Lecture #5: Continuum Normalization

Last time: Free Wavepacket
encoding of x_0, Δx, p_0, Δp

* use of the Gaussian functional form, $G(x; x_0, \Delta x)$, to avoid calculating integrals

* use of stationary phase to encode x_0 in $|g(k)|e^{i\alpha(k)}$

* use g(k) because it is automatic to put in $e^{-iE_k t/\hbar}$

For moving and spreading free wavepacket:
Δx is time dependent
Δp is not (because free wavepacket is not subject to any force)

Today: Normalization of eigenfunctions which belong to continuously (as opposed to discretely) variable eigenvalues.

- convenience of ortho-normal basis sets: generalization for continua
- we often talk about "density of states", but in order to do that we need to define what we mean by "state"
- computation of absolute probabilities — cannot depend on how we choose to define "state".

1. Identities for δ-functions.
2. $\Psi_{\delta k}$, $\Psi_{\delta p}$, $\Psi_{\delta E}$ for eigenfunctions that correspond to continuously variable eigenvalues.
3. finite box with countable number of discrete states taken to the limit $L \to \infty$. Normalization independent quantity:
$$P(x,\theta) = \left(\frac{\#\text{ states}}{\delta\theta}\right)\left(\frac{\#\text{ particles}}{\delta x}\right)$$
θ is the argument of the delta-function. So if we integrate over a region of θ and x, we have the absolute probability, $\iint d\theta dx\, P(x,\theta)$.
4. two examples — "predissociation" rate and smoothly varying spectral density.

In Quantum Mechanics, there are two very different classes of systems.

* SPATIALLY CONFINED:

- E is quantized
- can count states, easy to compute density of states $\frac{dn}{dE} = \rho_E$
- can normalize to $1 = \int_{-\infty}^{\infty} \psi_E^* \psi_E dx$

what is ρ_E good for?

T: classical period of oscillation

* # of encounters/sec: $\frac{1}{T}$

* fraction of time in region of length L: $\frac{L/|v|}{T}$ (v, classical velocity, is dependent on x)

* SPATIALLY UNCONFINED:

**

- E continuously variable
- can't count states, so how to compute $\frac{dn}{dE}$?
- can ask what is the absolute probability of finding the system between E, E + dE *and* x, x + dx

For confined systems, we can express ortho-normalization in terms of <u>Kronecker- δ</u>

$$\delta_{ij} = \int_{-\infty}^{\infty} \psi_i^* \psi_j \, dx$$

$$\delta_{ij} = 0 \qquad i \neq j \qquad \text{orthogonal}$$

$$\delta_{ij} = 1 \qquad i = j \qquad \text{normalized}$$

ψ has dimension of $L^{-1/2}$

δ_{ij} has dimension of pure number. (Kronecker-δ)

For unconfined systems, we are going to ortho-normalize states to <u>Dirac δ - functions</u>

In order to do this we need to know better what a δ - function is and what some of its mathematical properties are.

One of several equivalent definitions of a δ-function:

$$\delta(x - x') = \delta(x, x') = \frac{1}{2\pi} \int e^{-iu(x-x')} du.$$

What is it good for?

$$\int \delta(x,x')\psi(x)dx = \psi(x').$$

shifts a function evaluated at x to the same function evaluated at x′.

$\delta(x,x')$ has dimension of 1/x. (Dirac-δ function)

Some useful δ–function identities:

We do this so that we will be able to transform between δk, δp, and δE (where E = f(k)) delta-function normalization schemes.

1. $$\delta(ax,ax') = \frac{1}{|a|}\delta(x,x') \qquad \text{e.g., } \delta(p-p') = \delta(\hbar(k-k')) = \frac{1}{\hbar}\delta(k-k')$$

dimension of p^{-1}

dimension of 1/k

nonlecture proof of #1 above

$$\delta(ax,ax') = \frac{1}{2\pi}\int e^{-iu(ax-ax')}du \qquad \text{change variables}$$

$$v = au$$

$$dv = a\,du$$

$$\delta(ax,ax') = \frac{1}{2\pi}\frac{1}{a}\int e^{-iv(x-x')}dv = \frac{1}{a}\delta(x,x')$$

but, since $\delta(ax,ax') \equiv \delta(ax-ax') = \delta(ax'-ax) = \delta([-a](x-x'))$

