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Second Order Semiclassical Theory of Bloch Electrons in Uniform Electromagnetic Fields

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Second Order Semiclassical Theory of Bloch Electrons in Uniform Electromagnetic Fields

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Dedicated to my parents, Yujun Gao and Sumei Pan.

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Berry curvature appears in the semi-classical theory of Bloch electrons already to first order in electromagnetic fields, resulting in profound modification of the carrier velocity and phase space density of states. Here we derive the equations of motion for the physical position and crystal momentum to second order in the fields. The dynamics still has a Hamiltonian structure, albeit with noncanonical Poisson brackets between the physical variables. We are able to expand both the carrier energy and the Poisson brackets to second order in the fields with terms of clear physical meaning. To demonstrate the utility of our theory, we obtain with much ease the electromagnetic response and orbital magnetic susceptibility.

Table of Contents

1 Introduction

The essence of crystals is the periodic arrangement of atoms. The Born-Oppenheimer approximation seperates the motion of fast moving electrons and relatively inert ions [5]. Bloch waves express the structure of the electronic wave function in a crystal [1]. These two ideas give rise to the band structure, and lay down the foundation of the typical quantum mechanical treatment of crystals. Yet another elegant and intuitive treatment of Bloch electrons is the semiclassical theory.

Of course, the electronic motion is quantum mechanical in nature. The concept of 'classical' description comes from the construction of wavepackets as suggested by Paul Ehrenfest. However, the simple classical limit of Bloch electrons is not appropriate, since the variation of periodic potential is of the scale of interatomic distance and hence comparable with if not smaller than the typical spatial spread of the wave packet. Also, the semiclassical theory can not handle scattering from impurities or other imperfections in solids-it more naturally describes electrons moving between two subsequent collisions. For a long time, the semiclassical equations of motion for Bloch electrons read:

$$\dot{\boldsymbol{r}} = \frac{\partial \varepsilon(\boldsymbol{k})}{\partial \boldsymbol{k}}\,, \tag{1}$$

$$\dot{\boldsymbol{k}} = -e\boldsymbol{E} - e\dot{\boldsymbol{r}} \times \boldsymbol{B}\,, \tag{2}$$

where $\varepsilon(\boldsymbol{k})$ is the electronic band structure, $\boldsymbol{E}$ and $\boldsymbol{B}$ the external electromagnetic fields, and $\boldsymbol{k}$ the crystal momentum. Earlier works justifying the validity of these equations of motion (EOM) include Blount from phase space

quantum mechanics [3], Zak constructing the k-q representation [26, 27], and Chambers explicitly formulating a wavepacket with its center following the trajectory determined by Eq.(1)-(2). However, various Hall effects bring new challenges to the semiclassical theory.

A unified first order theory was developed by Sundaram and Niu [19]. They start by assuming that the Hamiltonian is slowly perturbed due to, for example, the external electromagnetic fields:

$$\hat{H} = H(\hat{\boldsymbol{p}} + e\boldsymbol{A}^{\boldsymbol{r}}(\hat{\boldsymbol{r}}, t)) - e\phi(\hat{\boldsymbol{r}}, t)\,, \tag{3}$$

and construct a wavepacket from a single band n:

$$|\Psi\rangle = \int_{BZ} \frac{d^3k}{8\pi^3} C(\boldsymbol{k}) e^{i\boldsymbol{k}\cdot\boldsymbol{r}} |u_{n\boldsymbol{k}}\rangle\,. \tag{4}$$

Here $\boldsymbol{A}^{\boldsymbol{r}}$ is the vector potential, $\boldsymbol{\phi}$ is the scalar potential, and $e^{i\boldsymbol{k}\cdot\boldsymbol{r}}|u_{n\boldsymbol{k}}\rangle$ the Bloch wave. Then they examine the Lagrangian defined by:

$$L = \langle\Psi| i\frac{d}{dt} |\Psi\rangle - \langle\Psi|\hat{H}|\Psi\rangle\,. \tag{5}$$

