

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$$E[\psi] = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \geq \epsilon_0$$

$$\hat{H} | \psi_i \rangle = \epsilon_i | \psi_i \rangle$$

$$\langle \psi_i | \hat{H} = \epsilon_i \langle \psi_i | \quad i=0, \dots, \infty$$

$$|\psi\rangle = \sum_{n=0, \dots, \infty} c_n |\psi_n\rangle$$

$$\langle \psi | = \sum_{m=0, \dots, \infty} c_m^* \langle \psi_m |$$

$$C_{22} = \langle \psi_{22} | \psi \rangle$$

$$= \sum_n c_n \langle \psi_{22} | \psi_n \rangle$$

$$= c_{22}$$

$$\langle \psi | \hat{H} | \psi \rangle =$$

$$= \sum_{m,n} c_m^* c_n \langle \psi_m | \hat{H} | \psi_n \rangle = \sum_{m,n} c_m^* c_n \epsilon_m \delta_{m,n}$$

$$= \sum_n \|c_n\|^2 \epsilon_n$$

$$= \sum_{m,n} c_m^* c_n \epsilon_n \delta_{m,n} = \sum_n c_n^* c_n \epsilon_n = \sum_n \|c_n\|^2 \epsilon_n$$

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$$\langle \psi | \psi \rangle = \sum_{m,n} c_m^* c_n \langle \psi_m | \psi_n \rangle =$$

$$= \sum_n \|c_n\|^2$$

$$\frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\sum_m \|c_m\|^2 \epsilon_m}{\sum_n \|c_n\|^2} \geq \frac{\sum_n \|c_n\|^2 \epsilon_0}{\sum_n \|c_n\|^2}$$

$$\|c_0\|^2 \epsilon_0 + \|c_1\|^2 \epsilon_1 + \|c_2\|^2 \epsilon_2 + \dots \geq$$

$$\epsilon_0 \frac{\sum_m \|c_m\|^2}{\sum_n \|c_n\|^2} \geq \epsilon_0$$

TO HAVE AN EQUAL, ...
YOU NEED $c_0 = 1,$
 $c_1, \dots, \infty = 0$

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Matrix Formulation (I)

$$\hat{H}|\psi\rangle = E|\psi\rangle$$

$$|\psi\rangle = \sum_{n=1, \dots, k} c_n |\varphi_n\rangle \quad \{|\varphi_n\rangle\} \text{ orthogonal}$$

$$\langle \varphi_m | \hat{H} |\psi\rangle = E \langle \varphi_m | \psi\rangle$$

$$= \sum_n c_n \langle \varphi_m | \hat{H} | \varphi_n \rangle = E \sum_n c_n \langle \varphi_m | \varphi_n \rangle$$

$$= \sum_n c_n H_{mn} = E c_m$$

$\langle \varphi_m | \varphi_n \rangle = \delta_{m,n}$
 $\sum_n c_n \langle \varphi_m | \varphi_n \rangle = c_m$

Matrix Formulation (II)

$$\mathbb{1} = \begin{pmatrix} 1 & & 0 \\ & \ddots & \\ 0 & & 1 \end{pmatrix}$$

$$\sum_{n=1, \dots, k} H_{mn} c_n = E c_m$$

$$\underline{H} \underline{c} = E \underline{c}$$

$$= E \underline{\mathbb{1}} \underline{c}$$

$$\begin{pmatrix} H_{11} - E & H_{12} & \dots & H_{1k} \\ H_{21} & H_{22} - E & \dots & H_{2k} \\ \vdots & \vdots & \ddots & \vdots \\ H_{k1} & \dots & \dots & H_{kk} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_k \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

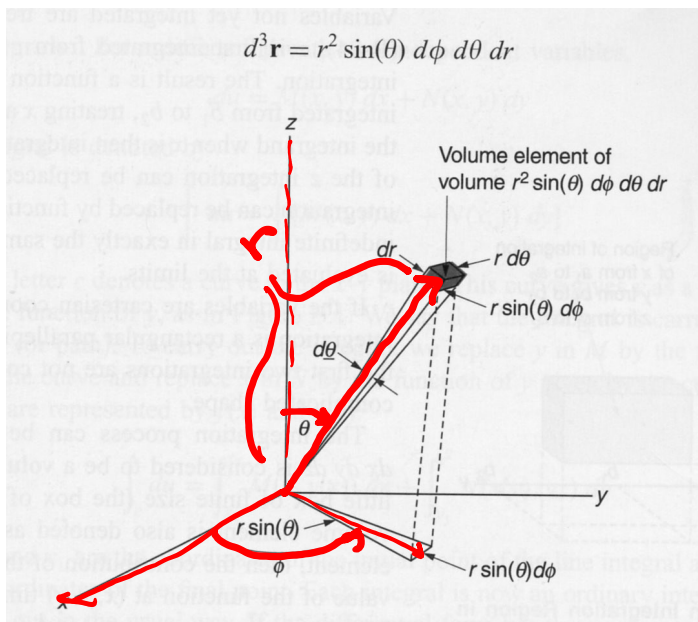
$$\det \|\underline{H} - E \underline{\mathbb{1}}\| = 0$$

Matrix Formulation (III)

$$\det \begin{pmatrix} H_{11} - E & \dots & H_{1k} \\ \cdot & H_{22} - E & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ H_{k1} & \dots & H_{kk} - E \end{pmatrix} = 0$$

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Spherical Coordinates



$$\int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} dz = \int_0^{\infty} dr \int_0^{\pi} d\theta \int_0^{2\pi} d\phi$$

$\cdot r^2 \sin\theta$

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

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Angular Momentum

Classical

Quantum

$$\vec{L} = \vec{r} \times \vec{p} \implies \vec{r} \times (-i\hbar \vec{\nabla})$$
$$\begin{aligned} L_x &= y p_z - z p_y & L_x &= y \left(-i\hbar \frac{\partial}{\partial z}\right) - z \left(-i\hbar \frac{\partial}{\partial y}\right) \\ L_y &= z p_x - x p_z \\ L_z &= x p_y - y p_x \end{aligned}$$