Lecture 6

13 Nov '23

Energy Normalization of Continuum States

We know that continuum states, i.e. those with $E>0$, are not normalizable — $\psi(r\to\infty)$ does not go to zero and $\int |\psi|^2 d^3r$ does not have a finite value. (in fact, it is guaranteed to diverge!) → easy to show that $\int \psi_E \psi_{E'} = 0$.

The standard way to "normalize" continuum states that you may have learned in QM is "Dirac" normalization,

$$\int \psi_k^*(\vec{r})\, \psi_{k'}(\vec{r})\, d^3r = \frac{\pi}{2}\, \delta(k-k').$$

A much more useful version used often in atomic physics problems is energy normalization. We have already seen the 'definition' of energy-normalized states in the Coulomb sol'ns; any wavefunction which satisfies

① $$\psi_E(r\to\infty) \sim \sqrt{\frac{2\pi}{mk}}\, \sin(kr+\delta), \quad E=\frac{k^2}{2m}$$

will also satisfy

② $$\int \psi_E^*(\vec{r})\, \psi_{E'}(\vec{r})\, d^3r = \delta(E-E').$$

Our goal now is to prove that (1) implies (2), and develop some useful tricks along the way.

We start with the SE:

$$\times \psi_{E'}^* \quad H\psi_E = E\psi_E$$

and, assuming H is Hermitian...

$$\times \psi_E \quad H\psi_{E'}^* = E'\psi_{E'}^*$$

With $H = T + U$, we get:

$$\psi_{E'}^* T \psi_E - \psi_E T \psi_{E'}^* = (E - E')\psi_E \psi_{E'}^*$$

$$\rightarrow \underbrace{\int \psi_{E'}^* \psi_E \, d^3r}_{I(E,E')} = \frac{1}{E-E'} \int \psi_{E'}^* T \psi_E - \psi_E T \psi_{E'}^* \, d^3r.$$

Let's specialize to spherical coordinates now:

$$I(E,E') = \frac{-1/2m}{E-E'} \int \underbrace{u_{E'l}\left(\frac{d^2}{dr^2}\right)u_{El} - u_{El}\left(\frac{d^2}{dr^2}\right)u_{E'l}}_{\text{This should ALWAYS make you want to I.B.P.!}} \, dr.$$

what we get

what we have

$$\frac{d}{dr}\left(u_{E'}\frac{d}{dr}u_E\right) = \frac{d}{dr}u_{E'}\frac{d}{dr}u_E + u_{E'}\frac{d^2}{dr^2}u_E$$

$$\frac{d}{dr}\left(u_E\frac{d}{dr}u_{E'}\right) = \frac{d}{dr}u_{E'}\frac{d}{dr}u_E + u_E\frac{d^2}{dr^2}u_{E'}$$

$$\rightarrow I(E,E') = \frac{-(2m)^{-1}}{E-E'} \cdot \left(\left[u_{E'}(u_E)' - u_E(u_{E'})' \right] \Big|_{r=0}^{r=\infty} \underset{\substack{\text{b/c} \\ \text{B.C.}}}{\downarrow{=0}} + \underbrace{\int (u_E)'(u_{E'})' - (u_E)'(u_{E'})' \, dr}_{\to 0} \right).$$

$$\rightarrow \boxed{I(E,E') = \frac{(2m)^{-1}}{E-E'} W(u_E, u_{E'}) \Big|_{R=\infty}.}$$

This is cool! We turned an integral evaluation into a Wronskian evaluation!

In general, calculating a Wronskian might be a tricky task. But here, we need only the value of W asymptotically, so we can use our asymptotic expressions for u_E!

Recall: if $V(r) \to 0$ quickly enough, our asymptotic solutions are:

$$u_{E\ell}(r) \longrightarrow A_{E\ell} \sin(kr \overbrace{- \ell\pi/2 + \delta_{E\ell}}^{\eta_{E\ell}})$$

$$u_{E'\ell}(r) \longrightarrow A_{E'\ell} \sin(k'r - \ell\pi/2 + \delta_{E'\ell})$$

(since we are interested in the divergent behavior as $E \approx E'$, we can assume $A_{E\ell} \sim A_{E'\ell}$ and $\eta_{E\ell} \sim \eta_{E'\ell}$.)

