Continuum Normalization

Last time: Gaussian Wavepackets

How to encode $\langle x \rangle$ in $\int g(k)e^{ikx}dk = \psi(x)$

$or\ \langle k \rangle$ in $\int \bar{g}(x)e^{-ikx}dx = \bar{\psi}(k)$

stationary phase: good for cooking or inspecting wiggly functions and for crudely evaluating integrals of wiggly integrands.

$v_{group} \neq v_{phase}$

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

convenience of ortho-normal basis sets

we often talk about "density of states", but in order to do that we need to define "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 corresponding to continuously variable eigenvalues.
3. finite box with countable discrete states taken to the limit $L \to \infty$.
   Normalization independent quantity:
   $$\left(\frac{\#\,\text{states}}{\delta\theta}\right)\left(\frac{\#\,\text{particles}}{\delta \text{x}}\right)$$
   δθ is the argument of the delta-function. So if we integrate over a region of θ and x, we have the absolute probability.
4. two examples — "predissociation" rate and smoothly varying spectral density.

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

* SPATIALLY CONFINED:

- E 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: $\frac{L/v}{T}$

* 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 Kronecker-δ

$$\delta_{ij} = \int_{-\infty}^{\infty} \psi_i^* \psi_j dx \qquad \begin{array}{lll} \delta_{ij} = 0 & i \neq j & \text{orthogonal} \\ \delta_{ij} = 1 & i = j & \text{normalized} \end{array}$$

For unconfined systems, we are going to ortho-normalize states to Dirac δ-functions

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 definition of 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′.

Prove some useful Identities

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

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

nonlecture proof

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

(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.

EXAMPLES

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

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

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′

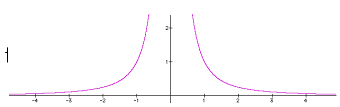
$$g(E) \approx \frac{1}{2}E'^{-1/2}(E - E').$$

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 $k \propto E^{1/2}$ $\qquad \delta(E-E') = \left(\dfrac{m}{2\hbar^2(E'-V_0)}\right)^{1/2}\delta(k-k')$

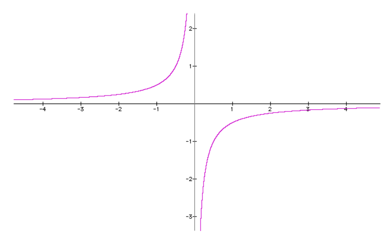
Another property of δ - functions: $\dfrac{d}{dx}\delta(x,x')$

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



$\therefore$ expect $\dfrac{d}{dx}\delta(x,x') \equiv \delta'(x,x')$

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



Non-lecture:

Use definition of derivative to prove that

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

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

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

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

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

δk * Our goal is to create ortho-normalized ψ's that look like e^{ikx}: "normalized to a δ-function in k"

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std. defn. of δ–function in k $\delta(k',k) = \int_{-\infty}^{\infty} \psi^*_{\delta k,k'} \psi_{\delta k,k} dx \equiv \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ix(k-k')}dx$

$$\therefore \quad \boxed{\psi_{\delta k,k} \equiv (2\pi)^{-1/2} e^{ikx}} \qquad \text{for } V(x) = \text{constant.}$$

$\psi_{\delta k,k}$ is said to be "normalized to $\delta(k,k')$".
What is the probability of finding the system, which is described by $\psi_{\delta k,k}$, to be located between $0 \le x \le L$?

$$\int_0^L \psi^*_{\delta k,k}\psi_{\delta k,k}dx = \frac{1}{2\pi}\int_0^L dx = \frac{L}{2\pi} = P_{\delta k}(L)$$

probability grows without limit as $L \to \infty$

But, more interestingly, what is the probability of finding a system in a δk-normalized state within a region of length equal to one de Broglie λ?

$$\lambda = h/p = \frac{2\pi}{k} \qquad P_{\delta k}(\lambda) = \frac{\lambda}{2\pi} = \frac{1}{k}$$

δk normalized states (for V(x) = constant) have: 1/k particle per λ of Δx

$\left(\text{or } \frac{1}{2\pi} \text{ particle per unit length}\right)$

What about ordinary space normalization?

$$\psi_k = N_k e^{ikx}$$

$$\psi_{k'} = N_k e^{ik'x}$$

$$\int \psi_k^* \psi_{k'} dx = |N_k|^2 \int_{-\infty}^{\infty} e^{i(k'-k)x} dx \quad \begin{cases} 0 \text{ if } k \neq k' \\ \infty \text{ if } k = k' \end{cases}$$

$\Uparrow$

THIS IS THE PROBLEM!

