

Band structures (overview)

Quantum mechanics: electrons as waves

Quantum mechanics begins with stating that particles such as electrons should really be treated as waves. These waves are described by the famous Schrodinger equation

$$i\hbar \partial_t \Psi = H\Psi,$$

where at this point Ψ is the “wave-function” and H is the Hamiltonian. The problem of analyzing this Schrodinger equation can be **reduced to the eigenvalue problem** in linear algebra, though in many cases the vector space might be infinite dimensional.

Schrodinger equation besides electrons

Our main focus is quantum-mechanical systems, however, as we will see, many ideas apply also in completely classical context of sound propagation and elasticity. To see this, let us convert a familiar wave-equation for a string into a Schrodinger-like form.

$$\partial_t^2 h - c^2 \partial_x^2 h = 0,$$

where $h(x,t)$ is the vertical displacement of the string. This wave-equation is second order in time. Let's try to make it first order like the Schrodinger equation by defining $h_1(x,t) = c^{-1} \partial_t h(x,t)$ and $h_2(x,t) = \partial_x h(x,t)$. After doing this we see that our wave-equation turns into a pair of equations that are linear order in time:

$$\partial_t h_2 = c \partial_x h_1$$

and

$$\partial_t h_1 = -c \partial_x h_2$$

We can turn this into the Schrodinger equation if we define:

$$\Psi(x,t) = \begin{pmatrix} h_1(x,t) \\ h_2(x,t) \end{pmatrix} \quad H = c \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} (-i\partial_x).$$

this indeed is the wave-function for helical Majorana particles.

Applying the Schrodinger equation

The wave-function Ψ in the Schrodinger equation that describes electrons is typically a complex though the Hamiltonian is not a matrix (thankfully):

$$H = -\frac{\hbar^2}{2m} \partial_x^2 + V(x),$$

where m is the mass of the electron and $V(x)$ is the background potential energy over which the electron is moving. We must remember about the wave equations for electrons, as below:

- $\Psi(x,t)$ is complex,
- H is a Hermitian matrix or operator
- density of electrons are related to $|\Psi(x,t)|^2$.
- If N is the number of electrons, one must occupy N orthogonal wave-functions.

The last point is more subtle and is called the **Pauli exclusion principle**.

Since we are interested in static properties of electrons in materials, it helps to make the simplifying ansatz: $\Psi = e^{-iEt/\hbar} \psi$. This ansatz simplifies the Schrodinger equation to a time-independent form:

$$H \psi = E \psi,$$

which is an eigenvalue problem in linear algebra.

We can often model electrons in materials within the **tight-binding** approximation where electrons are assumed to occupy a discrete set of orbitals. We then take ψ_a to be the wave-function of the electron on orbital a . The wave-functions ψ_a can be combined into ψ , which is then a vector. In this case, the Hamiltonian H becomes a matrix with components H_{ab} . These definitions transform the time-independent Schrodinger equation into a **matrix eigenvalue problem** from linear algebra.

Once we know how to set-up the matrix H_{ab} to model a particular material, we can extract the properties of the material from the wave-function components ψ_a and energy (eigenvalue) E . A few key properties of the Schrodinger equation $H \psi^{(n)} = E^{(n)} \psi^{(n)}$ are:

- if H is an $N \times N$ matrix, the eigenvalue index n goes from $n=1, \dots, N$.
- H is Hermitian i.e., $H_{ab} = H_{ba}^*$.
- **Eigenstates are orthogonal** i.e. $\psi^{(n)\dagger} \psi^{(m)} = 0$ for $m \neq n$
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Dirac **bra-ket** notation, wave-functions such as ψ are represented by **kets** i.e. $\psi \rightarrow |\psi\rangle$. We construct the ket $|\psi\rangle$ from the components of the wave-function ψ_a using the equation:

$$|\psi\rangle = \sum_a \psi_a |a\rangle.$$

Similarly, we turn the Hamiltonian H in to an **operator** using the equation :

$$H = \sum_{ab} H_{ab} |a\rangle \langle b|,$$

where H_{ab} are the elements of the matrix H from the last paragraph. We call the object $\langle b|$ a **bra** and together with the ket it forms a bra-ket with the property $\langle b|a\rangle = \delta_{ab}$. The Schrodinger equation now looks like

$$H|\psi\rangle = E|\psi\rangle,$$

which can be checked to be the same equation as the linear algebra form.

Eigenstates and Eigenvalues

Consider a general real-space operator, $A(x)$. When this operator acts on a general wavefunction $\psi(x)$ the result is usually a wavefunction with a completely different shape. However, there are certain special wavefunctions which are such that when A acts on them the result is just a multiple of the original wavefunction. These special wavefunctions are called *eigenstates*, and the multiples are called *eigenvalues*. Thus, if

$$A \psi_a(x) = a \psi_a(x), \quad (3.8.1)$$

where a is a complex number, then ψ_a is called an eigenstate of A corresponding to the eigenvalue a .