So: $W(u_E, u_{E'}) = \frac{A_{\varepsilon\ell}^2}{4} W\Big[\overbrace{e^{i(kr+\eta)}}^{a} - e^{-i(kr+\eta)}, \overbrace{e^{i(k'r+\eta)}}^{a'} - e^{-i(k'r+\eta)}\Big]$

$$= v \cdot \Big(\big(e^{ia} - e^{-ia}\big) \cdot ik'\big(e^{ia'} + e^{-ia'}\big) - ik\big(e^{ia} + e^{-ia}\big)\big(e^{ia'} - e^{-ia'}\big) \Big)$$

$$= v \cdot i\Big[k'\Big(e^{i(a+a')} + \big[e^{i(k-k')r} + e^{-i(k-k')r}\big] + e^{-i(a+a')}\Big) - k\Big(\underbrace{e^{i(a+a')}} - \underbrace{\big[e^{i(k-k')r} + e^{-i(k-k')r}\big]} + \underbrace{e^{-i(a+a')}}\Big)\Big]$$

U: these terms have the form

$(k'-k)\, e^{i(a+a')} = (k'-k)\, e^{i(k+k')r} e^{2\eta}$.

when $k \to k'$, these simply vanish. Boring!

U: These terms combine to form

$(k'+k)\, 2i \sin((k-k')r)$. Not boring!

So: $I(E,E') = \lim_{R\to\infty} \frac{A_{\varepsilon\ell}^2 (2m)^{-1}}{2(E-E')} \cdot (k+k')\sin[(k-k')R]$.

$E - E' = (2m)^{-1}(k^2 - k'^2) = (2m)^{-1}(k+k')(k-k')$

So: $= \lim_{R\to\infty} \frac{A_{\varepsilon\ell}^2}{2} R \underbrace{\frac{\sin[(k-k')R]}{(k-k')R}}$.

this sinc function oscillates like bananas as $R \to \infty$, so only its value at $k=k'$ → $\sin(0)$ → is relevant. Here, our expression looks like $R \cdot$ something $=1$ at $k=k'$. This feels a lot like a δ-function, and indeed you can prove it is (or look it up...)!

$$\rightarrow \lim_{R\to\infty} \frac{\sin(\Delta k R)}{\Delta k} = \pi\,\delta(\Delta k).$$

Finally then we have:

$$I(E,E') = A_{El}^2 \cdot \frac{\pi}{2} \cdot \underbrace{\delta(k-k')}_{\displaystyle = \delta\left[\frac{(E-E')\cdot 2m}{k+k'}\right]}.$$

When $E \to E'$, $k+k' \to 2k$ which is just a constant. Thus, using $\delta(ax) = \delta(x)/|a|$,

$$I(E,E') = A_{El}^2 \cdot \frac{\pi}{2} \cdot \frac{(\cancel{2}k)}{\cancel{2}m}\,\delta(E-E')$$

And <u>so</u>: If $A_{El} = \sqrt{\frac{2m}{\pi k}}$, $\underline{I(E,E') = \delta(E-E')}$.

This proves that ① => ②, as promised.

Important throughout: we are always thinking ahead to the point where we set $k \to k'$ ($E \to E'$). Anything far from that point is not important!

ASIDE: if you, like me, get worried about annoying little details like this Coulomb phase and its r-dependence, here's a quick reassurance that it's fine to not worry about it.

We have terms like:

$$\frac{d}{dr}\left(e^{i(kr - \frac{1}{k}\ln 2kr)}\right) = ik e^{ikr} e^{-i/k \ln 2kr} + e^{ikr} e^{-i/k \ln 2kr} \cdot (-2i/r)$$

This second term obviously vanishes as $r \to \infty$, while the first one will give, in the eventual sine function,

$$\sin\left((k-k')R + \underbrace{\frac{1}{k}\ln 2kR - \frac{1}{k'}\ln 2k'R}_{\ln\left[\frac{(2kR)^{1/k}}{(2k'R)^{1/k'}}\right]}\right).$$

as $k \to k'$ this goes to $\ln(1) = 0$.

So everything is fine - aside is over!

Using energy-normalized states will be very useful in the future. For now, we will just use some of the intermediate results to obtain something more immediately useful to Rydberg physics – the normalization of bound Rydberg states.

To be specific, we want to see what the value of

$$N_n^2 = \int_0^\infty u_{\varepsilon_n \ell}(r)^2 \, dr$$

is for the solutions we obtained earlier.

