Lecture 15

Tuesday, February 23, 2010

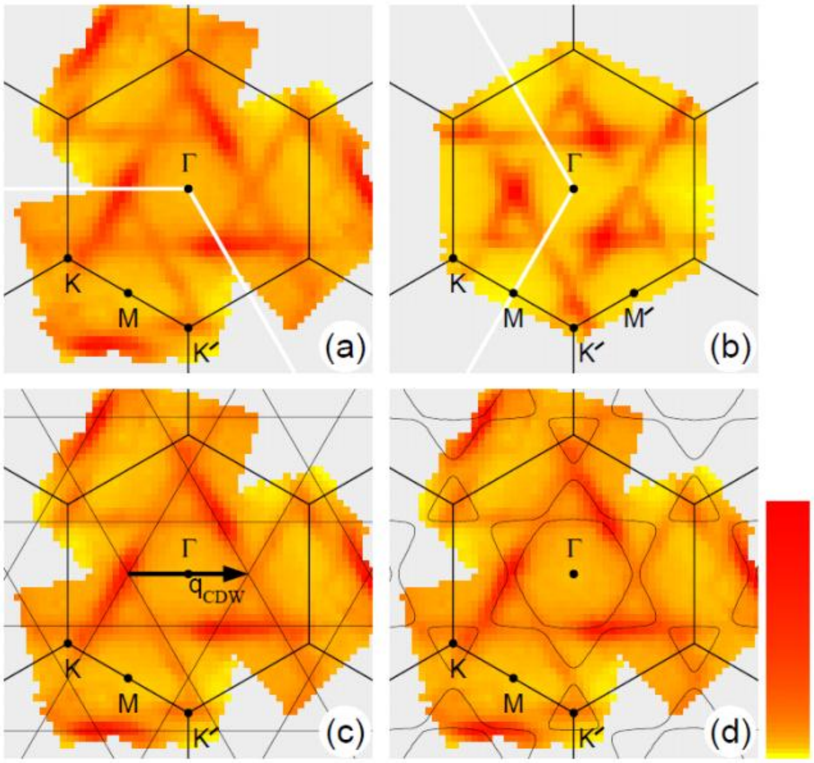
Now that we discovered the distinction between metals and insulators, we will discuss the defining feature of the metal -- Fermi surface -- a little bit. While we are doing that we would need to consider the semi-classical equation of motion and motion of electrons in the electric field and the magnetic field.

How to distinguish metals and non-metals?

In the previous lecture, we discussed how the existence of a partially filled band can distinguish metals from non-metals. We also made a statement about "Wilson's rule" based on this discussion. Accordingly, there is another method to distinguish metals from non-metals. **Metals have Fermi surface, while non-metals don't**. Insulators and semi-conductors have no Fermi surface at zero temperature. Semi-metals do not have Fermi surface at zero temperature; instead they have Fermi "points", the limit of finite volume/area Fermi surfaces just before they disappear. In practice, if the Fermi surface is very small, then the material can be considered a semi-metal.

How do we know that the FS exists?

There is a rather direct way of observing a Fermi surface. This method is angle resolved photoelectron spectroscopy (ARPES), which is the method of choice for yours truly. This method uses the photoelectric effect, to excite electrons out of the specimen with high flux beams of ultraviolet light. The interpretation of the photoelectric effect (electron + photon → more energetic electron) mainly involves only the energy conservation principle and the momentum conservation principle. Essentially, the electron that is taken out from the sample remembers the energy and the momentum it used to have inside the sample, and it is elementary for experimenters to compute them since the photon energy and the photon momentum involved in an ARPES experiment are very accurately known. The simplicity of the interpretation gives great power to the ARPES technique. From mid 90's, it has become quite routine to obtain "Fermi surface" maps, the intensity map at the chemical potential, where the high intensity region delineates the Fermi surface shape. The following is an example of such an early ARPES Fermi surface map, which was taken by yours truly for his Ph. D. thesis. The materials here are "Na/K purple bronzes" which have a strongly two dimensional electronic structure in a hexagonal unit cell. Shown here are the hexagonal BZ, ARPES maps, and theoretical predictions (c and d).



