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Lecture-28

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g^* is the conjugate of 'g'

Definitions and Theorems — I

- *Scalar product* of two complex functions f and g:

$$\langle g|f\rangle \doteq \int_\tau g^* f \, \mathrm{d}\tau$$

- The functions f, g are *orthogonal* if $\langle g|f\rangle = 0$. For any complex constants b , b_1 , b_2 , the following hold:

$$\langle f|g\rangle = \int_\tau f^* g \, \mathrm{d}\tau = \left(\int_\tau f g^* \, \mathrm{d}\tau\right)^* = \langle g|f\rangle^*$$

$$\langle g|bf\rangle = b\,\langle g|f\rangle\,, \qquad \langle bg|f\rangle = b^*\,\langle g|f\rangle$$

$$\langle g|b_1 f_1 + b_2 f_2\rangle = b_1\,\langle g|f_1\rangle + b_2\,\langle g|f_2\rangle$$

$$\langle b_1 g_1 + b_2 g_2|f\rangle = b_1^*\,\langle g_1|f\rangle + b_2^*\,\langle g_2|f\rangle$$

- The functions may result from an operator's application:

$$s \doteq \mathcal{D}f \;\Rightarrow\; \langle g|s\rangle = \int_\tau g^* \mathcal{D} f \, \mathrm{d}\tau\,, \quad \langle s|g\rangle = \int_\tau (\mathcal{D}f)^* g \, \mathrm{d}\tau$$

- The operator *adjoint* to $\mathcal{D}$ is indicated with $\mathcal{D}^\dagger$ and has the property

$$\langle g|\mathcal{D}f\rangle = \langle \mathcal{D}^\dagger g|f\rangle \qquad \forall f\,, g$$

- It may happen that $\mathcal{D}^\dagger = \mathcal{D}$. In this case, $\mathcal{D}$ is called *self-adjoint* or *Hermitian*, and $\langle g|\mathcal{D}f\rangle = \langle \mathcal{D}g|f\rangle = \langle g|\mathcal{D}|f\rangle$.

→ Checking whether Hamiltonian operator is Hermettian

Definitions and Theorems — II

- The definition of scalar product generalizes that between vectors. The definition of adjoint operator generalizes that of conjugate-transpose matrix.
- The Hamiltonian operator is Hermitian for any function vanishing at the boundary $\partial\tau$ of τ :

$$\langle g|\mathcal{H}f\rangle - \langle\mathcal{H}g|f\rangle = 0$$

$$= \int_\tau \left(-\frac{\hbar^2}{2m} g^* \nabla^2 f + g^* V f + \frac{\hbar^2}{2m} f \nabla^2 g^* - f V g^*\right) d\tau =$$

$$= \frac{\hbar^2}{2m} \int_\tau \left(f \nabla^2 g^* - g^* \nabla^2 f\right) d\tau = \text{ (by Green's theorem)}$$

$$= \frac{\hbar^2}{2m} \int_{\partial\tau} \left(f \frac{\partial g^*}{\partial \nu} - g^* \frac{\partial f}{\partial \nu}\right) d\partial\tau = 0 .$$

- The (second) Green theorem is demonstrated using $\boldsymbol{v} = \operatorname{grad} g$ in the identity $\operatorname{div}(f\boldsymbol{v}) = f \operatorname{div} \boldsymbol{v} + \boldsymbol{v} \bullet \operatorname{grad} f$, to find:

$$\operatorname{div}(f \operatorname{grad} g) = f\nabla^2 g + \operatorname{grad} f \bullet \operatorname{grad} g .$$

Interchanging f and g and subtracting from the above yields

$$f\nabla^2 g - g\nabla^2 f = \operatorname{div}(f \operatorname{grad} g - g \operatorname{grad} f) .$$

Integration over τ yields Green's theorem.

Definitions and Theorems — III

- The set of the eigenvalues of an operator is the operator's *spectrum*. The spectrum is *discrete* (*continuous*) if the eigenvalues depend on discrete (continuous) parameters only; otherwise it is *mixed*.

- An eigenvalue is *simple* if there is one and only one eigenfuction corresponding to it; it is *degenerate of order* s if there are s linearly independent eigenfuctions corresponding to it. The order of degeneracy may be ∞.