We use the boxed equation for $I(E,E')$:

$$N_n^2 = \lim_{R\to\infty} \lim_{\varepsilon'\to\varepsilon_n} \frac{W[u_{\varepsilon_n}, u_{\varepsilon'}]\big|_R}{2(\varepsilon_n - \varepsilon')}.$$

The large-R form of the radial functions is all we need again:

$$u_\varepsilon(R) \xrightarrow[R\to\infty]{} (\pi K)^{-1/2}\Big[\underbrace{\sin(\beta+\pi\mu)\,D^{-1}}_{\text{"b"}}R^{-\nu}e^{KR}$$
$$\underbrace{-\cos(\beta+\pi\mu)\,D}_{\text{"a"}}R^{\nu}e^{-KR}\Big],$$

$\beta = \pi(\nu - \ell)$.

Remember that $u_\varepsilon(R)$ diverges at large R due to the term on the first line, unless

$\varepsilon' = \varepsilon_n \rightarrow \beta + \pi\mu = n\pi$, where:

$$u_{\varepsilon_n}(R) \rightarrow \underbrace{-(\pi K)^{-1/2}\cos(\beta_n + \pi\mu_n)\,D}_{\text{"}a_n\text{"}}R^{+\nu_n}e^{-K_n R}.$$

Let's compute the Wronskian of these two sol'ns then

$$W[u_{\varepsilon_n}, u_{\varepsilon'}] = W\left[a_n R^{+\nu_n}e^{-K_n R},\ bR^{-\nu}e^{KR}\underline{+aR^{\nu}e^{-KR}}\right]$$

before diving in with derivatives, let's pay attention to the fact that resulting terms with the green underline will multiply terms which also decay at large R → these vanish at $R\to\infty$!

$$\rightarrow W[u_{\varepsilon_n}, u_{\varepsilon'}] = -(\pi K)^{-1}\cos(\beta_n + \pi\mu_n)\,D\,D^{-1}\sin(\beta+\pi\mu)$$
$$\cdot\, W\left[R^{+\nu_n}e^{-K_n R},\ R^{-\nu}e^{+KR}\right]$$

This Wronskian is:

$$W[\;] = R^{+\nu_n} e^{-\kappa_n R}\left(-\nu R^{-\nu-1} e^{\kappa R} + \kappa R^{-\nu} e^{\kappa R}\right) - R^{-\nu} e^{\kappa R}\left(\nu_n R^{+\nu_n-1} e^{-\kappa_n R} - \kappa_n R^{\nu_n} e^{-\kappa_n R}\right)$$

$$= -\nu R^{\nu_n-\nu-1} e^{(\kappa-\kappa_n)R} + \kappa R^{-\nu+\nu_n} e^{(\kappa-\kappa_n)R} - \nu_n R^{\nu_n-\nu-1} e^{(\kappa-\kappa_n)R} + \kappa_n R^{\nu_n-\nu} e^{(\kappa-\kappa_n)R}$$

In the $\varepsilon \to \varepsilon_n$ limit, $\nu_n \to \nu$, $\kappa \to \kappa_n$:

$$= -\nu R^{-1} + \kappa - \nu R^{-1} + \kappa$$

In the $R \to \infty$ limit all that survives is:

$$= 2\kappa.$$

Thus: $$N_n^2 = \lim_{\varepsilon' \to \varepsilon_n} \frac{2\kappa_n \sin[\beta(\varepsilon') + \pi\mu_{\varepsilon'}]\cos[\beta_n + \pi\mu_n]}{2(-\pi\kappa_n)(\varepsilon_n - \varepsilon')}.$$

Both $\sin[\;]$ and $\varepsilon_n - \varepsilon'$ go to $\emptyset$ as $\varepsilon' \to \varepsilon_n$, so this requires a trip to L'hopital:

$$N_n^2 = \frac{1}{\pi} \frac{d}{d\varepsilon'} \sin[\beta(\varepsilon') + \pi\mu_{\varepsilon'}]\cos[\beta_n + \pi\mu_n]\Big|_{\varepsilon' = \varepsilon_n}$$

$$= \frac{1}{\pi} \cos^2(\beta_n + \pi\mu_n) \cdot \left(\frac{d\beta}{d\varepsilon'} + \pi \frac{d\mu_{\varepsilon'}}{d\varepsilon'}\right)\Big|_{\varepsilon' = \varepsilon_n}$$

But: $\beta = \pi\nu \Rightarrow d\beta/d\varepsilon = \pi \frac{d\nu}{dE} = \pi\nu^3.$

And so finally:

$$N_n^2 = \frac{1}{\pi}\left(\pi \nu^3 + \pi \frac{d\mu}{d\varepsilon}\right)$$

So: $\overset{\text{normalized}}{u_{n\ell}(r)} = \left(\nu_n^3 + \mu'\right)^{1/2} u_{\varepsilon n \ell}(r)$

this term is huge!