Other methods of probing the Fermi surface

ARPES works very well for layered materials with quasi-2D electronic structure. These are crystals that are built up by loosely coupled layers, and the electrons spend much of their time within the layer than hopping between layers. This class of materials include high temperature superconductors and graphene/graphite, and so ARPES continues to receive much attention.

However, the applicability of ARPES to more traditional 3D materials is weak.

What are other methods of probing the Fermi surface? Quantum oscillation measurements at high magnetic field is a very sharp measurement tool. Also, in recent days, the scanning tunneling spectroscopy has been used to infer the Fermi surface shape. Other effects such as Kohn anomaly (homework 4.5) can give information about the Fermi surface. None of these methods are as direct as ARPES in the sense that, while ARPES can give the shape of the Fermi surface without any band theory input, all these methods must use some prior knowledge from theory in order to interpret the results since they cannot obtain the absolute position of the Fermi surface and the exact shape of the Fermi surface. Nevertheless, these methods are very useful, and more advantageous to the ARPES technique in terms of applicability to 3D materials. Of these, we will review the quantum oscillation measurements below. Before doing that, though, we need to do establish some important facts about how the electron (or the hole) moves under an applied field.

The semi-classical equation of motion

In real situations, a mono-chromatic wave with a very sharply defined crystal momentum is more a fantasy than a reality. Even when a theoretical description prefers to use a plane wave or a infinitely sharply defined Bloch state, one is advised to always remember that physical situations always involve wave packets due to intrinsic effects such as finite lifetime and extrinsic effects such as experimental conditions imposed (finite sample size, smearing by instrumental resolutions, etc.).

Let us then consider an electron wave packet, which is built up with a distribution of wave vectors, say centered at $\vec{k}$ with a width scale $\Delta\vec{k}$. When the spatial extent of this wave packet $\sim 1/\Delta k$, determined by Heisenberg uncertainty principle, is much smaller than the length scale (the wave length or the decay length) of the applied field, then we have the semi-classical approximation.

In addition, we also generally assume that Δk is not too large. If Δk is too large, then the spatial extent of the wave packet can be as small as the lattice constant, in which case the band structure begins to blur out severely. So, we assume that Δk small compared to the wave vector scale for the energy dispersion itself. If follows from this assumption that the wave packet moves with the group velocity $\vec{v}_g = \frac{1}{\hbar}\frac{d\epsilon_k}{d\vec{k}}$.

In this case, the following semi-classical equation of motion applies.

$$\hbar\frac{d\vec{k}}{dt} = \vec{F}(\vec{r}, \vec{v}_g)$$

where $\vec{r}$ is the mean position, and $\vec{v}_g$ is the group velocity ($\partial\epsilon/\partial\vec{k}$), of the wave packet, and $\vec{F}$ is the classical force at the position $\vec{r}$ and the velocity $\vec{v}_g$. For a particle with charge q, in the presence of the $\vec{E}, \vec{B}$ fields:

$$\hbar\frac{d\vec{k}}{dt} = q\vec{E} + \frac{q}{c}\,\vec{v}_g \times \vec{B}$$

Let us see how this can be derived. Consider $H = \frac{1}{2m}\left(\vec{p} - \frac{q}{c}\vec{A}\right)^2 + q\phi$ where we assume that the length scales associated with $\vec{A}$ and ϕ (wave lengths) are much larger than $1/\Delta k$ of the wave packet. Otherwise, we leave $\vec{A}, \phi$ as unrestricted: e.g. they can be time dependent.

Consider a $T_{\vec{R}}$ operator, where $T_{\vec{R}} f(\vec{r}) = f(\vec{r} - \vec{R})$, i.e. $T_{\vec{R}}$ is the translation by $\vec{R}$. Our restriction on $\vec{R}$ is that it is a small lattice vector such that $R \ll$ length scales of the field.

