

## 1.5: Eigenstates and Eigenvalues

Now let us discuss the most important corollaries of wave mechanics' linearity. First of all, it uses only linear operators. This term means that the operators must obey the following two rules: <sup>40</sup>

$$(\hat{A}_1 + \hat{A}_2) \Psi = \hat{A}_1 \Psi + \hat{A}_2 \Psi, \quad (1.5.1)$$

$$\hat{A} (c_1 \Psi_1 + c_2 \Psi_2) = \hat{A} (c_1 \Psi_1) + \hat{A} (c_2 \Psi_2) = c_1 \hat{A} \Psi_1 + c_2 \hat{A} \Psi_2, \quad (1.5.2)$$

where  $\Psi_n$  are arbitrary wavefunctions, while  $c_n$  are arbitrary constants (in quantum mechanics, frequently called  $c$ -numbers, to distinguish them from operators and wavefunctions). The most important examples of linear operators are given by:

- (i) the multiplication by a function, such as for the operator  $\hat{\mathbf{r}}$  given by Eq. (26), and
- (ii) the spatial or temporal differentiation, such as in Eqs. (25)-(27).

Next, it is of key importance that the Schrödinger equation (25) is also linear. (This fact was already used in the discussion of wave packets in the last section.) This means that if each of several functions  $\Psi_n$  are (particular) solutions of Eq. (25) with a certain Hamiltonian, then their arbitrary linear combination,

$$\Psi = \sum_n c_n \Psi_n \quad (1.5.3)$$

is also a solution of the same equation. <sup>41</sup>

Let us use the linearity to accomplish an apparently impossible feat: immediately find the general solution of the Schrödinger equation for the most important case when the system's Hamiltonian does not depend on time explicitly - for example, like in Eq. (41) with time-independent potential energy  $U = U(\mathbf{r})$ , when the Schrödinger equation has the form

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + U(\mathbf{r}) \Psi. \quad (1.5.4)$$

First of all, let us prove that the following product,

$$\Psi_n = a_n(t) \psi_n(\mathbf{r}), \quad (1.5.5)$$

qualifies as a (particular) solution of such an equation. Indeed, plugging Eq. (57) into Eq. (25) with any time-independent Hamiltonian, using the fact that in this case

$$\hat{H} a_n(t) \psi_n(\mathbf{r}) = a_n(t) \hat{H} \psi_n(\mathbf{r}), \quad (1.5.6)$$

and dividing both parts of the equation by  $a_n \psi_n$ , we get

$$\frac{i\hbar}{a_n} \frac{da_n}{dt} = \frac{\hat{H} \psi_n}{\psi_n}. \quad (1.5.7)$$

The left-hand side of this equation may depend only on time, while the right-hand side, only on coordinates. These facts may be only reconciled if we assume that each of these parts is equal to (the same) constant of the dimension of energy, which I will denote as  $E_n$ . <sup>42</sup> As a result, we are getting two separate equations for the temporal and spatial parts of the wavefunction:

$$\begin{aligned} \hat{H} \psi_n &= E_n \psi_n, \\ i\hbar \frac{da_n}{dt} &= E_n a_n. \end{aligned} \quad (1.5.8)$$

The latter of these equations, rewritten in the form

$$\frac{da_n}{a_n} = -i \frac{E_n}{\hbar} dt, \quad (1.5.9)$$

is readily integrable, giving

Stationary

state:

time

evolution

$$\ln a_n = -i\omega_n t + \text{const}, \quad \text{so that } a_n = \text{const} \times \exp\{-i\omega_n t\}, \quad \text{with } \omega_n \equiv \frac{E_n}{\hbar}.$$

Now plugging Eqs. (57) and (62) into Eq. (22), we see that in the quantum state described by Eqs. (57)(62), the probability  $w$  of finding the particle at a certain location does not depend on time:

$$w \equiv \psi_n^*(\mathbf{r})\psi_n(\mathbf{r}) = w(\mathbf{r}). \quad (1.5.10)$$

With the same substitution, Eq. (23) shows that the expectation value of any operator that does not depend on time explicitly is also time-independent:

$$\langle A \rangle \equiv \int \psi_n^*(\mathbf{r}) \hat{A} \psi_n(\mathbf{r}) d^3r = \text{const}. \quad (1.5.11)$$

Due to this property, the states described by Eqs. (57)-(62) are called stationary; they are fully defined by the possible solutions of the stationary (or "time-independent") Schrödinger equation (60).<sup>43</sup> Note that for the time-independent Hamiltonian (41), the stationary Schrödinger equation (60),