In the context of Bloch electrons, they find that:

$$L = -\varepsilon_M + e\phi(\boldsymbol{r}, t) + \boldsymbol{k}\cdot\dot{\boldsymbol{r}} + \dot{\boldsymbol{k}}\cdot\boldsymbol{A} - e\hat{\boldsymbol{r}}\cdot\boldsymbol{A}^{\boldsymbol{r}}\,, \tag{6}$$

$$\varepsilon_M = \varepsilon(\boldsymbol{k}) - \boldsymbol{B}\cdot\boldsymbol{m}\,, \tag{7}$$

where $\boldsymbol{A} = \langle u_{n\boldsymbol{k}}| i\partial/\partial\boldsymbol{k} |u_{n\boldsymbol{k}}\rangle$ is the Berry connection, and $\boldsymbol{m}$ is the magnetic moment:

$$\boldsymbol{m} = eIm\left[\left\langle \frac{\partial u_{n\boldsymbol{k}}}{\partial \boldsymbol{k}}\right| \times (\varepsilon - \hat{H}(\boldsymbol{k}) \left|\frac{\partial u_{n\boldsymbol{k}}}{\partial \boldsymbol{k}}\right\rangle\right]\,. \tag{8}$$

By applying the Euler-Lagrangian equations of motion, they are able to write down the correct first order equations of motion:

$$\dot{\boldsymbol{r}} = \frac{\partial \varepsilon_M}{\partial \boldsymbol{k}} - \dot{\boldsymbol{k}} \times \boldsymbol{\Omega} \,, \tag{9}$$

$$\dot{\boldsymbol{k}} = -e\boldsymbol{E} - e\dot{\boldsymbol{r}} \times \boldsymbol{B} \,. \tag{10}$$

where $\boldsymbol{\Omega} = \nabla_{\boldsymbol{k}} \times \boldsymbol{A}$ is the Berry curvature.

Comparing Eqs.(9)-(10) with Eqs.(1)-(2), two comments are in order: (1) the force equation remains the same; (2) electromagnetic fields modify the velocity equation in two ways: they modify the band energy by coupling to the electron magnetic moment in the n-th band, and also give rise to a new term by coupling to the Berry curvature in a symmetric way compared with the Lorentz force. This new term in the velocity equation is called the anomalous velocity. It is the cross product of the Berry curvature with $\hat{\boldsymbol{k}}$, the changing rate of $\boldsymbol{k}$-space parameter, and highly resembles the real space Lorentz force in the magnetic field. This resemblance suggests $\boldsymbol{\Omega}$ can be viewed as the $\boldsymbol{k}$-space magnetic field. To make the analogy more manifest, if one considers a two band toy model $H = \boldsymbol{h}(\boldsymbol{R}) \cdot \boldsymbol{\sigma}$, it can be shown that the vector form Berry curvature reads [22]:

$$\boldsymbol{\Omega} = \frac{1}{2} \frac{\boldsymbol{h}}{h^3} \,, \tag{11}$$

which is the field generated by a charge 1/2 monopole at the degenerate point $\boldsymbol{h} = 0$ in the parameter space. In this case, the implementation of Gauss theorem gives a delightful result which is useful beyond this simple toy model:

$$\int_{\Sigma} \Omega \cdot d\boldsymbol{S} = 2\pi \,. \tag{12}$$

The generalization is more easily addressed in the language of differential geometry. The playground for differential geometry in the context of crystals is the first Brillouin zone(BZ), because each point in the BZ will specify a possible electronic state. The BZ is a smooth, differentialable and oriented manifold. Interestingly, the real space periodicity is reflected also in the $\boldsymbol{k}$-space, which identifies any two points in the parameter space differing by a reciprocal lattice vector. This assigns a nontrivial torus topology to the BZ in the 2D case. The Bloch wave function has a $U(1)$ phase redundancy and $\mathcal{A} = \langle u|i\partial/\partial\boldsymbol{k}|u\rangle$ is the corresponding local connection. One can define an exact curvature form: $\omega = d\mathcal{A}$. Then the following integration can be proven to take only integer values:

$$N = \frac{1}{2\pi}\int_{BZ}\omega\,. \tag{13}$$

This leads to various interesting topics on exploring the topology of the band structure.