(δ is an even function), $\delta(ax,ax') = \frac{1}{|a|}\delta(x,x')$

2. $$\delta(g(x)) = \underbrace{\sum_{i}}_{\substack{\text{zeros}\\ \text{of } g(x)}} \left|\frac{dg(x_i)}{dx}\right|^{-1} \delta(x,x_i)$$

provided that $\frac{dg(x_i)}{dx} \neq 0$

expand g(x) in the region near each 0 of g(x),

i.e., x near x_i $$g(x) \cong \left.\frac{dg}{dx}\right|_{x=x_i}(x-x_i).$$

If there is only 1 zero, then identity #1 above gives the required result. It is clear that δ(g(x)) will only be nonzero when g(x) = 0. Otherwise we need to carry out the sum in identity #2.

g(x) = (x – a)(x – b) has zeroes at x = a and x = b.

$$\frac{dg}{dx}=\frac{d}{dx}\left[x^{2}-x(a+b)+ab\right]=2x-(a+b)$$

$$\left.\frac{dg}{dx}\right|_{x=a}=a-b \qquad \left.\frac{dg}{dx}\right|_{x=b}=b-a$$

$$\delta(g(x))=\sum_{i}\left|\frac{dg(x_{1})}{dx}\right|^{-1}\delta\left(x,x_{i}\right) \qquad \text{(zeroes of } g(x))$$

$$=\left|\frac{1}{a-b}\right|\left[\delta(x,a)+\delta(x,b)\right]$$

Other examples:

$$\delta\left(x^{2}-a^{2}\right)=\frac{1}{2|a|}\left[\delta(x,a)+\delta(x-a)\right]$$

$$\delta\left(x^{1/2}-a^{1./2}\right)=2a^{1/2}\delta(x-a) \quad (a>0)$$

See Merzbacher, Quantum Mechanics, 3rd Edition, pages 630-632.

EXAMPLES

A. g(x) = (x–a)(x–b) This has zeroes at x = a, and x = b.

You should show that $\delta(g(x)) = \frac{1}{|a-b|}\left[\delta(x,a)+\delta(x,b)\right]$.

B. $\delta\left(E^{1/2},E'^{1/2}\right)$

$g(E) = E^{1/2} - E'^{1/2}$ has one zero at E = E′, expand g(E) about E = E′, thus for E near E′

$$g(E) \pm \frac{1}{2}E'^{-1/2}(E-E').$$

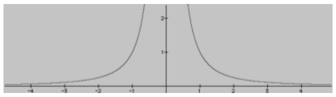
you should show that $\delta\left(E^{1/2},E'^{1/2}\right) = 2\left|E'^{1/2}\right|\delta(E,E')$

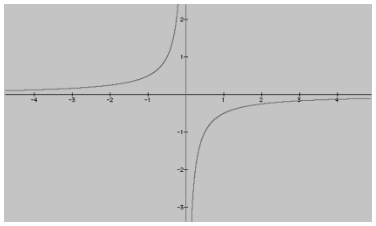
This is useful because k ∝ $E^{1/2}$ $\delta(E-E') = \left(\frac{m}{2h^2\left(E'-V_0\right)}\right)^{1/2}[\delta(k-k')+\delta(k+k')]$ for a free particle

$$or \quad \delta\left(k_E(x)-k_{E'}(x)\right) = \left(\frac{2h^2}{m}\right)^{1/2}(E'-V(x))^{1/2}\delta(E-E')$$

Another property of δ-functions: $\frac{\mathrm{d}}{\mathrm{dx}}\delta(x,x')$

$\delta(x,x')$ is an even function:





∴ expect $\frac{\mathrm{d}}{\mathrm{dx}}\delta(x,x') \equiv \delta'(x,x')$ to be an odd function:

This is useful because application of $\frac{d}{dx}\delta(x,x')$ to $f(x)$ is capable of picking out $\frac{df}{dx}$ evaluated at x′.