Can't specify N_k.

GENERALIZE

$$\delta(k,k') \equiv \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{iu(k-k')}du = \int_{-\infty}^{\infty} \psi_{\delta k,k}^* \psi_{\delta k,k'} dx$$

where $\boxed{\psi_{\delta k,k} \equiv (2\pi)^{-1/2} e^{ikx}}$, thus $\delta(k,k') = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i(k'-k)x}dx$

notation $\delta(k,k') = \delta(k-k') = \delta(k-k',0)$

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when $\delta(k,k')$ is multiplied onto $f(k)$ and integrated over all k, we get $f(k')$

$$\int_{-\infty}^{\infty} \delta(k,k') f(k) dk = f(k')$$

$\boxed{\delta(k,k') \text{ is "zero" when } k \neq k' \text{ and is "one" when } k = k'}$

$\psi_{\delta k,k_0}$ is eigenfunction of $\hat{k} = \frac{1}{i}\frac{\partial}{\partial x}$ with eigenvalue k_0: $\hat{k}\psi_{\delta k,k_0} = k_0 \psi_{\delta k,k_0}$

$\psi_{\delta x,x_0}$ is eigenfunction of $\hat{x} = x$ with eigenvalue x_0

Other normalization schemes for free particle

δp * $\psi_{\delta p,p} = N_p e^{ipx/\hbar}$ what is value of N_p?

$$\delta(p,p') = N^*_{p'} N_p \int \exp\left[ix\left(p/\hbar - p'/\hbar\right)\right]dx$$

$$= N^*_{p'} N_p\, 2\pi \underbrace{\delta(p/\hbar, p'/\hbar)}_{\left|\frac{1}{\hbar}\right|^{-1}\delta(p,p') \text{ using identity \#1}}$$

$$\boxed{\therefore \psi_{\delta p,p} = (2\pi\hbar)^{-1/2} e^{ipx/\hbar}}$$

$$\int_0^L \psi^*_{\delta p,p}\psi_{\delta p,p}dx = \frac{L}{2\pi\hbar}$$

$\nearrow$ $\frac{1}{p}$ particle per $\lambda = \frac{h}{p}$

$\searrow$ $\frac{1}{h}$ particle per unit * length

δE * $\psi^{\pm}_{\delta E} = N_E\left(e^{ikx} \pm e^{-ikx}\right)$ $\qquad k = \left|\left(\frac{2m(E-V_0)}{\hbar^2}\right)^{1/2}\right|$

↑ degenerate pair of states

you show that

$$\boxed{\begin{aligned} \psi^{+}_{\delta E,E} &= \left[\frac{m}{2E\pi^2\hbar^2}\right]^{1/4} \cos\left[\left(\frac{2mE}{\hbar^2}\right)^{1/2} x\right] \\ \psi^{-}_{\delta E,E} &= \left[\frac{m}{2E\pi^2\hbar^2}\right]^{1/4} \sin\left[\left(\frac{2mE}{\hbar^2}\right)^{1/2} x\right] \end{aligned}}$$

$\psi^{+}_{\delta E,E}$ is orthogonal to $\psi^{-}_{\delta E,E}$

$$\int_0^{\lambda} \psi^{+*}_{\delta E,E}\psi^{+}_{\delta E,E}dx = \frac{1}{2E} + \left(\text{another } \frac{1}{2E} \text{ from } \psi^{-}_{\delta E,E}\right) = \frac{1}{E}$$