μ is nearly indep. of ε → this term is tiny.

Remember what $u_{\varepsilon n\ell}(r)$ looks like in the classically allowed region in WKB:

$$u_{n\ell}(r) = \sqrt{\frac{2}{\pi k(r)}} \cdot \sin\left(\int k(r)\,dr + \pi/4\right)$$

careful! Although this form looks similar to the asymptotic exact $u_{\varepsilon\ell}(r)$ at $\varepsilon > 0$, they should not be confused. There, $k = \sqrt{2E}$, while here (for negative E) $k(r) = \sqrt{2E + \frac{2}{r} - \frac{\ell(\ell+1)}{2r^2}}$.

For small r, $2/r \gg E$ and this $u_{n\ell}(r)$ becomes indep. of E, and therefore n. So, the normalization contains all of the key ν-dependence at small r.

APPLICATION:
Rydberg atom oscillator strengths.

By definition, the oscillator strength from state $n l m$ to $n' l' m'$ is:

$$f_{n'l'm', nlm} = \frac{2m}{\hbar} \underbrace{\omega_{n'l', nl}}_{= (E_{n'l'} - E_{nl})/\hbar} \left| \langle n'l'm | x | nlm \rangle \right|^2$$

The average oscillator strength is:

$$\bar{f}_{n'l', nl} = \frac{2}{3} \omega_{n'l', nl} \frac{l_>}{2l+1} \left| \langle n'l' | r | nl \rangle \right|^2.$$

Swapping $l \leftrightarrow l'$ gives

$$\bar{f}_{n'l', nl} = -\frac{2l'+1}{2l+1} \bar{f}_{nl, n'l'}.$$

And in general, for transitions to the continuum...

$$df/dE = \frac{2m\,\omega_{nl,E}}{\hbar} \left| \langle \psi_E | x | \psi_{nlm} \rangle \right|^2.$$

Why bother with these? For one thing: they define several sum rules (Thomas-Reiche-Kuhn)

$$\sum_{n'l'm'} f_{n'l'm', nlm} = Z.$$

$$\sum_{n'} \overline{f_{n'l-1, nl}} = -\frac{1}{3}\frac{l(2l-1)}{2l+1}$$

$$\sum_{n'} \overline{f_{n'l+1, nl}} = \frac{1}{3}\frac{(l+1)(2l+3)}{2l+1}$$

$$\sum_{n'l'} \overline{f_{n'l', nl}} = 1, \quad l' = l \pm 1.$$

For the curious: let's derive that upper one, with a $Z=1$ atom for simplicity. We'll use $|1\rangle = |nlm\rangle$ and $|n\rangle \equiv |n'l'm'\rangle$ as labels. So:

$$S = \sum_n f_n + \int_0^\infty \frac{df}{dE}\,dE.$$

$$= m\sum_n \frac{2(E_n - E_1)}{\hbar^2}\langle\psi_1|z|\psi_n\rangle\langle\psi_n|z|\psi_1\rangle$$

$$+ m\int dE\,\frac{2(E-E_1)}{\hbar^2}\langle\psi_1|z|\psi_E\rangle\langle\psi_E|z|\psi_1\rangle.$$

Let's use the S.E. $H|\psi\rangle = E|\psi\rangle$ here to rewrite:

$$\frac{(E_n - E_1)m}{\hbar^2}\langle\psi_n|z|\psi_1\rangle = \frac{m}{\hbar^2}\Big(\langle H\psi_n|z|\psi_1\rangle - \langle\psi_n|z|H\psi_1\rangle\Big).$$

$$= \frac{m}{\hbar^2}\langle\psi_n|Hz - zH|\psi_1\rangle.$$

Since $[H,z] = \frac{1}{2m}[p^2,z] = \frac{1}{2m}\left(p[p,z] + [p,z]p\right) = -\frac{i\hbar}{m}p_z$,

$$= -\frac{i}{\hbar}\langle\psi_n|p_z|\psi_1\rangle.$$

Also: $(E_n - E_1)\langle\psi_1|z|\psi_n\rangle = \frac{i}{\hbar}\langle\psi_1|p_z|\psi_n\rangle \ldots$