We start from QM:

$$\frac{d\langle T_{\vec{R}}\rangle}{dt} = \frac{i}{\hbar}\langle [H, T_{\vec{R}}]\rangle$$

The left hand side here is trivial. $\langle T_{\vec{R}}\rangle \approx \langle e^{-i\vec{k}\cdot\vec{R}}\rangle = e^{-i\vec{k}\cdot\vec{R}}$.

So, $\frac{d\langle T_{\vec{R}}\rangle}{dt} \approx -i\dot{\vec{k}}\cdot\vec{R}e^{-i\vec{k}\cdot\vec{R}}$.

This is the leading order contribution, a term linear in $\vec{R}$. Our next task is to get the term of the same order on the right hand side.

Let us first consider the 2nd term in the Hamiltonian.

$$\frac{i}{\hbar}\langle [q\phi, T_{\vec{R}}]\rangle = \frac{i}{\hbar}q\langle \phi T_{\vec{R}} - T_{\vec{R}}\phi\rangle = \frac{iq}{\hbar}\langle \{\phi(\vec{r}) - \phi(\vec{r}-\vec{R})\}T_{\vec{R}}\rangle = \frac{iq}{\hbar}\vec{R}\cdot\langle \nabla\phi\, T_{\vec{R}}\rangle$$
$$\approx \frac{iq}{\hbar}\vec{R}\cdot\nabla\phi e^{-i\vec{k}\cdot\vec{R}}$$

[BEGIN]: Optional reading. The above is enough to show $\dot{\vec{k}} = q\vec{E}$.

Now, consider the first term in the Hamiltonian, which is more complicated.

$$\frac{i}{2m\hbar}\left\langle \left(\vec{p} - \frac{q}{c}\vec{A}\right)^2 T_{\vec{R}} - T_{\vec{R}}\left(\vec{p} - \frac{q}{c}\vec{A}\right)^2\right\rangle$$
$$= \frac{i}{2m\hbar}\left\langle \left\{\left(\vec{p} - \frac{q}{c}\vec{A}\right)^2 - \left(\vec{p} - \frac{q}{c}\vec{A}(\vec{r}-\vec{R})\right)^2\right\}T_{\vec{R}}\right\rangle$$
$$\approx \frac{i}{2m\hbar}\left\langle \left\{\left(\vec{p} - \frac{q}{c}\vec{A}\right)^2 - \left(\vec{p} - \frac{q}{c}\vec{A} + \frac{q}{c}(\vec{R}\cdot\nabla)\vec{A}\right)^2\right\}T_{\vec{R}}\right\rangle$$
$$\approx \frac{i}{2m\hbar}\left\langle \left\{-\frac{q}{c}\left(\vec{p} - \frac{q}{c}\vec{A}\right)\cdot(\vec{R}\cdot\nabla)\vec{A} - \frac{q}{c}\left((\vec{R}\cdot\nabla)\vec{A}\right)\cdot\left(\vec{p} - \frac{q}{c}\vec{A}\right)\right\}T_{\vec{R}}\right\rangle$$
$$\approx \frac{i}{2m\hbar}(-2)\frac{q}{c}\, m\vec{v}_g\cdot(\vec{R}\cdot\nabla)\vec{A}\, e^{-i\vec{k}\cdot\vec{R}}$$
$$= -\frac{iq}{\hbar c}\left\{\vec{R}\cdot(\vec{v}_g\times\vec{B}) + \vec{R}\cdot\left(\frac{d\vec{A}}{dt} - \frac{\partial\vec{A}}{\partial t}\right)\right\}e^{-i\vec{k}\cdot\vec{R}}$$

