QUANTUM MECHANICS B PHY-413 Note Set No. 3

SYMMETRY IN QUANTUM MECHANICS - PARITY.

All the examples of quantum wells you have met so far have energy eigenfunctions (stationary states with definite energy) which have a definite **symmetry** under the transformation $x \to -x$: they are either symmetric or antisymmetric:

$$\begin{array}{llrcl} \text{SYMMETRIC} & \text{(or Parity } +1\text{):} & \psi_E(-x) & = & +\psi_E(x) \quad (1) \\ \text{ANTISYMMETRIC} & \text{(or Parity } -1\text{):} & \psi_E(-x) & = & -\psi_E(x) \quad (2) \end{array}$$

Thus for the infinite square well the symmetric states are $\psi_E(x) = \cos n\pi x/L, n = 1,3,5\ldots$ for $-L/2 \leq x \leq L/2$ and $\psi_E(x) = 0$ for $-L/2 < x < L/2$; the antisymmetric ones $\psi_E(x) = \sin n\pi x/L, n = 2,4,6\ldots$ for $-L/2 \leq x \leq L/2$ and $\psi_E(x) = 0$ for $-L/2 < x < L/2$. Similarly for the finite square well and, as we shall see later, for the harmonic oscillator potential $V(x) = kx^2/2$. Inspection of these potentials (Figures 1 and 2) reveals that they are all *symmetric about the chosen origin of coordinates*,

$$\boxed{V(-x) = V(x)} \tag{3}$$

We now proceed to show that this is the key ingredient:
For all potentials which are symmetrical under reflections about some point the energy eigenfuntions have definite parity: they are either symmetric or antisymmetric under reflection of the axes about the symmetry point of the potential.[1]

This is the simplest example of one of the most important concepts in physics: symmetry under some transformation - here a mirror reflection about a suitably chosen origin - leads to a conservation law - here the conservation of the symmetry (or parity) of energy eigenstates. The following proofs establish these important results for this special case:
(1) First we show that for $V(-x) = V(x)$, energy eigenstates have definite symmetry under $x \to -x$.
The key step is to note that the symmetry of the potential implies the corresponding symmetry for the Hamiltonian because the kinetic energy term $-\hbar^2/2m\, \partial^2/\partial x^2$ is symmetric under $x \to -x$:

$$V(-x) = V(x) \quad \text{implies} \quad \widehat{H}(-x) = \widehat{H}(x) \tag{4}$$

Now consider an eigenstate of the Hamiltonian, a solution of the TISE

$$\boxed{\widehat{H}(x)\psi_E(x) = E\psi_E(x)} \tag{5}$$

where E is a number, the energy eigenvalue. Now replace x by $-x$ in this eigenvalue equation:

$$\widehat{H}(-x)\psi_E(-x) = E\psi_E(-x) \tag{6}$$

and then use the symmetry of the Hamiltonian to replace $\widehat{H}(-x)$ by $\widehat{H}(x)$,

$$\boxed{\widehat{H}(x)\psi_E(-x) = E\psi_E(-x)} \tag{7}$$

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[1] The symmetry of the wave functions is only obvious when we choose the origin to be the point about which the potential is symmetrical. If we were to choose the origin of the infinite square well problem to be at the left wall of the potential the eigenfuntions would be $\psi_E(x) = \sin n\pi x/L, n = 1,2,3,4,5,6\ldots$ for $0 \leq x \leq L$ and $\psi_E(x) = 0$ for $x < 0$ and $x > L$. This is clearly neither symmetric nor antisymmetric about $x = 0$ (draw the first two and see!), but is about $x = L/2$, the mid-point or symmetry point of the potential.