So: $$S = \underbrace{\left(\sum_n + \int dE\right)}\Big(\langle\psi_1|z\underbrace{|\psi_{E_n}\rangle\langle\psi_{E_n}|}-\frac{ip_z}{\hbar}|\psi_1\rangle + \langle\psi_1|\frac{ip_z}{\hbar}\underbrace{|\psi_{E_n}\rangle\langle\psi_{E_n}|}z|\psi_1\rangle\Big)$$

only E dependence here ⇒ use completeness!!

$$= \langle\psi_1|z\left(-\frac{ip_z}{\hbar}\right)|\psi_1\rangle + \langle\psi_1|\frac{ip_z}{\hbar}\cdot z|\psi_1\rangle$$

$$= -\frac{i}{\hbar}\langle\psi_1|\underbrace{zp_z - p_z z}_{[z,p_z] = i\hbar}|\psi_1\rangle$$

$$= \frac{-i}{\hbar}\cdot i\hbar\cdot\langle\psi_1|\psi_1\rangle = 1.$$

The other reason oscillator strengths are useful is because they are the key component of e.g.

Einstein A coefficient:

$$A_{n'l',nl} = -2\omega^2 \bar{f}_{n'l',nl}$$

Cross Section:

$$\sigma = 2\pi^2 \frac{d\bar{f}_{n'l',nl}}{d\varepsilon}.$$

And finally, from the small-r normalization we derived earlier, we can find e.g. $A_{n'l',nl}$ for the transition b/w a Rydberg state and the ground state.

$$A_{nl,gs} \sim \omega^3 \underbrace{|\langle nl|r|gs\rangle|^2}$$

$= \left|\int_0^{r_0} \psi_{gs}(r)\, \psi_{nl}(r)\, dr\right|^2$ r_0 is the (small) range of ψ_{gs}.

$= |n^{-3/2}|^2$

$$\sim \omega^3 n^{-3}.$$

Thus we see that Rydberg states have a lifetime $\tau \sim A^{-1} \sim n^3$, since ω becomes indep. of n at high n.

Note that this is <u>not</u> true for transitions between closeby Rydberg levels. For these,

$$\omega \sim -\frac{1}{2n^2} - \left(-\frac{1}{2n'^2}\right) \sim n^{-3},$$

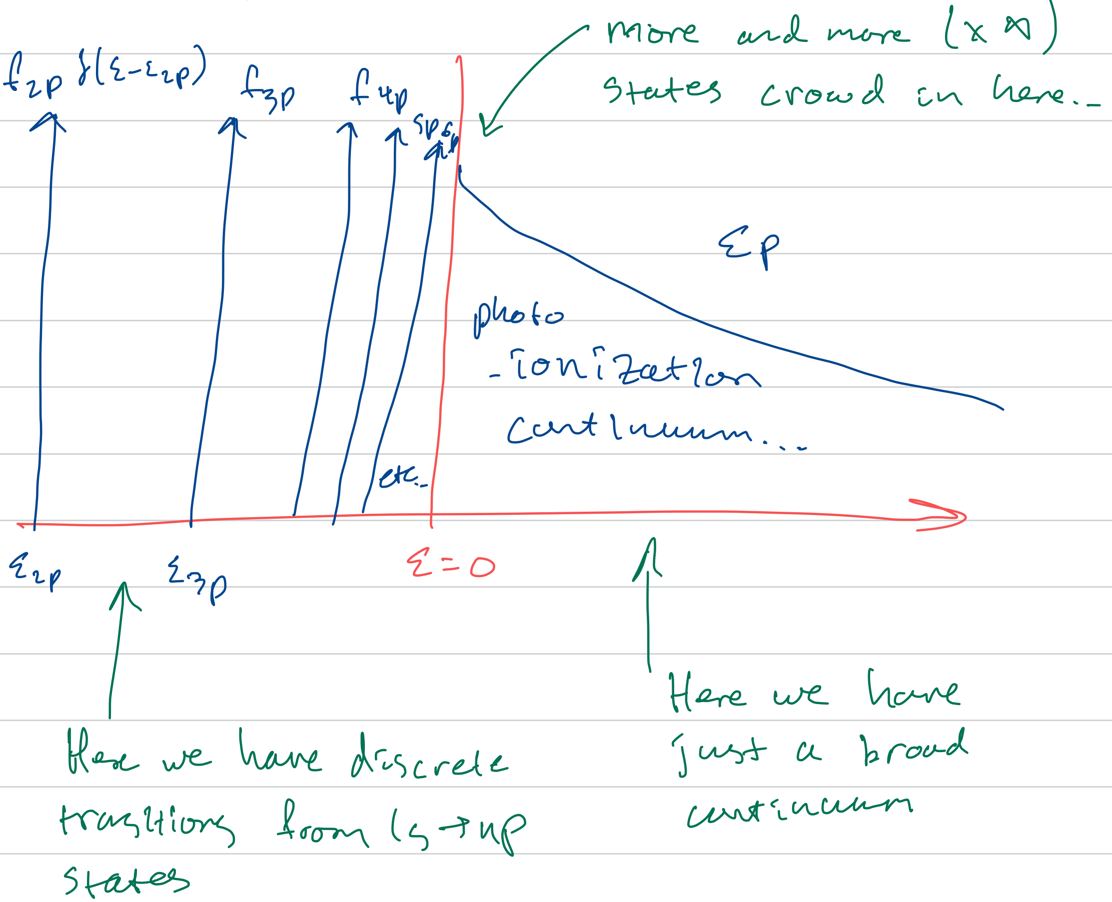
and also the overlap integral in $\langle n\ell | r | n'\ell' \rangle$ covers the whole range of allowed r values, which goes like $\sim n^2$. $\rightarrow |\langle n\ell | r | n'\ell' \rangle|^2 \sim n^4$