- For Hermitian operators, any two eigenfunctions belonging to different eigenvalues are orthogonal. Let $\mathcal{A}v = Av$ be the eigenvalue equation of $\mathcal{A}$. Assuming a discrete spectrum, let A_n, A_m be two different eigenvalues, and v_n, v_m two eigenfunctions corresponding to them:

$$\mathcal{A}v_n = A_n v_n\,, \qquad \mathcal{A}v_m = A_m v_m\,, \qquad \text{whence}$$

$$\langle v_m|\mathcal{A}v_n\rangle = A_n \langle v_m|v_n\rangle\,, \qquad \langle \mathcal{A}v_m|v_n\rangle = A_m^* \langle v_m|v_n\rangle\,.$$

As $\mathcal{A}$ is Hermitian, $(A_n - A_m^*)\langle v_m|v_n\rangle = 0$. But the eigenvalues of the Hermitian operators are all real, as is easily seen by letting $m = n$; as a consequence, $\langle v_m|v_n\rangle = 0$.

Definitions and Theorems — IV

Gram-Schmidt orthogonalization

- If an eigenvalue A_n has s linearly-independent eigenfunctions $v_n^{(1)}, \ldots, v_n^{(s)}$, then a linear combination of them is also an eigenfunction belonging to A_n :

$$\mathcal{A} \sum_{k=1}^{s} \alpha_k v_n^{(k)} = \sum_{k=1}^{s} \alpha_k \mathcal{A} v_n^{(k)} =$$

$$= \sum_{k=1}^{s} \alpha_k A_n v_n^{(k)} = A_n \sum_{k=1}^{s} \alpha_k v_n^{(k)} .$$

- The eigenfunctions $v_n^{(1)}, \ldots, v_n^{(s)}$ are not necessarily orthogonal to each other; however, it is possible to build-up linearly-independent combinations of them that are mutually orthogonal (*Gram-Schmidt orthogonalization*):

$$u_n^{(1)} = v_n^{(1)} , \qquad u_n^{(2)} = v_n^{(2)} + a_{21} u_n^{(1)}$$

where a_{21} is such that $\langle u_n^{(1)} | u_n^{(2)} \rangle = 0$:

$$\langle u_n^{(1)} | v_n^{(2)} \rangle + a_{21} \langle u_n^{(1)} | u_n^{(1)} \rangle = 0 , \quad a_{21} = - \frac{\langle u_n^{(1)} | v_n^{(2)} \rangle}{\langle u_n^{(1)} | u_n^{(1)} \rangle} .$$

(continues)

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Definitions and Theorems — V

Gram-Schmidt orthogonalization

- (cont.) The next function is found be letting

$$u_n^{(3)} = v_n^{(3)} + a_{31} u_n^{(1)} + a_{32} u_n^{(2)}$$

with $\langle u_n^{(1)} | u_n^{(3)} \rangle = 0$, $\langle u_n^{(2)} | u_n^{(3)} \rangle = 0$:

$$\langle u_n^{(1)} | v_n^{(3)} \rangle + a_{31} \langle u_n^{(1)} | u_n^{(1)} \rangle = 0 , \quad a_{31} = - \frac{\langle u_n^{(1)} | v_n^{(3)} \rangle}{\langle u_n^{(1)} | u_n^{(1)} \rangle} .$$

$$\langle u_n^{(2)} | v_n^{(3)} \rangle + a_{32} \langle u_n^{(2)} | u_n^{(2)} \rangle = 0 , \quad a_{32} = - \frac{\langle u_n^{(2)} | v_n^{(3)} \rangle}{\langle u_n^{(2)} | u_n^{(2)} \rangle} .$$

- In general:

$$u_n^{(k)} = v_n^{(k)} + \sum_{i=1}^{k-1} a_{ki} u_n^{(i)} , \quad a_{ki} = - \frac{\langle u_n^{(i)} | v_n^{(k)} \rangle}{\langle u_n^{(i)} | u_n^{(i)} \rangle} .$$

where $\langle u_n^{(i)} | u_n^{(i)} \rangle = \int_\tau |u_n^{(i)}|^2 \, d\tau \doteq ||u_n^{(i)}||^2$ is the square of the norm of $u_n^{(i)}$.