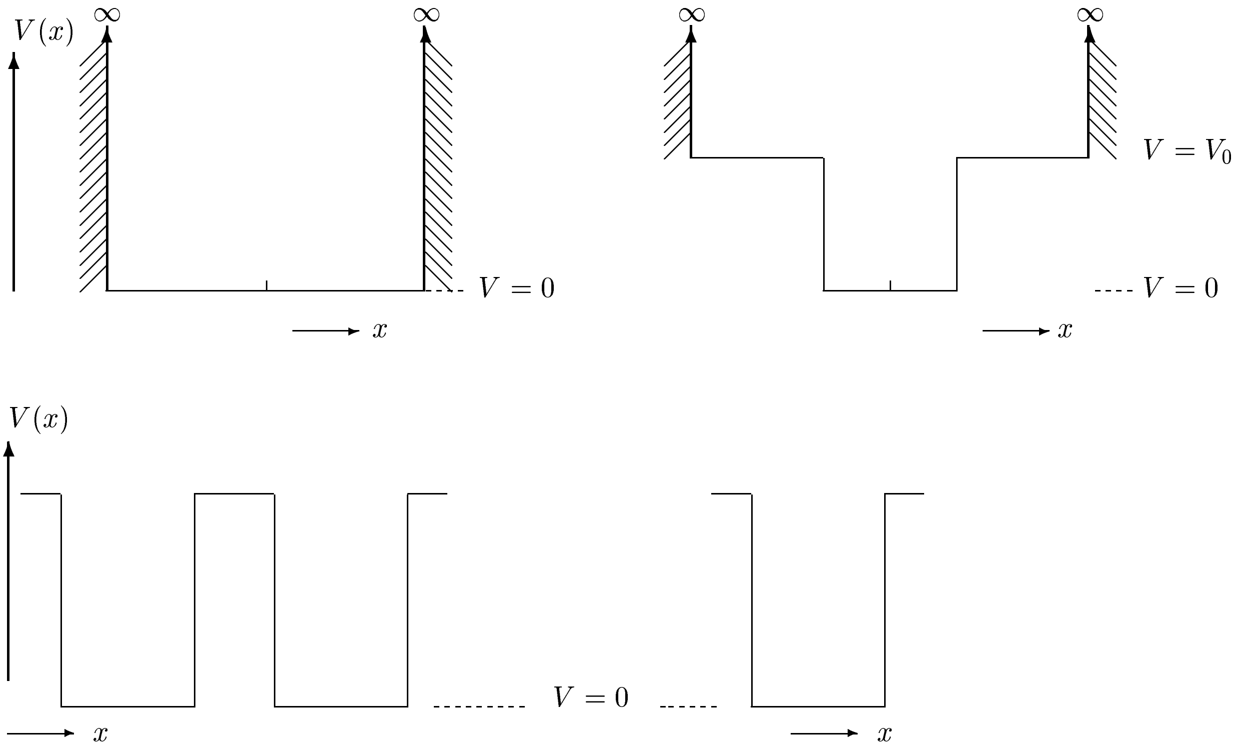

Figure 1: Some examples of symmetric potentials.

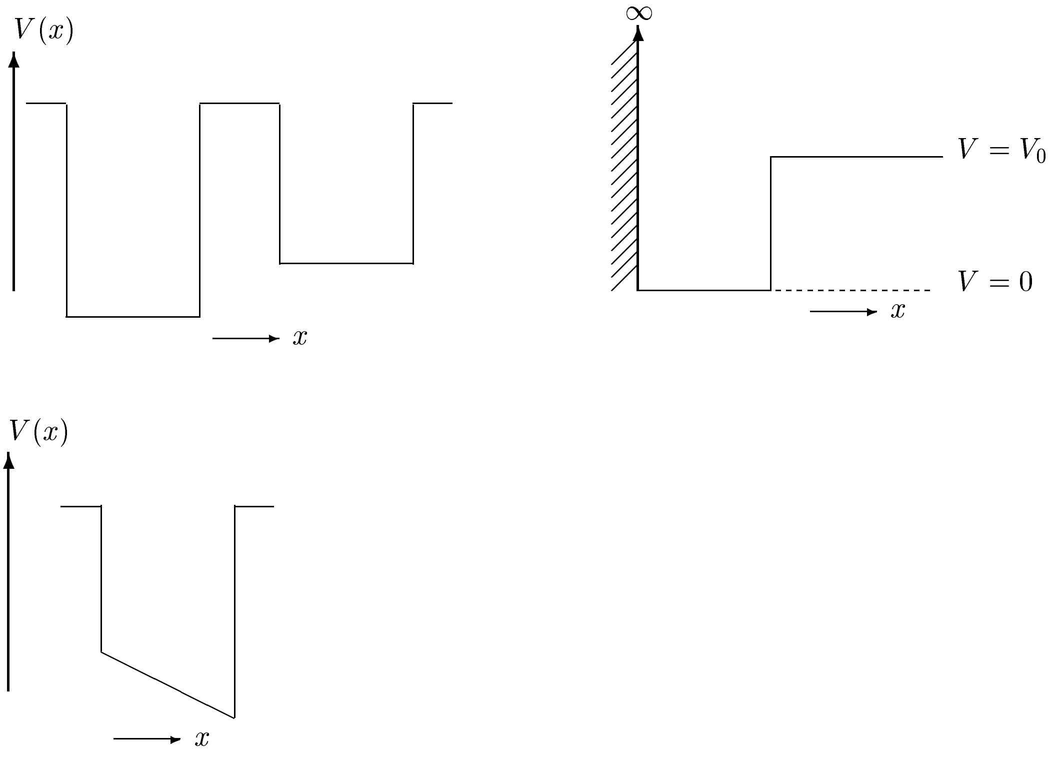

Figure 2: Some examples of non-symmetric potentials.