$\vec{p} - \frac{q}{c}\vec{A} \approx m\vec{v}_g$ for the wave packet

$$\vec{v}\cdot(\vec{R}\cdot\nabla)\vec{A} = v_j R_i \partial_i A_j = \delta_{il}\delta_{jk}v_k R_l \partial_i A_j = (\epsilon_{mij}\epsilon_{mlk} + \delta_{ik}\delta_{jl})v_k R_l \partial_i A_j$$
$$= (\vec{R}\times\vec{v})\cdot(\nabla\times\vec{A}) + \vec{R}\cdot(\vec{v}\cdot\nabla)\vec{A} = (\vec{R}\times\vec{v})\cdot\vec{B} + \vec{R}\cdot\left(\frac{d\vec{A}}{dt} - \frac{\partial\vec{A}}{\partial t}\right) = \vec{R}\cdot(\vec{v}\times\vec{B}) + \vec{R}\cdot\left(\frac{d\vec{A}}{dt} - \frac{\partial\vec{A}}{\partial t}\right)$$

So, collecting all terms:

$$-i\dot{\vec{k}}\cdot\vec{R} = \frac{iq}{\hbar}\vec{R}\cdot\nabla\phi - \frac{iq}{\hbar c}\left\{\vec{R}\cdot(\vec{v}_g\times\vec{B}) + \vec{R}\cdot\left(\frac{d\vec{A}}{dt} - \frac{\partial\vec{A}}{\partial t}\right)\right\}$$

Taking $\vec{R}$ to be $\vec{a}, \vec{b}, \vec{c}$, of the Bravais lattice, we have the vector identity:

$$\hbar\dot{\vec{k}} = -q\nabla\phi + \frac{q}{c}\left(\vec{v}_g \times \vec{B} + \frac{d\vec{A}}{dt} - \frac{\partial\vec{A}}{\partial t}\right)$$

With $\vec{E} = -\nabla\phi - \frac{1}{c}\frac{\partial\vec{A}}{\partial t}$, we have $\frac{d}{dt}\left(\hbar\vec{k} - \frac{q}{c}\vec{A}\right) = q\vec{E} + \frac{q}{c}\vec{v}_g \times \vec{B}$.

While this form is consistent with the classical limit ($\hbar\vec{k}$ is an average of the canonical momentum for each plane wave component of the wave packet, up to a constant reciprocal vector, and so $\frac{d}{dt}\left(\hbar\vec{k} - \frac{q}{c}\vec{A}\right) \approx \frac{d}{dt}\left(m\vec{v}_g\right)$), it is not $\frac{d}{dt}\left(\hbar\vec{k}\right) = \vec{F}\left(\vec{r}, \vec{v}_g\right) = q\vec{E} + \frac{q}{c}\vec{v}_g \times \vec{B}$. Also, our derivation resulted in a gauge dependent form, which is clearly not desirable. The resolution of this problem is complicated, and is sketched in the following paragraph.