Non-lecture:

Use definition of derivative to prove that

$$\int_{-\infty}^{\infty}\delta'(x,x')f(x)dx = -f'(x')$$

$$\frac{d}{dx}\delta(x,x') = \lim_{\varepsilon\to 0}\frac{\left[\delta(x+\varepsilon,x')-\delta(x,x')\right]}{\varepsilon}$$

$$\int \delta(x+\varepsilon,x')f(x)dx = f(x'-\varepsilon)$$

$$\int \delta(x,x')f(x)dx = f(x')$$

$$\therefore \int \lim_{\varepsilon\to 0}\frac{\left[\delta(x+\varepsilon,x')-\delta(x,x')\right]}{\varepsilon}f(x)dx = \lim_{\varepsilon\to 0}\frac{f(x'-\varepsilon)-f(x')}{\varepsilon} = -f'(x')$$

There are several useful ways to normalize wavefunctions.

Bound states. Particle is confined in space (with tunneling tails outside the box). Space normalized. 1 particle (mostly) in box.

Box normalized $\psi_{L,E_i}(x)$ (box of length L)

$$\int_{-\infty}^{\infty} dx\, \psi^*_{L,E_i} \psi_{L,E_j} = \delta_{ij} \qquad \text{Kronecker - delta}$$

OK for bound states, but not continua.

dimension of $\psi_{L,E}$ is $L^{-1/2}$

dimension of δ_{ij} or $\delta_{E_iE_j}$ is 1.

Continua. We need some other form of normalization.

e.g. $\int_{-L/2}^{L/2} dx\left(e^{ikx}\right)^* e^{ik'x} = \int_{-L/2}^{L/2} dx e^{-i(k-k')x}$

if $k = k'$ we get L

if $k \neq k'$ we expect to get 0 (in limit $L \rightarrow \infty$)

So we can normalize to a delta function in E, p, or k.

$$\delta\,\mathbf{E}: \quad \int_{-\infty}^{\infty} dx \psi^*_{\delta E,E_i} \psi_{\delta E,E_j} \equiv \delta\left(E_i - E_j\right)$$

$\delta\,(E_i - E_j)$ has the useful δ-function property:

$$\int dE\,\delta\left(E - E_j\right)\psi_{\delta E,E} = \psi_{\delta E,E_j}$$

This implies that $\delta(E - E_j)$ has the dimension of 1/E and that $\psi_{\delta E,E}$ has dimension of $L^{-1/2}E^{-1/2}$

$$\delta\,\mathbf{p}: \quad p_E(x) = \left[2m\left(E - V(x)\right)\right]^{1/2} \qquad P_E^2/2m = E - V(x)$$

$$\int_{-\infty}^{\infty} dx\psi^*_{\delta p,p_{E_i}} \psi_{\delta p,p_{E_j}} = \delta\left(p_{E_i}(x) - p_{E_j}(x)\right)$$

$\boxed{\delta\left(p - p'\right) \text{ has dimension of } 1/p}$

$\psi_{\delta p,p_E}$ has dimension of $L^{-1/2}p^{-1/2}$

$$\delta\,\mathbf{k}: \quad k_E(x) = \left[\frac{2m}{\hbar^2}\left(E - V(x)\right)\right]^{1/2} \qquad \frac{\hbar^2 k_E^2}{2m} = E - V(x)$$

$$\int_{-\infty}^{\infty} dx\psi^*_{\delta k,k_{E_i}} \psi_{\delta k,k_{E_j}} = \delta\left(k_{E_i}(x) - k_{E_j}(x)\right)$$

$\delta\left(k - k'\right)$ has units of 1/k

$\boxed{\psi_{\delta k,k} \text{ has units of } L^{-1/2}k^{-1/2}}$

What are all of these normalization schemes good for?