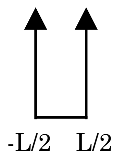
probability for δE - normalized state per λ

* Volume of N-dimensional phase space occupied by a δp normalized state is h^N

Thus there are $\frac{1}{E}$ particles per λ for a δE - normalized state.

$$\left[\text{or } \frac{2}{h}\left(\frac{m}{2E}\right)^{1/2} \text{ particles per unit length}\right]$$

So we have assembled all the basic stuff we will need, at least for V(x) = constant problems. Now use it to examine a problem we understand perfectly.



$$\psi_{E_n} = \left(\frac{2}{L}\right)^{1/2} \begin{Bmatrix}\sin\\ \cos\end{Bmatrix} \left[\left(\frac{2mE_n}{\hbar^2}\right)^{1/2} x\right]_{\text{n odd}}^{\text{n even}}$$

$$k_n = \left(\frac{2mE_n}{\hbar^2}\right)^{1/2}$$

$$E_n = \left(\frac{h^2}{8mL^2}\right)n^2$$

1 particle per box of length L

$$\left.\begin{matrix}\frac{1}{L} \text{ particle per unit length} \\ \frac{\lambda}{L} \text{ particle per } \lambda\end{matrix}\right\} \rightarrow 0 \text{ as } L \rightarrow \infty$$

4 normalization schemes (δk, δp, δE, box): each gives different #/L or #/λ.

Why - because each scheme defines "state" differently.

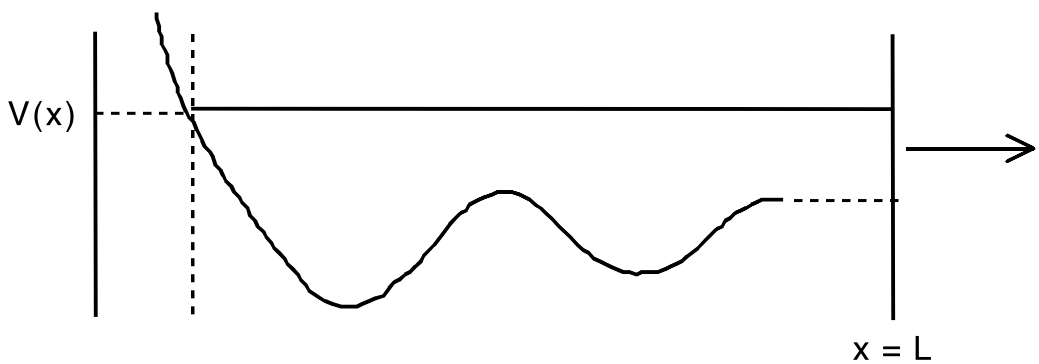
However, expect that $\left(\frac{\#\ \text{particles}}{\delta x}\right)\left(\frac{\#\ \text{states}}{\underbrace{\delta\theta}_{\text{k, p, E or box}}}\right)$ must be independent of normalization scheme

Why? Because the probability of finding a system between x, x + dx AND θ, $\theta + d\theta$ is observable. We have completely specified what counts as an observation.

Normalization-Independent Quantity for general V(x):

$$\lim_{L\to\infty} \underbrace{\left(\frac{dn}{d\theta}\right)}_{\substack{\text{density of}\\ \text{states}\\ \text{(\# states per}\\ \text{unit } \theta}} \left[\frac{1}{L}\int_{-L/2}^{L/2} \psi_{\delta\theta}^{*}\psi_{\delta\theta}dx\right] = \left(\frac{\#\ \text{states}}{\delta\theta}\right)\left(\frac{\#\ \text{particles}}{\delta x}\right)$$

The infallible way to get the invariant reference density is to box normalize (so that one can count states) and then take limit $L \to \infty$. Why? Because most realistic potentials become smooth and flat at large enough x.