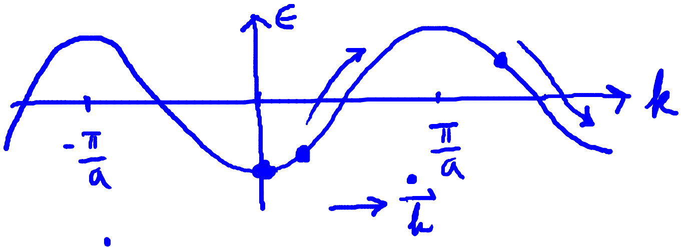
According to Zak, Phys. Rev. 168, 686 ('68), the semi-classical equation of motion should read as $\hbar\frac{d}{dt}\left[\vec{k}\right] = q\vec{E} + \frac{q}{c}\left[\frac{\partial\epsilon_n(\vec{k})}{\partial\vec{k}}\right] \times \vec{B}$ where [] means replacing $\vec{k} \to \vec{k} - i\frac{q}{2\hbar c}\vec{B} \times \frac{\partial}{\partial\vec{k}}$ (his derivation is for a constant $\vec{B}$ field and single band). $\vec{A} = \frac{1}{2}\vec{B} \times \vec{r}$ for a constant $\vec{B}$ field, and so $\vec{k} - i\frac{q}{2\hbar c}\vec{B} \times \frac{\partial}{\partial\vec{k}}$ can be thought of as related to $\vec{k} - \frac{q}{\hbar c}\vec{A}$ since one might expect $\vec{r}$ to be something like $i\frac{\partial}{\partial\vec{k}}$. As a matter of fact, Zak works in the representation that diagonalize both $T\left(\vec{R}\right) = e^{-i\vec{p}\cdot\vec{R}/\hbar}$ (translation operator in real space) and $T^*\left(\vec{G}\right) = e^{-i\vec{x}\cdot\vec{G}}$ (translation operator in momentum space). Since these two operators commute, it is possible to find the $\vec{k}, \vec{q}$ representation, where $\vec{k}$ labels the eigenvalue of $T\left(\vec{R}\right)$, $e^{-i\vec{k}\cdot\vec{R}}$, and $\vec{q}$ labels the eigenvalue of $T^*\left(\vec{G}\right)$, $e^{-i\vec{q}\cdot\vec{G}}$. In this representation, he obtains $\vec{p} = -i\hbar\frac{\partial}{\partial\vec{q}}$ and $\vec{r} = i\frac{\partial}{\partial\vec{k}} + \vec{q}$. He further finds that, in the presence of the magnetic field, the semi-classical equation $\hbar\frac{d}{dt}\vec{k} = q\vec{E} + \frac{q}{c}\ v_g\left(\vec{k}\right) \times \vec{B}$ has to be interpreted as $\vec{k}$ meaning $\left[\langle\vec{k}\rangle\right]$, where [] means the replacement of $\vec{k} \to \vec{k} - i\frac{q}{2\hbar c}\vec{B} \times \frac{\partial}{\partial\vec{k}}$. So, it is not really $\vec{k}$ when there is a magnetic field. However, this can be understood as a simple "re-mapping" or "re-labeling" of $\vec{k}$. Besides, the magnitude of the 2nd term is generally very small: $\frac{q}{2\hbar c}Ba \sim \frac{e\hbar}{2mc}B\frac{mc^2}{(\hbar c)^2}a \sim \mu_B B\ \frac{1}{4\ \text{eV Å}} \sim O(10^{-3})\ \text{Å}^{-1}$ (a is the lattice constant $\sim O\left(\frac{\partial}{\partial\vec{k}}\right)$, and μ_B is the Bohr magneton $= 6 \times 10^{-9}$ eV/gauss. The strongest B field that one can generate in a laboratory $\sim 10^6$ gauss; On the other hand, the term $\frac{q}{\hbar c}A \sim \frac{q}{\hbar c}Br$ is *not* necessarily small, since $r \gg a$.)

[END]: Optional reading.

Bloch Oscillation

Surprisingly, the semi-classical equation above predicts that if a partially filled band is subjected to a constant DC electric field, then an AC response may be obtained.

This is easy to see if there was one wave packet moving on a single band in one dimension.



$$\dot{\vec{k}} = \frac{q}{\hbar}\vec{E} = \text{const.}$$

According to the semi-classical EOM, **the wave vector simply changes at a constant rate**, under a constant $\vec{E}$ field, but without the $\vec{B}$ field. So, given a band sketched above, the wave packet will simply trace the dispersion relation, going up and coming down and repeating indefinitely, while the wave vector changes steadily. Why does this mean an AC current? The current density is $nq\vec{v}_g$ ($q = -e$ for the electron wave packet), where $n =$ number density, and $\vec{v}_g$ is the group velocity. Notice how the group velocity increases to a positive number, decreases to zero at $k = \pi/a$, and then reverses its direction, and then decreases further before increasing to 0 again ($k = 2\pi/a$). Thus the current is definitely an AC current. Given the band structure (which may not be a single cosine function in general), we expect that the AC current will contain harmonics of the $2\pi/T$, where T is the period: the time it takes for $\Delta k = 2\pi/a$. Since the rate at which k changes is constant ($|qE|/\hbar$), $T = \frac{2\pi\hbar}{a|qE|}$. This is the so-called **Bloch oscillation**.

