

## 4 Degeneracy, Symmetry and Conservation Laws

### 4.1 Distinguishing between eigenstates, Quantum numbers as labels

How can we distinguish between quantum states  $|\alpha_n\rangle$  which have degenerate values of A? The obvious way is to measure the quantised observables and use them to label the state. We must be sure not to make measurements which change the state. Thus all measurements should correspond to commuting operators (Compatible observations: see QP3). In the non-degenerate case measuring energy is sufficient, but in hydrogen, for example, we used quantum numbers  $n$  (for energy, operator  $\hat{H}$ ),  $l$  (for total angular momentum,  $\hat{\mathbf{L}}^2$ ) and  $m_l$  (one component of angular momentum,  $\hat{L}_z$ ).

Continuing the example of twofold degeneracy (3.6), suppose that some operator  $\hat{B}$  is compatible with  $\hat{A}$ . This means that  $[A, B] = 0$  and  $\hat{A}$  and  $\hat{B}$  have a common eigenbasis. i.e. some  $\theta$  and  $\theta + \pi/2$  give eigenstates of both  $\hat{A}$  and  $\hat{B}$  in the form  $|\alpha(\theta)\rangle = (\cos\theta|\alpha_1\rangle + \sin\theta|\alpha_2\rangle)$ .

To find the appropriate value of  $\theta$ , we have a similar problem to that encountered in 3.1 and must solve for the eigenvectors of:

$$\begin{pmatrix} \langle\alpha_1|\hat{B}|\alpha_1\rangle & \langle\alpha_1|\hat{B}|\alpha_2\rangle \\ \langle\alpha_2|\hat{B}|\alpha_1\rangle & \langle\alpha_2|\hat{B}|\alpha_2\rangle \end{pmatrix}$$

The eigenvalues of this equation are the quantised measurable values of  $\hat{B}$ . If both of these are equal, there must be another measurable C which will distinguish the two states.

The generalisation to many degenerate levels is straightforward. If there are  $n$  orthogonal degenerate eigenstates of  $\hat{A}$ , (therefore an  $n$ -dimensional space in which every unit vector is an eigenstate of  $\hat{A}$ ), compatibility of eigenbases means there are at least  $n$  eigenstates of  $\hat{B}$ . It is now possible that all these have different B eigenvalues, or that at least two have the same eigenvalue, in which case if we want a specific set of orthogonal eigenstates, we must look for another compatible operator  $\hat{C}$ .

When the set of operators is sufficiently large that there is a unique set of eigenvalues for each eigenstate, we call it a complete commuting set of operators. An example is  $\hat{H}$ ,  $\hat{\mathbf{L}}^2$ ,  $\hat{S}_z$  and  $\hat{L}_z$  in hydrogen. The complete commuting set is not unique for a given Hamiltonian, for hydrogen we could have used  $\hat{H}$ ,  $\hat{\mathbf{L}}^2$ ,  $\hat{S}_x$  and  $\hat{L}_x$  or  $\hat{H}$ ,  $\hat{\mathbf{L}}^2$ ,  $\hat{J}$  and  $\hat{L}_z$ . If one of the quantum numbers can be written in terms of the others then it is redundant. If two of the quantum numbers come from non-commuting operators, then the set does not define a state since the full set of measurements could not be performed without changing the wavefunction.

### 4.2 Example

Consider the 2D harmonic oscillator  $V_0 = \frac{1}{2}m\omega^2(x^2 + y^2)$ . If we measure the energy and find it to be  $2\hbar\omega$ , then the state could be  $|n_x = 1, n_y = 0\rangle$  or  $|n_x = 0, n_y = 1\rangle$  or any linear combination. To fully define any state we require any two quantum numbers:  $n_x, n_y$  and  $E = (n_x + n_y + 1)\hbar\omega$ .