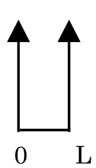


x_(E) - inner turning point

Procedure:

1. Box normalize ψ_{E_n} (E is quantized)
2. Compute $\frac{dn}{dE}$ from E(n)
3. take limit $L \to \infty$ $\left(\frac{dn}{dE} \to \infty\right)\left(\text{but } \frac{1}{L}\frac{dn}{dE} \text{ remains finite}\right)$

example:



$$\psi_E = \left(\frac{2}{L}\right)^{1/2} \sin\left[\left(\frac{2mE_n}{\hbar^2}\right)^{1/2} x\right]$$

$\int_0^L \psi_{E_n}^{*}\psi_{E_n} dx = 1$ by construction (for box normalization)

$$E_n = n^2 \frac{h^2}{8mL^2} \qquad \frac{dE}{dn} = \frac{2nh^2}{8mL^2} \qquad n = \left[\frac{8mE_nL^2}{h^2}\right]^{1/2}$$

$$\rho_E(E) = \frac{dn}{dE} = \frac{2L}{h}\left(\frac{m}{2E}\right)^{1/2}$$

REFERENCE DENSITY

$$\lim_{L\to\infty}\left(\underbrace{\frac{dn}{dE}}_{\frac{\#}{\Delta E}}\underbrace{\frac{1}{L}\int_0^L \psi_E^*\psi_E dx}_{\frac{\#}{L}}\right) = \frac{2}{h}\left(\frac{m}{2E}\right)^{1/2} = \underbrace{\left[\frac{2m}{h^2E}\right]^{1/2}}_{\text{indep. of L}} = \frac{P(x, x+\delta x;\ E, E+\delta E)}{\delta x\ \ \delta E}$$

THIS SECTION TO BE REPLACED

$$\frac{dn_{\delta E}}{dE} \text{ for } \psi_{\delta E}\ ,\quad \frac{dn_{\delta p}}{dp} \text{ for } \psi_{\delta p}\ ,\quad \frac{dn_{\delta k}}{dk} \text{ for } \psi_{\delta k}$$

$\delta E^{\pm}$

$$\underbrace{\left[\frac{2m}{h^2E}\right]^{1/2}}_{\text{above derived reference density}} = \lim_{L\to\infty}\frac{dn_{\delta E}}{dE}\underbrace{\frac{1}{L}\int_0^L \psi_{\delta E}^*\psi_{\delta E}dx}_{\left[\frac{m}{2h^2E}\right]^{1/2} \text{ derived earlier}}$$

$$\therefore \frac{dn_{\delta E}}{dE} = 2(E/E) = 2$$

2 because each E is doubly degenerate

δp

$$\frac{1}{L}\int_0^L \psi_{\delta p}^*\psi_{\delta p}dx = \frac{1}{h}$$

$$\frac{dn_{\delta p}}{dp}\frac{1}{h} = \left[\frac{2m}{h^2E}\right]^{1/2}$$

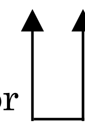
$$\therefore \frac{dn_{\delta p}}{dp} = \left[\frac{2m}{E}\right]^{1/2} = \frac{2m}{p} = \frac{p}{E}$$

δk $$\frac{1}{L}\int_0^L \psi^*_{\delta k}\psi_{\delta k}\,dx = \frac{1}{2\pi}$$

$$\frac{dn_{\delta k}}{dk} = \frac{2m}{\hbar^2 k} = \frac{k}{E}$$

	$dn_{\delta\theta}/d\theta$
δE	$2E/E$
δp	p/E
δk	k/E

see the pattern?

These results are only valid for  $\to\ \infty$ problem. They illustrate all continuum normalization problems where it is desired to calculate probabilities.