showing that $\psi_E(-x)$ is also an eigenstate of the Hamiltonian $\widehat{H}(x)$ *with the same eigenvalue* as $\psi_E(x)$. We have therefore found *two* solutions of the TISE with the *same* energy eigenvalue E. But the solutions of the TISE are unique, at least for the cases we have studied so far, where for each eigenstate there is a unique energy, eg. $E_n = n^2\pi^2\hbar^2/2mL^2$ for the infinite square well. [2] Thus the two eigenfunctions are not independent and can therefore only differ by a numerical factor, say λ,

$$\psi_E(-x) = \lambda\psi_E(x) \tag{8}$$

Now replace x by $-x$ in this equation, and then use this equation again to get rid of $\psi_E(-x)$ in favour of $\psi_E(x)$:

$$\begin{aligned} \psi_E(x) &= \lambda\,\psi_E(-x) \\ &= \lambda^2\psi_E(x) \end{aligned} \tag{9}$$

Comparison of the first and last items immediately yields,

$$\lambda^2 = 1 \quad \text{which immediately implies} \quad \lambda = \pm 1 \tag{10}$$

thereby establishing the result promised:

$$\boxed{\psi_E(-x) = \pm\,\psi_E(x)} \tag{11}$$

viz. that the energy eigenstates are either symmetric or antisymmetric under mirror reflection about the symmetry point of the potential.

(2) We now establish a result which we shall see repeatedly in general form when we deal with the angular momentum operators and with the hydrogen atom. First we must introduce the parity operator $\widehat{\mathcal{P}}$ which carries out the mirror reflection on the wave functions; it is *defined* by:

$$\boxed{\widehat{\mathcal{P}}\psi_E(x) \overset{df}{=} \psi_E(-x)} \tag{12}$$

First we see that our result above implies that the eigenvalues of $\widehat{\mathcal{P}}$ are ± 1: equation (11) can be rewritten using the definition of the parity operator to yield

$$\boxed{\widehat{\mathcal{P}}\psi_E(x) = \pm\,\psi_E(x)} \tag{13}$$

This is just the statement that the eigenvalue of the parity operator is $+1$ for symmetric wave functions and -1 for antisymmetric wave functions; we say that the energy eigenstates are also parity eigenstates and *have parity* ± 1. **Thus we see that the energy eigenstates in a symmetric potential are simultaneously eigenstates of both the Hamiltonian and the parity operator.**

In addition we will now show that **the symmetry of the potential implies that $\widehat{\mathcal{P}}$ commutes with the Hamiltonian.**
We saw above that $\psi_E(-x)$ is an eigenstate of the Hamiltonian,

$$\begin{aligned} \widehat{H}(x)\,\psi_E(-x) &= E\,\psi_E(-x) \\ \text{ie.}\quad \widehat{H}(x)\widehat{\mathcal{P}}\,\psi_E(x) &= E\,\psi_E(-x) \end{aligned} \tag{14}$$

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[2] When there is more than one wave function for a given energy we have **degeneracy** - the TISE does not have a unique solution. The result we prove here still holds true, but the proof is a little trickier; see the Appendix to these notes.

where we used the definition of the parity operator on the left. Now let us operate with $\widehat{\mathcal{P}}$ on both sides of the TISE for $\psi_E(x)$,

$$\begin{aligned} \widehat{\mathcal{P}}\widehat{H}(x)\,\psi_E(x) &= E\,\widehat{\mathcal{P}}\psi_E(x) \\ &= E\,\psi_E(-x) \end{aligned} \tag{15}$$

where we used the definition of the parity operator to rewrite the right hand side, which is now equal to that of the previous equation. We therefore discover that the order of $\widehat{H}$ and $\widehat{\mathcal{P}}$ does not matter:

$$\begin{aligned} \widehat{\mathcal{P}}\widehat{H}(x)\,\psi_E(x) &= \widehat{H}(x)\widehat{\mathcal{P}}\,\psi_E(x) \\ \text{ie.}\quad [\widehat{\mathcal{P}},\widehat{H}(x)]\psi_E(x) &= 0 \end{aligned} \tag{16}$$