Each wave packet causes such an AC current, and the frequency of the current will not change when the same type of AC current is caused by a very many number of electron wave packets.

When would a Bloch oscillation be observed? $T \ll \tau$, where τ is the relaxation time. For a small T, one would like to have a large a (a nanoscale superstructure -- an artificial crystal -- rather than a natural crystal) and a large $|E|$ (semi-conductor instead of a metal). In semiconductors, τ is on the order of pico-seconds, and a superstructure with $a \sim 50$ Å and $E \sim 5 \times 10^4$ V/cm, giving $T \sim 0.2$ pico-seconds, will be enough.

Motion of charged particle in a $\vec{B}$ field

$T \sim 0.2$ pico-seconds, will be enough.

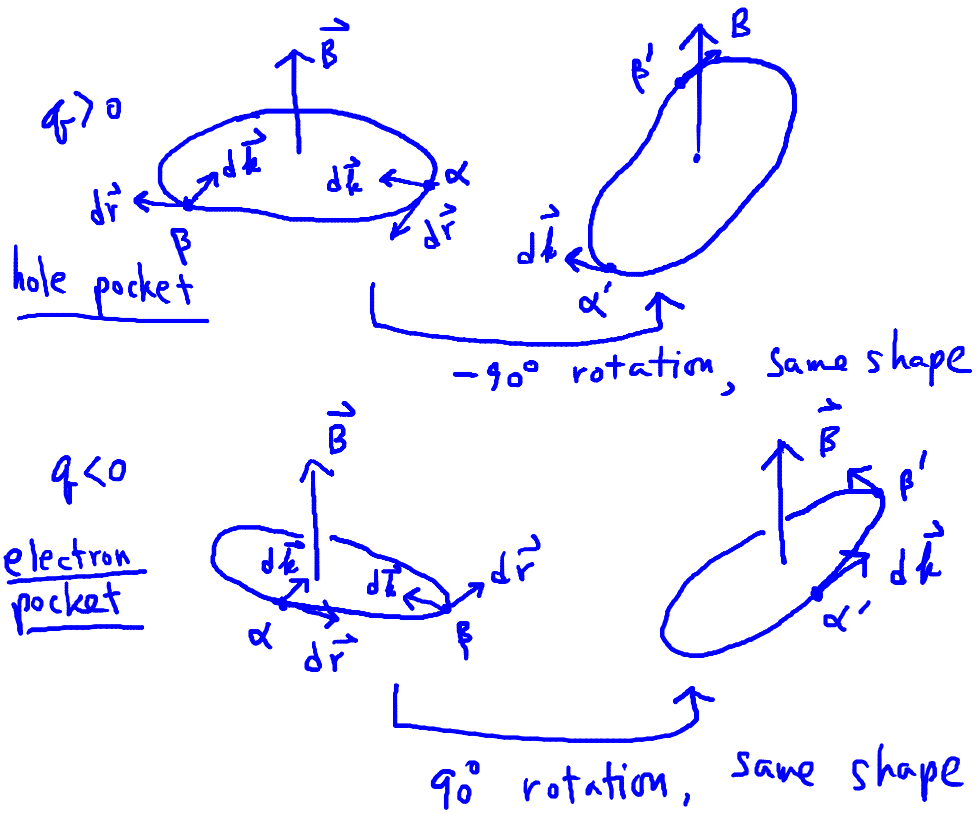
Motion of charged particle in a $\vec{B}$ field

Let us consider a complementary situation when $\vec{E} = 0$ but $\vec{B} =$ constant. Classically, we know that this means a circular motion with the cyclotron frequency $\omega_c = \frac{qB}{mc}$. We shall now see what happens in the quantum case.