Definitions and Theorems — VI

Completeness (a)

fundamental property of set of Eigen functions of operators is Completeness

For a function $f(x)$ defined in $[-\alpha/2, +\alpha/2]$ and such that $\int_{-\alpha/2}^{+\alpha/2} |f(x)|\, dx < \infty$, Fourier's expansion holds:

$$f(x) = \frac{1}{2}a_0 + \sum_{n=1}^{\infty} [a_n \cos(2\pi nx/\alpha) + b_n \sin(2\pi nx/\alpha)] \;,$$

with $a_0/2 = \bar{f} \doteq (1/\alpha) \int_{-\alpha/2}^{+\alpha/2} f(x)\, dx$. The equality above indicates convergence in the mean; letting $g \doteq f - \bar{f}$:

$$\lim_{N\to\infty} \int_{-\alpha/2}^{+\alpha/2} \left\{ g - \sum_{n=1}^{N} [a_n \cos(2\pi nx/\alpha) + b_n \sin(\ldots)] \right\}^2 dx = 0.$$

Defining $\chi_n \doteq \sqrt{2/\alpha}\cos(2\pi nx/\alpha)$, $\sigma_n \doteq \sqrt{2/\alpha}\sin(2\pi nx/\alpha)$, the following hold:

orthogonality

$$\begin{aligned}
\langle \sigma_m | \chi_n \rangle &= 0\,, & n, m &= 0, 1, 2, \ldots, \\
\langle \sigma_m | \sigma_n \rangle = \langle \chi_m | \chi_n \rangle &= 0\,, & n, m &= 0, 1, 2, \ldots, \quad m \neq n \\
\langle \sigma_n | \sigma_n \rangle = \langle \chi_n | \chi_n \rangle &= 1\,, & n &= 1, 2, \ldots,
\end{aligned}$$

showing that σ_n, χ_n, $n = 0, 1, 2, \ldots$ form an *orthonormal* system of functions. The system is also *complete* with respect to any g for which the expansion above is allowed.

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Definitions and Theorems — VII

Completeness (b)

The coefficients of Fourier's expansion are given by:

$$a_n = \frac{2}{\alpha}\int_{-\alpha/2}^{+\alpha/2} \cos(2\pi n x/\alpha)\, f(x)\, \mathrm{d}x\,, \qquad n = 1, 2, \ldots$$

$$b_n = \frac{2}{\alpha}\int_{-\alpha/2}^{+\alpha/2} \sin(2\pi n x/\alpha)\, f(x)\, \mathrm{d}x\,, \qquad n = 1, 2, \ldots$$

whence $\boxed{f = \bar{f} + \Sigma_{n=1}^{\infty}\left(\langle\chi_n|f\rangle\chi_n + \langle\sigma_n|f\rangle\sigma_n\right)}$ or, observing that $\langle\sigma_n|\mathrm{const}\rangle = \langle\chi_n|\mathrm{const}\rangle = 0\,,$

$$\boxed{g = \sum_{n=1}^{\infty}\left(\langle\chi_n|g\rangle\chi_n + \langle\sigma_n|g\rangle\sigma_n\right)}\,.$$

Letting

$$c_{2n-1} \doteq \langle\chi_n|g\rangle\,, \quad c_{2n} \doteq \langle\sigma_n|g\rangle\,, \quad w_{2n-1} \doteq \chi_n\,, \quad w_{2n} \doteq \sigma_n\,,$$

the expansion takes the more compact form

$$\boxed{g = \sum_{m=1}^{\infty} c_m w_m\,,} \qquad \underline{c_m = \langle w_m|g\rangle}\,.$$

Definitions and Theorems — VIII

Examples of Completeness

Normalized Solution for Schrodinger eqn for particle in a Box

1. From the expansion into Fourier's series one sees that the system made of the $\sigma_n = \sqrt{2/\alpha}\,\sin(2\pi n x/\alpha)$ only is complete with respect to any function that is *odd* in $[-\alpha/2, +\alpha/2]$, hence it is complete with respect to any function in $[0, +\alpha/2]$.

   On the other hand, the system of the σ_n (apart from the normalization coefficient) is the set of the eigenfunctions for the Hamiltonian of a particle in a box. In conclusion, the system of eigenfunctions of such Hamiltonian is complete within $[0, +\alpha/2]$.

2. The eigenfunctions of a free particle are, for any $\boxed{k = \sqrt{2mE}/\hbar}$ and apart from an arbitrary multiplicative constant, $w_{+k} = \exp(jkx)$ and $w_{-k} = \exp(-jkx)$. In an equivalent form they may be written as $w_k = \exp(jkx)$, where k can also be negative. Taking the multiplicative constant equal to $1/\sqrt{2\pi}$, the expansion of a function f such that $\int_{-\infty}^{+\infty} |f|\,\mathrm{d}x < \infty$ reads

   'C' is projection of 'f' on 'w'$_k$

   $$f(x) = \int_{-\infty}^{+\infty} c_k w_k(x)\,\mathrm{d}k\,, \qquad c_k \doteq \langle w_k | f \rangle$$

   These expressions are equivalent to the Fourier-transform formulæ

   $$c(k) = \int_{-\infty}^{+\infty} \frac{\exp(-jkx)}{\sqrt{2\pi}}\, f(x)\,\mathrm{d}x, \quad f(x) = \int_{-\infty}^{+\infty} \frac{\exp(jkx)}{\sqrt{2\pi}}\, c(k)\,\mathrm{d}k,$$

   this showing that the eigenfunctions of a free particle form a complete system.