Altogether then, $A_{n\ell \to n'\ell'}$ goes like $\omega^3 n^4 = n^{-5}$.

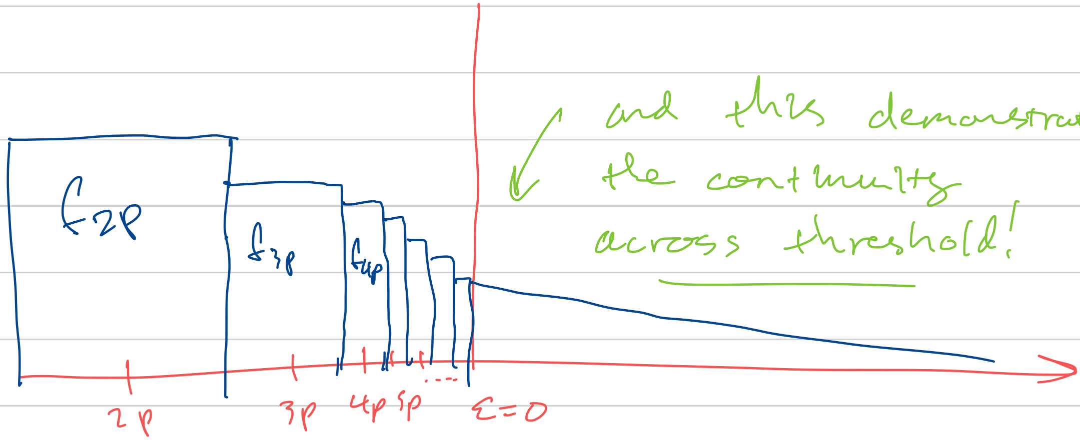
Note that a <u>circular</u> Rydberg state, which has $\underline{\ell = n-1}$, can only decay to the state $n' = n-1,\ \ell' = n'-1 = n-2$ with a single photon. Thus these states have a lifetime which is <u>much</u> longer than low-ℓ states: $\underline{\tau \sim n^5!}$

The last topic for here involves the continuity - or discontinuity - of observables across thresholds.

Let's plot the oscillator strengths for H 1s photoabsorption:



But a helpful way to visualize this (due to Fano + Cooper) is to represent the δ-functions as boxes $\rightarrow$ i.e. $f_n \delta(\varepsilon - \varepsilon_n) \rightarrow$ box of width $\Delta\varepsilon = \varepsilon_n - \varepsilon_{n-1}$ w/ height $f_n / \Delta\varepsilon$, so the area of the box is f_n.



and this demonstrates the continuity across threshold!