The fruitful implications of the anomalous velocity in the semiclassical theory is largely explored by Di Xiao *et al.* [24]. The key message is that it breaks the canonicality between the semiclassical phase space variables $\boldsymbol{r}$ and $\boldsymbol{k}$. Indeed, in the derivation provided by Sundaram and Niu, $\boldsymbol{r}$ and $\boldsymbol{k}$ are taken as independent degrees of freedom, so there is no reason they happen to be canonical. From the quantum mechanical point of view, this fact is due to the projection P of the whole Hilbert space to a subspace spanned by Bloch

states from only one band, so that

$$P[\hat{\boldsymbol{r}}, \hat{\boldsymbol{k}}]P \neq [P\hat{\boldsymbol{r}}P, P\hat{\boldsymbol{k}}P]\,. \tag{14}$$

A direct consequence is that Liouville's theorem is violated and the phase space density of states will pick up an additional term:

$$1 \to 1 + \boldsymbol{B} \cdot \boldsymbol{\Omega}\,. \tag{15}$$

However, the total number of states is fixed, so the Fermi surface is shifted. Since various transport properties of solids are effects determined by processes in the neighbourhood of the Fermi surface, this shift is then of great significance - for example, in the understanding of anomalous Hall conductivity and orbital magnetization. Despite its success, the semiclassical theory up to now has had a serious limitation: it is only accurate to the first order in external fields. Therefore it cannot deal with quantities that require second order accuracy. In this work, I will generalize the semiclassical equations of motion to the second order accuracy in external fieds, and use it to examine various polarizabilities and susceptibilities in solids. To realize the generalization, an alternative formalism of quantum mechanics called phase space quantum mechanics would be more useful.

2 Phase Space Quantum Mechanics

The role of statistical concepts has bothered the founders of quantum mechanics. In 1927, Hermann Weyl [21] designed a transformation, which maps each Hilbert space operator to a phase space function. This map is a new and complete representation of quantum mechanics in the sense that it is also assembled with a star product between two functions which mimics the operator product in the Hilbert space. Since the star product possesses an asymptotic expansion with the expanding parameter $\hbar$, it actually describes the quantum mechanics as a deformation of classical mechanics mediated by the Planck constant. In 1932, Eugene Wigner [10] introduced the Wigner quasi-probability distribution to study quantum corrections to classical statistical mechnics. It is the phase space analog of quantum mechanical wavefunctions which encode all expectation information. However, Wigner has noticed that this distribution function cannot be made positive all the time. So he emphasises that it is only a useful mathematical tool. In 1949, José Enrique Moyal [16] explored in depth the possibility of reformulating quantum mechanics in the statistical language. Here I will just sketch his major ideas and main results.

One should focus on the measurable quantities in a system, i.e. the expectation values of physical observables. In the statistical language, it is:

$$\langle G \rangle = \int dx G(x) \rho(x;t)\,, \tag{16}$$

where $G(x)$ is the observable of physical interest, and $\rho(x;t)$ the distribution

function.

From this, it is obvious that to map the quantum mechanics into a statistical theory, one needs to resolve three problems: (1) How to get a distribution function that describes the state of a quantum system; (2) How to get the appropriate function for observables; (3) How does the distribution function evolve.

Assuming $\hat{p}$ is a complete set of commutating obserbles, it is usually not enough to specify the dynamical properties of the system. One needs to find a complementary set $\hat{q}$, which do not commute with $\hat{p}$, and together they characterize a given system dynamically and span the phase space. This idea can also be stated in a more intuitive way: one prepares a sample as an eigenstate of some operator, however the measurement process usually corresponds to an observable which does not commute with the original one. One example is that $\hat{q}$ can be the Cartesian coordinates and $\hat{p}$ the conjugate momenta (for simplicity, the following derivation will make this identification). So the first problem amounts to finding the phase space distribution function $\rho(p, q)$.

Moyal [16] anwsered the first question by transfering the concept of the characteristic function in statistics, i.e. by looking for the Fourier inverse of $\rho(p, q)$:

$$M(\tau, \theta) = \iint \rho(p, q) e^{i(\tau q + \theta p)} dp dq \,. \tag{17}$$

So the characteristic function is the expectation value of the phase space function $e^{i(\tau q+\theta p)}$. The connection with the quantum mechanics comes from substituting q and p by its operator form $\hat{q}$ and $\hat{p}$. Then one can identify Eq.(17) with

the quantum mechanical expectation value of the operator kernel $e^{i(\tau\hat{q}+\theta\hat{p})}$. If the wavefunction Ψ is given, the result is:

$$M(\tau,\theta) = \langle\Psi|e^{i(\tau\hat{q}+\theta\hat{p})}|\Psi\rangle\,. \tag{18}$$

By taking the Fourier transform, the distribution function is obtained:

$$\rho(p,q) = \frac{1}{4\pi^2}\iint\langle\Psi|e^{i(\tau\hat{q}+\theta\hat{p})}|\Psi\rangle e^{-i(\tau q+\theta p)}d\tau d\theta\,. \tag{19}$$