Since the result holds for any eigenstate, [3] it must hold for the operators alone:

$$\boxed{[\widehat{\mathcal{P}},\widehat{H}(x)] = 0} \tag{17}$$

Summary: For a symmetric potential, $V(-x) = V(x)$, and therefore symmetric Hamiltonian, $\widehat{H}(-x) = \widehat{H}(x)$,
(a) eigenfunctions of $\widehat{H}$ are simultaneously eigenfunctions of $\widehat{\mathcal{P}}$ with eigenvalues ± 1;
(b) the parity operator $\widehat{\mathcal{P}}$ commutes with the Hamiltonian, $[\widehat{\mathcal{P}},\widehat{H}(x)] = 0$;

Of course these results also hold in 3-dimensions, where the reflection entails reversing all three components of the coordinate vector $\mathbf{r} = (x,y,z) \to -\mathbf{r} = (-x,-y,-z)$. Two examples of 3-dimensional symmetric potentials are the escape-proof parallelepiped and central potentials including the coulomb potential for the hydrogen atom; we treat both cases in this course so you may confirm explicitly that the energy eigenfunctions we obtain do indeed have definite parity ± 1, ie. they are simultaneously eigenfunctions of the Hamiltonian and the parity operator.

Generalisation: The above discussion presented the simplest example of the consequences of invariance or symmetry in QM. The entire discussion can be generalised to any operator which commutes with the Hamiltonian: eigenstates of energy will also be eigenstates of such an operator. Indeed, the result can be generalised even further: any two commuting operators have common eigenstates.[4] We shall meet an example of each of these cases in this course: the squared orbital angular momentum, $\widehat{\mathbf{L}}^2$ commutes with its $z-$component, $\widehat{L}_z$, so they have common eigenstates; and for a central potential $\widehat{\mathbf{L}}^2$ also commutes with the Hamiltonian: so eigenstates of $\widehat{\mathbf{L}}^2$ are *also* eigenstates of energy. Thus we will discover that in a central potential, the energy eigenstates are also eigenstates of $\widehat{\mathbf{L}}^2$ and $\widehat{L}_z$.

Observables which commute are known as **compatible observables**, and their eigenvalues provide a way of labelling quantum states. A **complete set of compatible observables** all commute with each other; their eigenvalues provide a complete set of labels for the quantum states of the system. For the hydrogen atom (ignoring hyperfine magnetic interactions) the complete set is $\{\widehat{H},\widehat{\mathbf{L}}^2,\widehat{L}_z,\widehat{S}_z\}$ with eigenvalues $\{E_n,\hbar^2\ell(\ell+1),\hbar\, m_\ell,\hbar m_s\}$; the wave functions are labelled with the quantum numbers corresponding to these eigenvalues, $\{n,\ell,m_\ell,m_s\}$. We shall establish all these results later in the course.

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[3] A mathematical point: the eigenstates make up a complete set of functions. This is the expansion theorem and means that any function may be expanded as a linear combination of energy eigenstates. So the equation holds for any function, and hence must be a property of the operators alone.

[4] In fact it is easy to prove that (a) two operators with common a eigenfunction commute; and (b) if two operators commute they have common eigenfunctions. See Bransden/Joachain p.206 for proofs.

APPENDIX: The case of Degeneracy.

We have **degeneracy** when distinct quantum states have the same energy. Examples are (a) the energy eigenstates of the 3-dimensional escape-proof box (parallelepiped) with two or more equal faces and (b) the spin up and spin down spin states of an electron in the absence of a magnetic field. In these cases the solutions to the TISE are not unique. The proof is easily modified to take account of this as follows. Recall that we have found that both $\psi_E(x)$ and $\psi_E(-x)$ are solutions of the same TISE; but if there is degeneracy these wave functions may be different. In that case all we do is construct the following two states:

$$\psi_s(x) \equiv \psi_E(x) + \psi_E(-x) \tag{18}$$

$$\psi_a(x) \equiv \psi_E(x) - \psi_E(-x) \tag{19}$$

These states
(a) are eigenstates of $\widehat{H}(x)$ with energy E because they are just linear combinations of eigenstates with the same eigenvalue - we are using the superposition principle here, a consequence of the linearity and homogeneity of the TISE;
(b) are states of definite parity, $+1$ for ψ_s; -1 for ψ_a.

This therefore proves the result: in the case of degeneracy we can always construct energy eigenstates of definite parity.[5]

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[5] Notice that the assumption required to obtain this result is that the Hamiltonian is invariant under $x \to -x$. It is this assumption which shows that $\psi_E(-x)$ is also a solution of the TISE with the same energy. This will *not* happen with a non-symmetric potential for which $\psi_E(-x)$ will *not* be a solution to the TISE. In that case ψ_s and ψ_a will *not* be solutions to the TISE.