When you make a measurement on a continuum (unbound) system, you ask

What is the probability of finding a particle between

x, x + dx
and **θ, θ + dθ ?** **θ can be E, p_E(x), or k_E(x)**

The probability is $P(x,\theta)dxd\theta$

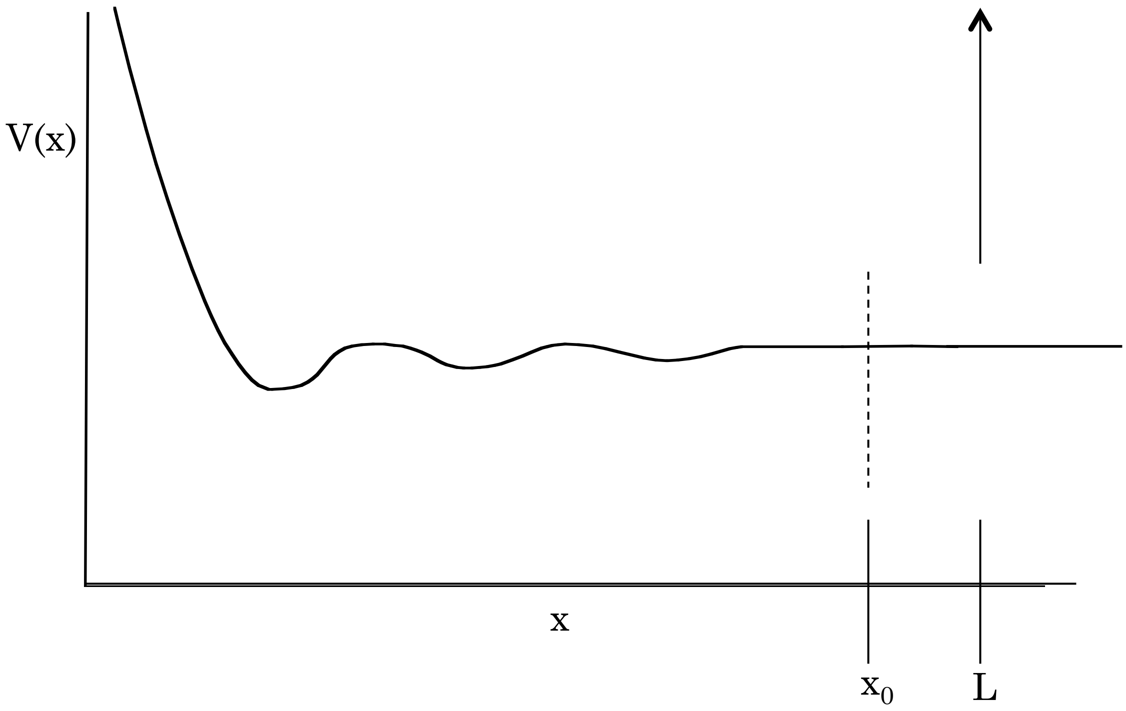
Want $P(x,\theta)$. Has dimensions $L^{-1}\,\theta^{-1}$ $\left(\text{as shown for } \psi_{\delta,\delta E}, \psi_{\delta_{p,pE}}, \text{ and } \psi_{\delta_{k,kE}}\right)$

$$P(x,\theta) = \psi^*_{\delta\theta,\theta}(x)\psi_{\delta\theta,\theta}(x) \qquad !$$

There is another less abstract way to get this kind of information. “Discretize the continuum” by adding an infinite barrier at x = L and taking the limit L→∞. This way we can use box-normalized states, and actually count the states.

The WKB quantization condition (will be derived in Lecture #7) gives

$$\frac{dn}{dE} = \frac{(2m)^{1/2}}{h}\int_{x_-(E)}^{x_+(E)} dx\left(E - V(x)\right)^{-1/2}$$



We have a complicated V(x) for $x < x_0$ and constant for $x > x_0$.

In the region where V(x) is constant at $V(x_0) = V_0$.