A more useful form of Eq.(19) would require the Baker-Hausdorff formula:

$$e^{X+Y} = e^X e^Y e^{-\frac{1}{2}[X,Y]}e^{\frac{1}{6}(2[Y,[X,Y]]+[X,[X,Y]])}\cdots\,. \tag{20}$$

And the phase space distribution function takes a form:

$$\rho(p,q) = \frac{1}{2\pi}\int\Psi^*(q-\frac{1}{2}\hbar\tau)e^{-i\tau p}\Psi(q+\frac{1}{2}\hbar\tau)d\tau\,. \tag{21}$$

The next step is to find the mapping of Hilbert space operators and phase space functions. Given a phase space function $G(p,q)$, the measurement of G yields:

$$G = \iint G(p,q)\rho(p,q)dpdq = \left\langle\Psi\left|\iint g(\tau,\theta)e^{i(\tau\hat{q}+\theta\hat{p})}d\tau d\theta\right|\Psi\right\rangle\,, \tag{22}$$

where

$$g(\tau,\theta) = \frac{1}{4\pi^2}\iint G(p,q)e^{-i(\tau q+\theta p)}dpdq\,. \tag{23}$$

So one can take the corresponding Hilbert space operator to be:

$$\hat{G} = \iint g(\tau,\theta)e^{i(\tau\hat{q}+\theta\hat{p})}d\tau d\theta\,. \tag{24}$$

Here, the operator kernel in the Fourier inverse combined with the Fourier transform actually yields a Dirac delta analogue:

$$\frac{1}{4\pi^2}\iint e^{-i(\tau(q-\hat{q})+\theta(p-\hat{p}))}d\tau d\theta = \delta(q-\hat{q})\delta(p-\hat{p})\,. \tag{25}$$

Another useful expression for $\hat{G}$ from $G(p,q)$ is:

$$\hat{G} = e^{\hbar/(2i)\partial^2/\partial p\partial q}\hat{G}_0(\hat{q},\hat{p})\,, \tag{26}$$

where $\hat{G}_0(\hat{q},\hat{p})$ is obtained from the ordinary function $G(p,q)$ by writing all the operator $\hat{p}$ to the right, and this order is maintained when applying the operator $e^{\hbar/(2i)\partial^2/\partial p\partial q}$. Later, it is pointed out that this is just another way to write down $\hat{G}$ in the fully symmetrized form.

The inverse problem is more difficult. Given a Hilbert space operator, to find its phase space correspondance, one needs to use the Schwartz kernel theorem, which asserts that for a linear operator, one can find its kernel:

$$\hat{G}\varphi(q) = \int K_G(q;q')\varphi(q')dq'\,, \tag{27}$$

where $\hat{G}$ is a linear operator and φ is a wavefunction. Then the phase space function is given by:

$$G(p,q) = \frac{1}{\sqrt{2\pi}}\int d\tau e^{-i\tau q}K_G(p+\tau/2, p-\tau/2)\,. \tag{28}$$

As for the evolution of the distribution function, Moyal [16] found that it should not be done in the framework of classical statistical mechanics, which

is a 'crypto-deterministic' theory, but appears more like a special case of dynamical stochastic processes, i.e. a Markov process. After some lengthy derivation, his result is:

$$\frac{\partial}{\partial t}G(p,q;t) = \frac{2}{\hbar}\sin\frac{\hbar}{2}\left[\frac{\partial}{\partial p_G}\frac{\partial}{\partial q_H} - \frac{\partial}{\partial q_G}\frac{\partial}{\partial p_H}\right]G(p,q;t)H(p,q)\,, \tag{29}$$

where $H(p,q)$ is the phase space function of the Hamiltonian operator, the subscript G or H means acting on $G(p,q;t)$ or $H(p,q)$, and the sine function is in the sense of Taylor series expansion. Above processes complete the construction of the phase space representation of quantum mechanics. Now one is ready to apply this formalism to solid state physics.

3 Bloch Electrons in Uniform Electromagnetic Fields

Consider these three different types of Hamiltonian that may be used in solid state physics (for simplicity, the natural units $e = \hbar = c = 1$ are adopted):

(a) Schrödinger Hamiltonian:

$$\hat{H} = \frac{\hat{\boldsymbol{p}}^2}{2m} + U(\hat{\boldsymbol{r}})\,, \tag{30}$$

where m is the mass of the electron and U the periodic crystalline potential.

