Suppose that an instant of time, the wave function of a quantum particle

$$\psi = \sum c_n \psi_n,$$

where ψ_n are normalized eigenfunctions of particle's Hamiltonian, *i.e.* $\hat{H}\psi_n = E_n\psi_n$, and c_n's are numbers (complex, in general). Let us find the average value of the energy of that particle

$$\langle E \rangle = \langle \psi, \hat{H}\psi \rangle.$$

Plugging in the linear combination representing ψ and using properties of the inner product, we find

$$\langle \psi, \hat{H}\psi \rangle = \langle \sum c_m \psi_m, \hat{H} \sum c_n \psi_n \rangle = \sum_m \sum_n c_m^* c_n \langle \psi_m, \hat{H}\psi_n \rangle.$$

But ψ_n's are eigenfunctions of the Hamiltonian ($\hat{H}\psi_n = E_n\psi_n$). Hence

$$\sum_m \sum_n c_m^* c_n \langle \psi_m, \hat{H}\psi_n \rangle = \sum_m \sum_n c_m^* c_n E_n \langle \psi_m, \psi_n \rangle.$$

Now, recall that $\hat{H}$ is Hermitian, and eigenfunctions that belong to different eigenvalues are orthogonal, that is $\langle \psi_m, \psi_n \rangle = \delta_{mn}$. Hence

$$\sum_m \sum_n c_m^* c_n E_n \langle \psi_m, \psi_n \rangle = \sum_m \sum_n c_m^* c_n E_n \delta_{mn} = \sum_n E_n \cdot |c_n|^2.$$

Eventually,

$$\langle E \rangle = \sum_n E_n \cdot |c_n|^2.$$

When you recall how we calculate average values in the theory of probability, then the non-negative numbers $|c_n|^2$ on the rhs exactly correspond to the probability that the value E_n is obtained in a measurement of the energy of the particle

$$\Pr(E = E_n) = |c_n|^2.$$

Of course the same discussion can be repeated for $\psi = \sum c_n \phi_n$, that is a linear combination of eigenfunctions of any Hermitian operator $\hat{A}$ representing a physical quantity A. Then $|c_n|^2$ will be the probability that a measurement of A gives the value a_n (where $\hat{A}\phi_n = a_n\phi_n$).