**Some general results concerning impurities in metals**

**Friedel’s Sum Rule**

If we have Fermionic particles in a box, and we add some sparse potentials – say like δ function potentials – then the energy levels will change (remember these energy levels will be discrete even if the δ potential is repulsive because we have boundary conditions for our box of volume V). Further, the allowed k values, won’t simply reduce simply to k = 2π**n**/a, for instance. Consider the situation in 1D, for the case of a delta function potential. As we’ll recall from the Quantum Mechanics folder, a delta function potential in the middle of a 1D box as the following eigenfunctions.



Let’s see if we can work out the k values, under some approximation, for the even parity wavefunctions. Might say something like:



So this is our dimensionless equation for x,



Let’s say V0 < 0. Then we have:



And let’s say |x0| << 1, so a weak potential, basically. Can we have x << |x0|? If so, then,



But this would make x negative. So that doesn’t work. What about x ~ |x0|? Then,



And this wouldn’t really be consistent either. So then x >> |x0|. And then our solution would be:



If |x0| << 1, then even n = 1 would count as large. And so we can do expansion,



So we see contraction of the k’s. Translating back to k’s:



Or well, absolute value of. Can see we may write,



where δ(k) is evaluated at k = 2πn/a, and small V0/large k approximation is used. Maybe could’ve just started off with this from the very beginning, as a first order approximation. Well anyway, the number of extra states would be increase in the range of k’s divided by the approximate spacing of the states:



Now let’s consider an impurity in a metal. Say the metal atoms give up one electron to the conduction band, and the impurity atoms give up two electrons. Then the metal atom ions will have charge +1, while the impurity atom ions will have charge + 2. The difference we’ll call Z, in this case equal to 2 – 1 = 1. The extra charge, Z, on the impurity will be the cause of the net impurity potential, which will give rise to a scattering phase shift δ(k). This Z will be screened by the conduction electrons. The extra states needed to accommodate the electrons to screen the potential are those extra states calculated above from δ(k). This is Friedel’s theorem, that the number of extra states just equals the valence difference, Z. So, in 1D, adding a factor of two for spin degeneracy,



What about in 3D? We’ll recall that free states in 3D spherical potentials generically take on the form,



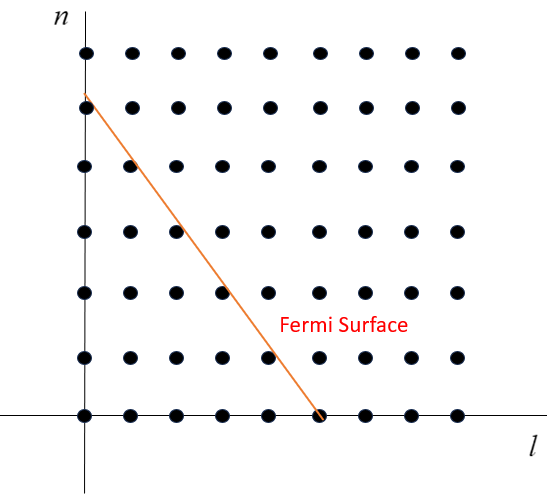
where the ℓ quantum number is a whole number that can range from 0 to ∞. If we enclose this within an infinte potential spherical border (trying to model the wavefunction of a single impurity potential within a solid), then boundary conditions will require,



Using the past as a guide, approximate solutions to this equation would be just,



where the k in the δℓ(k) is evaluated at (πn + ℓπ/2)/R. The (n, ℓ) states occupy the first quadrant. The Fermi surface would look like a straight line, I guess, for a spherical model.