   'k' depends on Energy and is also continuous.

Norm of function = Sum of Norm of coefficients

Parseval Theorem and Dirac Notation

Considering the expansion of a complex function f with respect to an orthonormal, discrete system of functions w_n ,

$$f = \sum_n c_n w_n \,, \qquad c_n = \langle w_n | f \rangle \,, \qquad \langle w_n | w_m \rangle = \boxed{\delta_{nm}} \,,$$

$\delta_{nm} = 1 \quad n = m$

$\quad = 0 \quad n \neq m$

the squared norm of f reads

Squared Norm of function

$$\int_\tau |f|^2 \, \mathrm{d}^3 r = \langle f | f \rangle = \langle \sum_n c_n w_n | \sum_m c_m w_m \rangle =$$

$$= \sum_n c_n^* \sum_m c_m \langle w_n | w_m \rangle = \sum_n c_n^* \sum_m c_m \, \delta_{nm} = \sum_n |c_n|^2 \,.$$

Sum of Squared Norm of coefficients

For a continuous set of eigenfunctions, the above become

$$f = \int_\alpha c_\alpha w_\alpha \, \mathrm{d}\alpha \,, \qquad c_\alpha = \langle w_\alpha | f \rangle \,, \qquad \boxed{\langle w_\alpha | w_\beta \rangle = \delta(\alpha - \beta) \,,}$$

dirac delta & it should be used only inside an Integral

$$\int_\tau |f|^2 \, \mathrm{d}^3 r = \langle f | f \rangle = \langle \int_{-\infty}^{+\infty} c_\alpha w_\alpha \, \mathrm{d}\alpha | \int_{-\infty}^{+\infty} c_\beta w_\beta \, \mathrm{d}\beta \rangle =$$

$$= \int_{-\infty}^{+\infty} c_\alpha^* \, \mathrm{d}\alpha \int_{-\infty}^{+\infty} c_\beta \, \delta(\alpha - \beta) \, \mathrm{d}\beta = \int_{-\infty}^{+\infty} |c_\alpha|^2 \, \mathrm{d}\alpha \,.$$

The notation using brackets to indicate the scalar products is due to Dirac. The two terms $\langle g|$ and $|f\rangle$ of the scalar product $\langle g|f\rangle$ are called *bra vector* and *ket vector*, respectively.

row vector

column vector

Capitolo 12

Equazione di Schrödinger dipendente dal tempo

Superposition Principle — I

The De Broglie postulate associates the monochromatic wave function $w(\boldsymbol{r})\exp(-j\omega t)$ to the motion of a particle with definite and constant energy $E = \hbar\omega$. The analogy with the e.m. case suggests that a more general type of wave function —still related to the conservative case— can be expressed as a superposition of monochromatic wave functions. Considering the discrete case, *it is then postulated that*

$$\boxed{\psi(\boldsymbol{r},t) = \sum_n c_n w_n \exp(-jE_n t/\hbar)}\,, \qquad \boxed{\mathcal{H} w_n = E_n w_n}\,,$$

with c_n complex coefficients. The latter are found thanks to the completeness of the eigenfunctions:

$$\psi_{t=0} = \psi(\boldsymbol{r},0) = \sum_n c_n w_n\,, \qquad c_n = \langle w_n | \psi_{t=0} \rangle\,.$$

- ▷ The interference of monochromatic waves allows for the localization of $|\psi|^2$ (wave packet).
- ▷ The wave function $\psi(\boldsymbol{r},t)$ is uniquely determined by the initial value $\psi_{t=0}$.
- ▷ As all possible energies E_n appear in the expression of ψ, the latter does not describe a motion with definite energy.