$$\int_{x_0}^{L} [E - V(x)]^{-1/2} dx = [E - V_0]^{-1/2} (L - x_0) \propto L$$

and box normalization causes $|\psi|^2 \propto \frac{1}{L}$

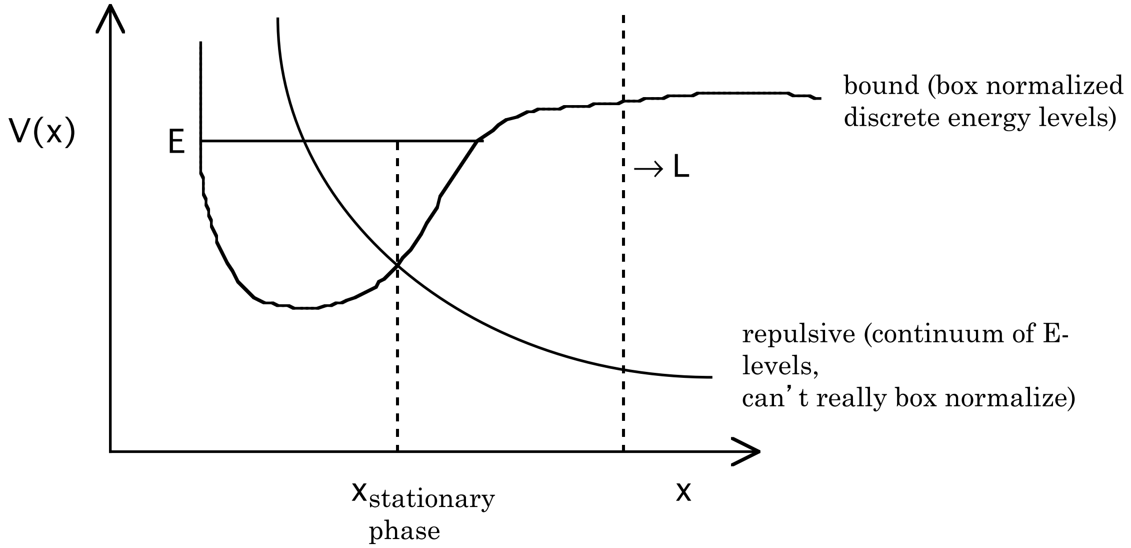
so we get $$\underbrace{P(x,E)}_{\substack{\text{dimension} \\ L^{-1}E^{-1}}} = \lim_{L\to\infty} \underbrace{\left(\frac{dn_L}{dE}\right)}_{\substack{\text{dimension} \\ E^{-1}}} \underbrace{\psi^*_{L,E}(x)\psi_{L,E}(x)}_{\substack{\text{dimension} \\ L^{-1}}}$$

---

2 Schematic Examples

- * Bound → free transition probabilities
- * Constant spectral density across a dissociation or ionization limit.

Bound-Free Transition (predissociation)



At t = 0, system is prepared in $\Psi(x,0) = \psi_{\text{bound}}(x)$

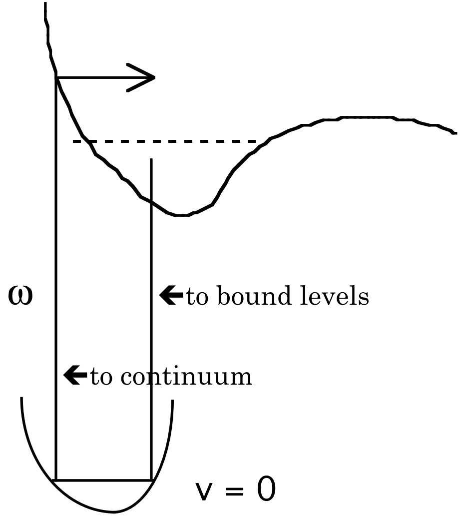
Fermi' s Golden Rule:

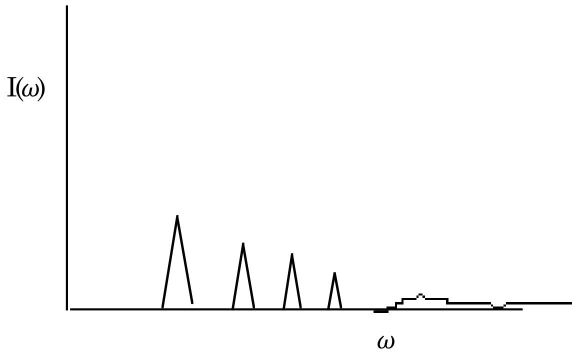
$$Rate = \Gamma_{\text{bound}\to\text{free}} = \frac{2\pi}{\hbar}\left|\int \psi^{free*}_{\delta E}(E)\hat{\mathbf{H}}\psi^{bound}_{L,E}dx\right|^2 \rho_{\delta E}(E)$$

$\rho_{\delta E} = \frac{dn_{\delta E}(E)}{dE}$ derive this key quantity by box normalizing repulsive state and taking $\lim_{L\to\infty}\left(\frac{1}{L}\frac{dn_L}{dE}\right)$

Then compute the $\hat{\mathbf{H}}$ integral using two box normalized functions.

Constant spectral density on both sides of a bound/free limit





$\frac{\text{Intensity}(\omega)}{\Delta E} \sim$ smooth function of ω, no discontinuity at onset of continuum

5.73 Quantum Mechanics I
Fall 2018