Per ℓ, the number of extra states induced by this potential would be:



(because δ(k=0) typically goes to 0 in 3D, as can verify for a couple of our examples in the QM folder)

We can repeat the argument. But for a given ℓ, we have 2ℓ(ℓ+1) solutions too, due to presumed spin (ms) and z angular momentum quantum number (mℓ) degeneracy. So repeating our arguments from before, we’d say that in 3D we have:



Presumably, the sum over ℓ only encompasses the ℓ’s which lie on the Fermi surface? If the potential were more like a Coulomb potential, then the n’s and ℓ’s would be, I suppose, *those* quantum numbers. And again, only the n’s, ℓ’s that lie on the Fermi surface would be included. So for instance, a transition metal impurity might have an s and multiple d orbitals that touch the Fermi surface, so we’d include ℓ = 0, 1 for those. Also, if not all the mℓ’s of a given ℓ were on the Fermi surface, then I suppose the degeneracy wouldn’t be (2ℓ+1).

**Example**

An impurity with a charge of 2e is placed in a three-dimensional metal. Assume that the Friedel sum rule holds for this system, and only the scattering phase shifts from the electrons contribute to this sum (we don't need to consider ion phase shifts). This metal has a spherical Fermi surface with Fermi wave vector kF. The only degeneracy for the electrons at the Fermi surface is spin (two-fold) and angular momentum (2ℓ+1) for each angular momentum channel. Ignore scattering for ℓ > 2,  and assume that the scattering doesn't depend on the spin degree of freedom. Denote the scattering phase shift at the Fermi wave vector in the ℓth channel as δℓ(kF). If δ0(kF) = 11π/31, and and δ1(kF) = π/29, what is δ2(kF)?

Well, we need,



**Funni’s Theorem**

I guess here is a good spot to throw in Funni’s theorem. So we already saw that adding impurity potentials changes the allowed k’s, and so changes the allowed energy levels. So naturally, this will lead to a change in the ground state energy Let’s try to motivate this by considering a delta function in the middle of a 1D periodic box. We considered this potential in the file Quantum Mechanics Folder/Time-Independent/Delta function in a periodic box. The results were:



Note that when V0 = 0, the even solution’s k = 2πn/a. So we duplicate the energies. This makes sense because a free particle in a periodic box has two levels at the same energy (parabolic spectrum). When V0 = ∞, then we have k = 2π(n+1/2)/a. So then they’re halfway in between ψ-(x)’s k values. So we’ll observe that whatever ψ+(x)’s k values are, they’re going to be inbetween ψ-(x)’s k values. So we can approximately say that E+(k)’s are:



Then could say,



And since k ≈ 2πn/a, because as we saw above, when V0 = ∞, this only shifts the k’s to k = 2π(n+1/2)/a, and n is presumed large, we can say,



This approximation becomes better and better, I think, as *a* → ∞. Anyway, now we can say:



(Note I had a different justification for this formula somehow, also with no minus sign, in an earlier version of this file, that made no sense to me, so I rewrote as this) So now,



Adding a factor of two for spins, we have:



So there we go! We’ll also note that since we saw ψ+(x)’s k values were interspersed with ψ-(x)’s k values, we won’t expect kF to change in any significant way, especially as *a* → ∞. Also note, finally, that for our δ potential δ(k) = tan-1(stuff), so ΔE will be a positive quantity for a repulsive potential, and negative for an attractive potential, which kind of makes sense. We can generalize to 3D. In that case, the free wavefunctions of an infinite potential V0, of radius R radial box, are given by:



where the radial wavefunction is approximately,



and the energies are:



where δℓ(k) is evaluated at k = (πn + πℓ/2)/R. So for smallish δ(k), we have:



which we could write as:



where our k now denotes the free particle wavevectors. But for a given ℓ, we have 2ℓ(ℓ+1) solutions too, stemming from the azimuthal and spin d.o.f. So we can say, the shift in energy of our system is:



So we come to Funni’s theorem, where we change the sum to an integral and account for the fact that the spacing of k-points is π/R, so Σ -> ∫dk/(π/R):



where Ni is the number of such potentials present. I imagine that kF is ℓ-dependent in this setup, just as it was in the 3D Friedel theorem example examined up above?