Suppose we measure the energy and find  $3\hbar\omega$ : there is a *partial* collapse of the wavefunction and there are three degenerate possibilities. Suppose we then apply a perturbation  $\Delta V = \lambda x^2$  (see 2.6). This breaks the symmetry and collapses the wavefunction onto either  $|1, 1\rangle$ ,  $|2, 0\rangle$  or  $|0, 2\rangle$ . The perturbation matrix (see 3.1)  $\langle n_x, n_y | \Delta V | n_x, n_y \rangle$  is diagonal provided we choose the basis with  $x$  along the direction of the perturbation, and it has eigenvalues  $(n_x + \frac{1}{2})\lambda\hbar/m\omega$ . If we then measure the energy and find  $E = 3\hbar\omega + \lambda\hbar/2m\omega$  then we know that the state is  $|0, 2\rangle$ : a *complete* collapse onto a single wavefunction.

**Aside:** Consider mixing with the non-degenerate states. By symmetry  $\langle 1, 0 | \lambda x^2 | 2, 0 \rangle = 0$ : the perturbation does not mix  $n_x = 0$  and  $n_x = 1$  states, nor does it affect  $n_y$  (see 2.3). Thus applying the perturbation may induce a transition from  $|0, 2\rangle$  to  $|2, 2\rangle$ ,  $|4, 2\rangle$  etc. but not to  $n_x = \text{odd}$  or  $n_y \neq 2$ . This gives rise to selection rules

### 4.3 Translational Symmetry and Conservation of Momentum

Consider a transformation operator in 1 dimension  $\hat{D}$  which acts on the coordinates of a system as a displacement  $\hat{D}[f(x)] = f(x+l)$ . The eigenfunctions of  $\hat{D}$  satisfy  $\hat{D}|\phi(x)\rangle = d|\phi(x)\rangle = |\phi(x+l)\rangle$ . The general solutions to this equation are  $\phi(x) = e^{ikx}u(x)$  where  $u(x)$  satisfies  $u(x) = u(x+l)$  and  $k$  is complex.

This kind of translational symmetry exists when we have a crystal structure. Now consider a 1D closed loop of  $N$  atoms: Uniqueness of the wavefunction requires that  $\phi(x) = \phi(x + Nl) \Rightarrow e^{ikx} = e^{ik(x+Nl)}$ . Thus possible wavefunctions must have real  $k$  and the form

$$\phi(x) = e^{2\pi nix/Nl}u(x); \quad k = 2\pi n/Nl$$

The momentum of this state is given by:

$$-i\hbar \int \phi^*(x) \frac{d\phi(x)}{dx} dx = \int \phi^*(x) \left[ \frac{2\pi\hbar n}{Nl} + \frac{u'(x)}{u(x)} \right] \phi(x) dx$$

The RHS first term gives is the familiar  $\hbar k$ , which we associate with the momentum. If  $u(x)$  has some definite parity, then  $u'(x)$  will have opposite parity and the second term will be the integral of an odd function (i.e. zero by symmetry). Thus  $k$  is a quantum number associated with translational symmetry, which in turn has an operator  $\hat{D}$  which commutes with the Hamiltonian and is thus a constant of the motion. Translational symmetry is associated with conservation of momentum.

For which the TISE, with the atom described by a potential  $V(x)$ , and a particular value of  $k$ , can be written

$$\hat{H}_k u_k(x) = \frac{\hbar^2}{2m} \left[ \left( k - i \frac{d}{dx} \right)^2 + V(x) \right] u_k(x) = E_k u_k(x)$$

since the phase has been eliminated, we simply have a particle in a fixed volume  $u_k(x) = u_k(x+l)$ , which means a series of discrete energy levels (bands). Thus all states can be labelled by  $k$  and a band index  $n$ .

We can write the semiclassical group velocity of the wavefunction as

$$v_g = \frac{d\omega}{dk} = \frac{1}{\hbar} \frac{dE}{dk}$$

using  $E = \hbar\omega$ . A formal proof using the velocity operator gives the same result for the velocity. Assuming that  $E$  does vary with  $k$ , this means we have a time-independent state which nevertheless has a permanent, non-zero velocity through the lattice.