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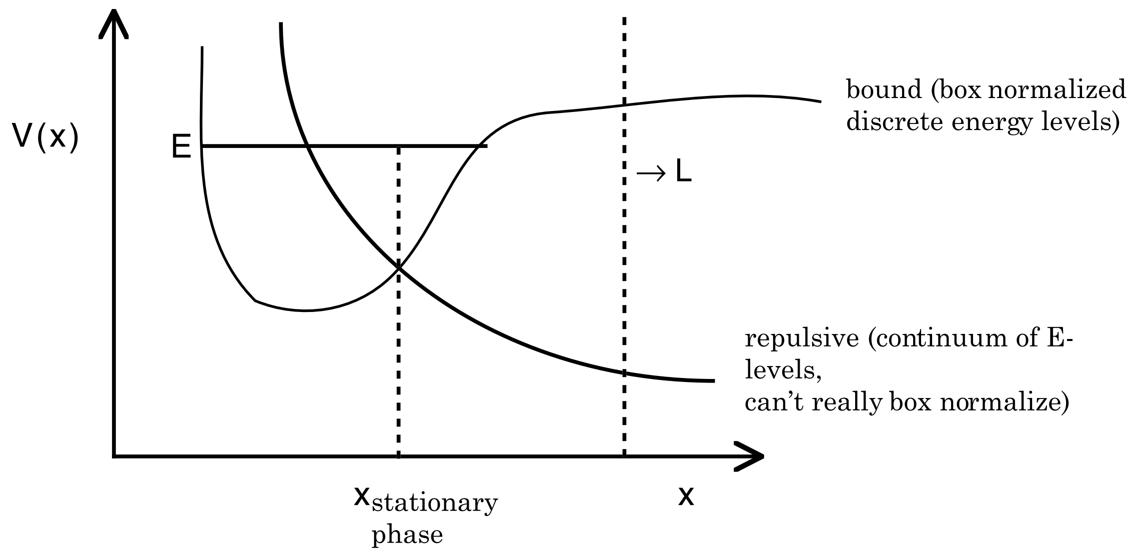
2 Schematic Examples

* Bound $\rightarrow$ free transition probabilities

* Constant spectral density across a dissociation or ionization limit.

Bound-Free Transition (predissociation)



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

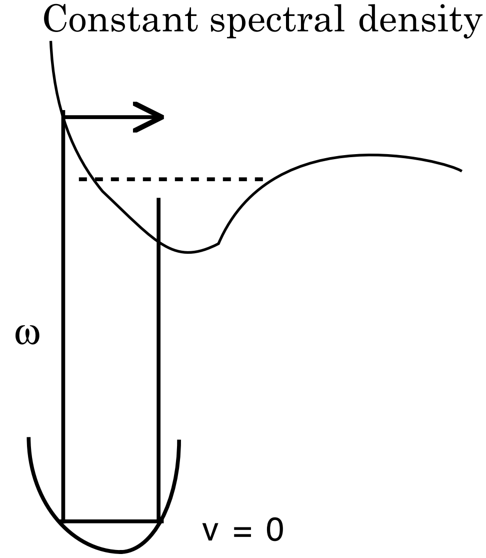
Fermi's Golden Rule:

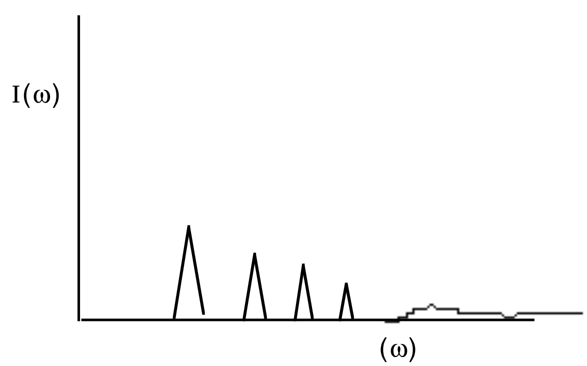
$$\text{Rate} = \Gamma_{\text{bound}\to\text{free}} = \frac{2\pi}{\hbar}\left|\int \psi_{\delta E}^{\text{free}*}(E)\hat{\mathbf{H}}\psi_{E}^{\text{bound}}dx\right|^2 \rho_{\delta E}(E)$$

$\rho_{\delta E} = \dfrac{n_{\delta E}(E)}{dE}$ derive this key quantity by box normalizing repulsive state and taking $\lim\limits_{L\to\infty}\left(\dfrac{1}{L}\dfrac{dn}{dE}\right)$

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

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





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