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_n + U(\mathbf{r}) \psi_n = E_n \psi_n, \quad (1.5.12)$$

is a linear, homogeneous differential equation for the function  $\psi_n$ , with a priori unknown parameter  $E_n$ . Such equations fall into the mathematical category of eigenproblems,<sup>44</sup> whose eigenfunctions  $\psi_n$  and eigenvalues  $E_n$  should be found simultaneously, i.e. self-consistently.<sup>45</sup> Mathematics<sup>46</sup> tells us that for such equations with space-confined eigenfunctions  $\psi_n$ , tending to zero at  $r \rightarrow \infty$ , the spectrum of eigenvalues is discrete. It also proves that the eigenfunctions corresponding to different eigenvalues are orthogonal, i.e. that space integrals of the products  $\psi_n \psi_{n'}^*$  vanish for all pairs with  $n \neq n'$ . Due to the Schrödinger equation's linearity, each of these functions may be multiplied by a proper constant coefficient to make their set orthonormal:

$$\int \psi_n^* \psi_{n'} d^3r = \delta_{n,n'} \equiv \begin{cases} 1, & \text{for } n = n', \\ 0, & \text{for } n \neq n'. \end{cases} \quad (1.5.13)$$

Moreover, the eigenfunctions  $\psi_n(\mathbf{r})$  form a full set, meaning that an arbitrary function  $\psi(\mathbf{r})$ , in particular the actual wavefunction  $\Psi$  of the system in the initial moment of its evolution (which I will always, with a few clearly marked exceptions, take for  $t = 0$ ) may be represented as a unique expansion over the eigenfunction set:

$$\Psi(\mathbf{r}, 0) = \sum_n c_n \psi_n(\mathbf{r}) \quad (1.5.14)$$

The expansion coefficients  $c_n$  may be readily found by multiplying both sides of Eq. (67) by  $\psi_n^*$ , integrating the results over the space, and using Eq. (66). The result is

$$c_n = \int \psi_n^*(\mathbf{r}) \Psi(\mathbf{r}, 0) d^3r. \quad (1.5.15)$$

Now let us consider the following wavefunction

$$\Psi(\mathbf{r}, t) = \sum_n c_n a_k(t) \psi_k(\mathbf{r}) = \sum_n c_n \exp\left\{-i \frac{E_n}{\hbar} t\right\} \psi_n(\mathbf{r}). \quad (1.5.16)$$

Since each term of the sum has the form (57) and satisfies the Schrödinger equation, so does the sum as the whole. Moreover, if the coefficients  $c_n$  are derived in accordance with Eq. (68), then the solution (69) satisfies the initial conditions as well. At this moment we can use one more bit of help from mathematicians, who tell us that the linear, partial differential equation of type (65), with fixed initial conditions, may have only one (unique) solution. This means that in our case of time-independent potential Hamiltonian, Eq. (69) gives the general solution of the Schrödinger equation (25).

So, we have succeeded in our apparently over-ambitious goal. Now let us pause this mad mathematical dash for a minute, and discuss this key result.

<sup>40</sup> By the way, if any equality involving operators is valid for an arbitrary wavefunction, the latter is frequently dropped from notation, resulting in an operator equality. In particular, Eq. (53) may be readily used to prove that the linear operators are commutative:  $\hat{A}_2 + \hat{A}_1 = \hat{A}_1 + \hat{A}_2$ , and associative:  $(\hat{A}_1 + \hat{A}_2) + \hat{A}_3 = \hat{A}_1 + (\hat{A}_2 + \hat{A}_3)$ .

<sup>41</sup> At the first glance, it may seem strange that the linear Schrödinger equation correctly describes quantum properties of systems whose classical dynamics is described by nonlinear equations of motion (e.g., an anharmonic oscillator - see, e.g., CM Sec. 5.2). Note, however, that statistical equations of classical dynamics (see, e.g., SM Chapters 5 and 6) also have this property, so it is not specific to quantum mechanics.

<sup>42</sup> This argumentation, leading to variable separation, is very common in mathematical physics - see, e.g., its discussion in CM Sec. 6.5, and in EM Sec. 2.5 and beyond.

<sup>43</sup> In contrast, the full Schrödinger equation (25) is frequently called time-dependent or non-stationary.

<sup>44</sup> From the German root *eigen*, meaning "particular" or "characteristic".

<sup>45</sup> Eigenvalues of energy are frequently called eigenenergies, and it is often said that the eigenfunction  $\psi_n$  and the corresponding eigenenergy  $E_n$  together determine the  $n^{\text{th}}$  stationary eigenstate of the system.

<sup>46</sup> See, e.g., Sec. 9.3 of the wonderful handbook by G. Korn and T. Korn, listed in MA Sec. 16(ii).

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