### 4.4 Application - electron in a crystalline solid

The above is the 1D statement of Bloch's Theorem, the basis of study of electrons in solids. If we imagine applying an electric field ( $\mathcal{E}$ ) in the  $x$ -direction, then the rate at which work is done is:

$$-e\mathcal{E}v_g = \frac{dE}{dt} = \frac{dE}{dk} \frac{dk}{dt}$$

Using the expression for  $v_g$  we find that the rate of change of  $\hbar k$  is proportional to the external force, rather like Newton's second law.

$$-e\mathcal{E} = F = \hbar \frac{dk}{dt}$$

If we now consider acceleration:

$$a = \frac{dv_g}{dt} = \frac{dv_g}{dk} \frac{dk}{dt} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} F$$

we find a quantity  $\hbar^2 / \frac{d^2 E}{dk^2}$  which is known as the *effective mass*, relating external force to acceleration in a solid, and allowing us to avoid further consideration of the effect of the lattice.

#### 4.5 The Kronig-Penney Model

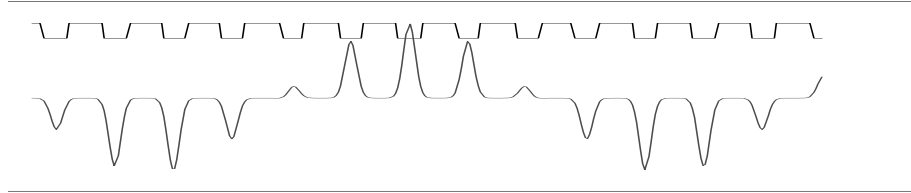


Figure 2: The Kronig-Penney potential and a Bloch function

In 4.1  $u(x)$  is still completely general. The *Kronig-Penney model* considers a periodically repeating square potential defined in one cell by  $V(x) = 0$  ( $0 < x < b$ );  $V(x) = V_0$  ( $b < x < l$ ), then we can solve for  $u(x)$  in one cell. Like the finite square well, this is a tedious boundary condition problem where matching value and slope of the wavefunction at the potential edge gives a 4x4 matrix to diagonalise. The details are given in wikipedia(!) and lead to an equation the LHS of which is drawn below:

$$\cos k_1 b \cos k_2(l - b) - \frac{k_1^2 + k_2^2}{2k_1 k_2} \sin k_1 b \sin k_2(l - b) = \cos kl$$

where  $k_1 = \sqrt{2mE}/\hbar$  and  $k_2 = \sqrt{2m(E - V_0)}/\hbar$ , the appropriate free particle wavevectors, thus for  $E < V_0$ ,  $k_2$  is imaginary. As the figure shows, multiple solutions are possible for all  $k$ , giving certain “bands” of energy, but not others.