Superposition Principle — II

- The wave function $\psi(\boldsymbol{r}, t) = \sum_n c_n w_n \exp(-jE_n t/\hbar)$ provides the probability density $|\psi|^2$ used to identify the position of the particle. Here a normalizeable wave function is assumed:

$$\int_\tau |\psi|^2 \, \mathrm{d}^3 r = \sum_n |c_n|^2 = 1 \,.$$

Parseval's Relation

- If an energy measurement is carried out, and is completed at $t = t_E$ to find the eigenvalue E_m , then for $t > t_E$ it must be

$$\psi(\boldsymbol{r}, t) = w_m \exp[-jE_m(t - t_E)/\hbar] \,.$$

- This is interpreted as follows: the measurement filters out the term corresponding to E_m; as a consequence, the coefficients c_n whose values were previously set by the original ψ are changed by the measurement into $\boxed{c_n = \delta_{nm}}$. Again it is $\sum_n |c_n|^2 = |c_m|^2 = 1$. If another energy measurement is carried out, the probability of the outcome E_m is 1 due to the form of ψ for $t \geq t_E$.
It is then sensible to interpret $|c_n|^2$ as the probability that a measurement of energy finds the result E_n .

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Time-Dependent Schrödinger Equation

- The Superposition Principle prescribes the form of the general wave function for the conservative case. Considering a discrete set of eigenfunctions, the time derivative of ψ reads

$$\frac{\partial \psi}{\partial t} = \sum_n c_n w_n \frac{E_n}{j\hbar} \exp(-jE_n t/\hbar) \, .$$

As $\mathcal{H} w_n = E_n w_n$, the above becomes

$$j\hbar \frac{\partial \psi}{\partial t} = \sum_n c_n \mathcal{H} w_n \exp(-jE_n t/\hbar) \quad \Rightarrow \quad \boxed{j\hbar \frac{\partial \psi}{\partial t} = \mathcal{H} \psi \, .}$$

Time dependent schrodinger eq^n

- The latter is the time-dependent Schrödinger equation, that provides the time evolution of ψ starting from the initial value $\psi_{t=0}$. The boundary conditions are the same as those of the eigenfunctions w_n .
- *It is postulated that the same equation also holds in the non conservative cases* ($\mathcal{H} w_n = E_n w_n$ does not hold then). Due to the form of the Schrödinger equation, the state of the particle (i.e., its wave function) is uniquely determined by the initial value $\psi_{t=0}$.

This eq^n is seperable if the situation is conservative but even in Non coservative case, it is still useful.

$\mathcal{H}^* = \mathcal{H}$

$|\psi|^2 = \psi^* \psi$

Norm Conservation

From the time-dependent Schrödinger equation it follows

$$\boxed{\frac{\partial |\psi|^2}{\partial t} = \psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t} = \psi^* \frac{\mathcal{H}\psi}{j\hbar} - \psi \frac{\mathcal{H}\psi^*}{j\hbar},}$$

with $\psi^* \mathcal{H}\psi - \psi \mathcal{H}\psi^* = -\hbar^2/(2m)\,(\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*)$. Using the identity $\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^* = \mathrm{div}(\psi^* \, \mathrm{grad}\, \psi - \psi \, \mathrm{grad}\, \psi^*)$:

$$\frac{\partial |\psi|^2}{\partial t} + \mathrm{div}\, \boldsymbol{J}_\psi = 0\,, \quad \boldsymbol{J}_\psi \doteq \frac{j\hbar}{2m}(\psi \, \mathrm{grad}\, \psi^* - \psi^* \, \mathrm{grad}\, \psi)\,.$$

The above has the form of a continuity equation. As $|\psi|^2$ is the probability density, $\boldsymbol{J}_\psi$ must be given the meaning of *density of the probability flux*. This result also provides a physical explanation of the continuity of the first derivatives of ψ. Integrating over a volume yields the norm conservation:

$$\boxed{\frac{\mathrm{d}}{\mathrm{d}t}\int_\tau |\psi|^2 \, \mathrm{d}\tau = -\int_{\partial\tau} \boldsymbol{J}_\psi \bullet \boldsymbol{\nu}\, \mathrm{d}\partial\tau} \Rightarrow \frac{\mathrm{d}}{\mathrm{d}t}\int_\infty |\psi|^2 \, \mathrm{d}\tau = 0\,.$$

Norm conservation

The definition of $\hat{\boldsymbol{p}} = -j\hbar\, \mathrm{grad}$ also yields the alternative form

$$\boldsymbol{J}_\psi = \frac{1}{2m}\left[\psi\,(\hat{\boldsymbol{p}}\psi)^* + \psi^* \hat{\boldsymbol{p}}\psi\right] = \frac{1}{m}\Re\,(\psi^* \hat{\boldsymbol{p}}\psi)\,.$$

(Momentum operator) we studied earlier

Integrating over a volume is the probability of finding the particle in that volume.

$H = T + V$

$T = \frac{\hat{p}^2}{2m} = \frac{-\hbar^2}{2m}\nabla^2$