Suppose that A is an Hermitian operator corresponding to some physical dynamical variable. Consider a particle whose wavefunction is ψ_a . The expectation of value A in this state is simply [see Equation ([e3.55])]

$$\langle A \rangle = \int_{-\infty}^{\infty} \psi_a^* A \psi_a dx = a \int_{-\infty}^{\infty} \psi_a^* \psi_a dx = a, \quad (3.8.2)$$

where use has been made of Equation ([e3.107]) and the normalization condition ([e3.4]). Moreover,

$$\langle A^2 \rangle = \int_{-\infty}^{\infty} \psi_a^* A^2 \psi_a dx = a \int_{-\infty}^{\infty} \psi_a^* A \psi_a dx = a^2 \int_{-\infty}^{\infty} \psi_a^* \psi_a dx = a^2, \quad (3.8.3)$$

so the variance of A is [cf., Equation ([e3.24a])]

$$\sigma_A^2 = \langle A^2 \rangle - \langle A \rangle^2 = a^2 - a^2 = 0. \quad (3.8.4)$$

The fact that the variance is zero implies that every measurement of A is bound to yield the same result: namely, a . Thus, the eigenstate ψ_a is a state that is associated with a unique value of the dynamical variable corresponding to A . This unique value is simply the associated eigenvalue.

It is easily demonstrated that the eigenvalues of an Hermitian operator are all real. Recall [from Equation ([e3.84])] that an Hermitian operator satisfies

$$\int_{-\infty}^{\infty} \psi_1^* (A \psi_2) dx = \int_{-\infty}^{\infty} (A \psi_1)^* \psi_2 dx. \quad (3.8.5)$$

Hence, if $\psi_1 = \psi_2 = \psi_a$ then

$$\int_{-\infty}^{\infty} \psi_a^* (A \psi_a) dx = \int_{-\infty}^{\infty} (A \psi_a)^* \psi_a dx, \quad (3.8.6)$$

which reduces to [see Equation ([e3.107])]

$$a = a^*, \quad (3.8.7)$$

assuming that ψ_a is properly normalized.

Two wavefunctions, $\psi_1(x)$ and $\psi_2(x)$, are said to be *orthogonal* if

$$\int_{-\infty}^{\infty} \psi_1^* \psi_2 dx = 0. \quad (3.8.8)$$

Consider two eigenstates of A , ψ_a and $\psi_{a'}$, which correspond to the two different eigenvalues a and a' , respectively. Thus,

$$\begin{aligned} A \psi_a &= a \psi_a, \\ A \psi_{a'} &= a' \psi_{a'}. \end{aligned}$$

Multiplying the complex conjugate of the first equation by $\psi_{a'}$, and the second equation by ψ_a^* , and then integrating over all x , we obtain

$$\begin{aligned}\int_{-\infty}^{\infty} (A \psi_a)^* \psi_{a'} dx &= a \int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx, \\ \int_{-\infty}^{\infty} \psi_a^* (A \psi_{a'}) dx &= a' \int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx.\end{aligned}$$

However, from Equation ([e3.111]), the left-hand sides of the previous two equations are equal. Hence, we can write

$$(a - a') \int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx = 0. \quad (3.8.9)$$

By assumption, $a \neq a'$, yielding

$$\int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx = 0. \quad (3.8.10)$$

In other words, eigenstates of an Hermitian operator corresponding to different eigenvalues are automatically orthogonal.

Consider two eigenstates of A , ψ_a and ψ'_a , that correspond to the same eigenvalue, a . Such eigenstates are termed *degenerate*. The previous proof of the orthogonality of different eigenstates fails for degenerate eigenstates. Note, however, that any linear combination of ψ_a and ψ'_a is also an eigenstate of A corresponding to the eigenvalue a . Thus, even if ψ_a and ψ'_a are not orthogonal, we can always choose two linear combinations of these eigenstates that are orthogonal. For instance, if ψ_a and ψ'_a are properly normalized, and

$$\int_{-\infty}^{\infty} \psi_a^* \psi'_a dx = c, \quad (3.8.11)$$

then it is easily demonstrated that

$$\psi''_a = \frac{|c|}{\sqrt{1 - |c|^2}} (\psi_a - c^{-1} \psi'_a) \quad (3.8.12)$$

is a properly normalized eigenstate of A , corresponding to the eigenvalue a , that is orthogonal to ψ_a . It is straightforward to generalize the previous argument to three or more degenerate eigenstates. Hence, we conclude that the eigenstates of an Hermitian operator are, or can be chosen to be, mutually orthogonal.

It is also possible to demonstrate that the eigenstates of an Hermitian operator form a complete set : that is, any general wavefunction can be written as a linear combination of these eigenstates. However, the proof is quite difficult, and we shall not attempt it here.

In summary, given an Hermitian operator A , any general wavefunction, $\psi(x)$, can be written

$$\psi = \sum_i c_i \psi_i, \quad (3.8.13)$$

where the c_i are complex weights, and the ψ_i are the properly normalized (and mutually orthogonal) eigenstates of A : that is,

$$A \psi_i = a_i \psi_i, \quad (3.8.14)$$

where a_i is the eigenvalue corresponding to the eigenstate ψ_i , and

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j dx = \delta_{ij}. \quad (3.8.15)$$

Here, δ_{ij} is called the *Kronecker delta-function*, and takes the value unity when its two indices are equal, and zero otherwise.

It follows from Equations ([e3.123]) and ([e3.125]) that

$$c_i = \int_{-\infty}^{\infty} \psi_i^* \psi dx. \quad (3.8.16)$$

Thus, the expansion coefficients in Equation ([e3.123]) are easily determined, given the wavefunction ψ and the eigenstates ψ_i . Moreover, if ψ is a properly normalized wavefunction then Equations ([e3.123]) and ([e3.125]) yield

$$\sum_i |c_i|^2 = 1. \quad (3.8.17)$$