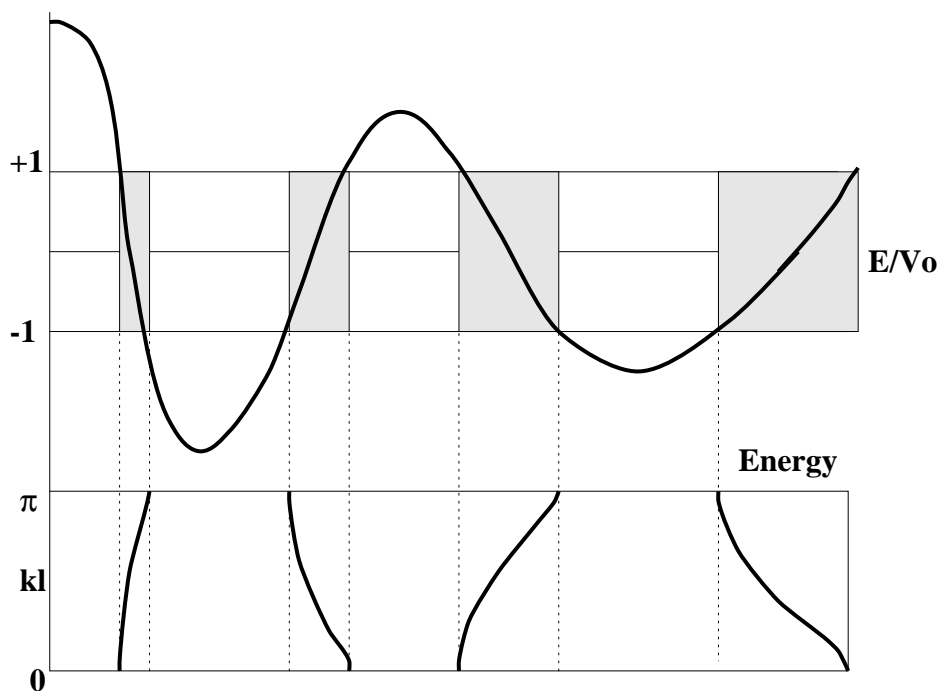


Figure 3: Graph of function arising from multiple square-well problem: Allowed energy solutions exist only where  $|\cos kl| \leq 1$ .

The key point about this equation is that it cannot be solved for certain values of  $E$ , around  $k_1 b = m\pi$ . A plot of the left hand side of the equation against  $E/V_0$  illustrates this, solutions for some value of  $k$  can be found only in the shaded regions of  $E$ . Moreover each shaded region contains  $N$  allowed  $k = 2\pi n/Nl$  values. Thus if each atom contributes two electrons the lower ‘valence’ band will be filled (one of each spin in each state) and the upper ‘conduction’ band will be empty. To get an electron to move (change to a different  $k$ -state) requires a lot of energy, so this represents an insulator.

In the limit of  $V_0 = 0$ , we get  $k = k_1 = k_2 = \sqrt{2mE}/\hbar$ , the free electron result, while for very large  $V_0 \gg E$  solutions are possible only for values of  $E$  which satisfy  $\sin(k_1 b) \approx 0$ , i.e. the square well.

The wavefunction is a complex exponential of  $k_1 x$  or  $k_2 x$ , depending on whether it is in a well or not. It is *not* an eigenfunction of the momentum operator. Thus although  $\hbar k$  looks like a momentum, it isn’t the eigenvalue of the momentum operator. It is called “crystal momentum” and along with the “effective mass” gives a pair of quantities with which we can apply Newtonian dynamics thinking to a crystal, ignoring the effects of the lattice.

In three dimensions, the topology of the bands becomes much more complicated: this is a topic for solid state physics.

#### 4.6 Radioactive decay and imaginary potentials

If the number of particles in a given state is reduced in time, then the total intensity of that state is reduced. Consider a particle moving in a region of imaginary potential  $V(r) = -iV_0$ . The TDSE is:

$$i\hbar \frac{\partial}{\partial t} |\Phi, t\rangle = [H_0 - iV_0] |\Phi, t\rangle$$

Assume that the time independent part of the state is an combination of eigenstates of the real part of the Hamiltonian:

$$|\Phi, t\rangle = \sum_n c_n(t) \exp(-iE_n t/\hbar) |\phi_n\rangle; \quad \text{where} \quad H_0 |\phi_n\rangle = E_n |\phi_n\rangle$$

Following the same analysis as for TDSE, premultiplying by  $\langle m|$ , and for constant  $V_0$ ,  $V_{mn} = \delta_{mn} V_0$  we obtain:

$$i\hbar \dot{c}_m = -iV_0 c_m \quad \Rightarrow \quad |c_m(t)|^2 = |c_m(0)|^2 e^{-2V_0 t/\hbar}$$

Thus the probability amplitude of the state decreases in time. An imaginary potential can be used to represent destruction of particles, either by absorption (in a scattering process, perhaps) or by radioactive decay. Obviously the ket is not a full description of the system, since that should include information about the decay products. The lifetime of the state is  $\tau = \hbar/2V_0$ .

Notice that  $-iV_0$  is not a Hermitian operator, and so it is not possible to perform a single measurement of half life.