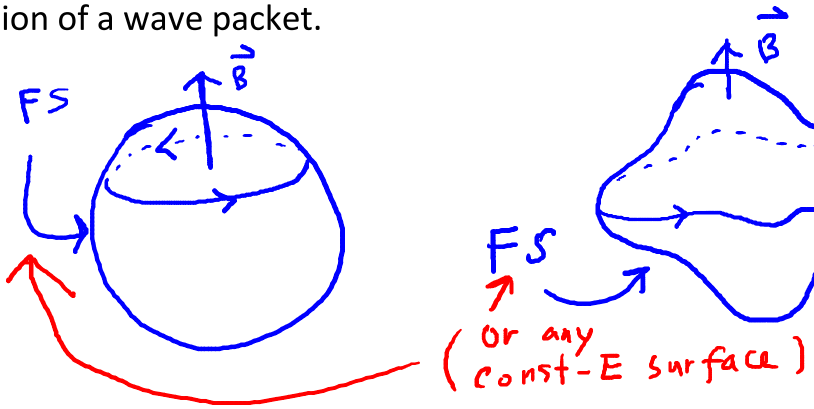
First, let us look at the equation of motion: $\hbar\dot{\vec{k}} = \frac{q}{c}\vec{v} \times \vec{B}$. Rewriting this $\hbar\frac{d\vec{k}}{dt} = \frac{q}{c}\frac{d\vec{r}}{dt} \times \vec{B}$, we get

$$d\vec{k} = \frac{q}{\hbar c} d\vec{r} \times \vec{B}$$

What does this mean? Suppose $q > 0$. Let us say that there is a real space path that is followed by this wave packet $(d\vec{r})$. We consider a planar motion only, where the plane is perpendicular to the field. [The particle can have a finite constant velocity parallel to the field.] This equation means that the path of the particle in that plane is replicated (with a different scale $\frac{qB}{\hbar c}$).



It is important to realize that the shape of the orbit above is determined by the crossection of the constant energy surface. Why? (1) $\hbar\dot{\vec{k}} = \frac{q}{c}\vec{v}\times\vec{B}$ means that $\dot{\vec{k}}\cdot\vec{B} = 0$, meaning that the $\vec{k}$ component along the direction of $\vec{B}$ is constant (so the motion in $\vec{k}$ space is strictly two dimensional, while the motion in $\vec{r}$ space can be three dimensional with a constant velocity along the direction of $\vec{B}$). (2) $\frac{d\epsilon_{\vec{k}}}{dt} = \frac{\partial\epsilon_{\vec{k}}}{\partial\vec{k}}\cdot\dot{\vec{k}} = \vec{v}\cdot\dot{\vec{k}} = \frac{q}{c}\vec{v}\cdot\left(\vec{v}\times\vec{B}\right) = 0$. That is, the magnetic field doesn't do any work, as well-known. So a given band structure completely determines the motion of a wave packet.



Quantum Oscillations (dHvA, SdH measurements)

We continue to consider the constant $\vec{B}$ case without any $\vec{E}$ field. As Landau found out, the $\vec{B}$ field causes an additional quantization, which becomes very essential for quantum oscillation measurements (de Haas van Alphen effect etc.).

Recall the Bohr-Sommerfeld quantization condition from the semi-classical point of view: $\oint d\vec{r}\cdot\vec{p} = (n+\gamma)h$ (Kittel has a typo for this equation; there is no 2π if using h). Here, γ is a sort of "greedy factor" that we use to fit the semi-classical theory even for the ground state. For this problem, $\gamma = 1/2$ like in a simple Harmonic oscillator, but we won't need it.

We will consider the free electron case only, the generalization to the band case is straightforward.

Recall that the canonical momentum is given by $m\vec{v} + \frac{q}{c}\vec{A} = \hbar\vec{k} + \frac{q}{c}\vec{A}$. (In the case of a wave packet of Bloch states, this identity would be valid for each sub-wave packet (with each $\vec{k}$ belonging to the same cell in the extended zone scheme) up to a constant $\vec{G}$; that would be sufficient for the following derivation since the integral that we consider is independent of any constant offset in $\vec{k}$.)

... to be continued ...