(b) Pauli Hamiltonian which is the Schrödinger Hamiltonian with the spin-orbit coupling:

$$\hat{H} = \frac{\hat{\boldsymbol{p}}^2}{2m} + \frac{1}{4m^2}\hat{\boldsymbol{p}} \cdot \boldsymbol{\sigma} \times \nabla U(\hat{\boldsymbol{r}}) + U(\hat{\boldsymbol{r}})\,, \tag{31}$$

where $\boldsymbol{\sigma}$ is the Pauli matrices.

(c) Relativistic Dirac Hamiltonian:

$$\hat{H} = \boldsymbol{\alpha} \cdot \hat{\boldsymbol{p}} + U(\hat{\boldsymbol{r}})\,, \tag{32}$$

where $\boldsymbol{\alpha}$ is the four-component spinor.

For these Hamiltonians, one can define a total velocity operator $\hat{\mathcal{V}}$ as follows:

$$\hat{\mathcal{V}} = -i[\hat{\boldsymbol{r}}, \hat{H}]\,. \tag{33}$$

When uniform external electromagnetic fields are turned on, one should add a scalar potential $\boldsymbol{E} \cdot \hat{\boldsymbol{r}}$, and use the mechanical momentum to substitute the

canonical momentum in these three Hamiltonians:

$$\hat{\boldsymbol{p}} \to \hat{\boldsymbol{p}} + \frac{1}{2}\boldsymbol{B} \times \hat{\boldsymbol{r}}\,. \tag{34}$$

Here $\boldsymbol{E}$ and $\boldsymbol{B}$ are electromagnetic fields. The symmetric gauge is chosen for the vector potential. These Hamiltonians under EM fieds can be put in a unified form:

$$\hat{H} = \hat{H}_0 + \frac{1}{4}\{\hat{\mathcal{V}} \cdot \boldsymbol{B} \times \hat{\boldsymbol{r}}\} + \frac{(\boldsymbol{B} \times \hat{\boldsymbol{r}})^2}{8m}\,, \tag{35}$$

except that for the Dirac case one must set $1/m = 0$ and the last term disappears. Here $\hat{H}_0$ is the Hamiltonian without external fields. If one treats the second and third terms as perturbations, a serious issue is that $\hat{\boldsymbol{r}}$ is involved in the vector potential, which is an unbound operator. So convential perturbation technique is not applicable here. Yet the smallness of external fieds means that the scalar and vector potential varies slowly from cell to cell. Based on this observation, E.I.Blount [2, 3] tackled this kind of perturbation in the framework of phase space quantum mechanics.

To get the phase space function for the Hamiltonian operator, it is convinent to use the Bloch wavefunction, which is the eigenstate for the unperturbed Hamiltonian. Note that any operator $\hat{O}$ under the Bloch basis takes the form $O_{mn}(\boldsymbol{p}_1, \boldsymbol{p}_2)$, where m and n are band indices, $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ the crystal momentum. Rewrite $O_{mn}(\boldsymbol{p}_1, \boldsymbol{p}_2)$ as follows:

$$O_{mn}(\boldsymbol{p}; \boldsymbol{p}') \equiv O_{mn}(\boldsymbol{p} + \boldsymbol{p}'/2, \boldsymbol{p} - \boldsymbol{p}'/2) = O_{mn}(\boldsymbol{p}_1, \boldsymbol{p}_2)\,. \tag{36}$$

The the phase space function is found by:

$$O_{mn}(\boldsymbol{p}, \boldsymbol{q}) = \int d\boldsymbol{p}' O_{mn}(\boldsymbol{p}; \boldsymbol{p}') e^{i\boldsymbol{q}\cdot\boldsymbol{p}'}\,. \tag{37}$$

In the phase space representation, the quantum nature of any function lies in the deformation of the matrix product, i.e. the multiplication rule. Given two Hilbert space operators $\hat{N}$ and $\hat{O}$, whose phase space functions are $N(\boldsymbol{p},\boldsymbol{q})$ and $O(\boldsymbol{p},\boldsymbol{q})$ respectively, the counterpart of $\hat{N}\hat{O}$ is obtained by the following asymptotic expansion:

$$\begin{aligned} N \star O = NO + \frac{i}{2}\{N,O\}_{PB} \\ - \frac{1}{8}\left(\frac{\partial^2 N}{\partial p_i \partial p_j}\frac{\partial^2 O}{\partial q_i \partial q_j} - 2\frac{\partial^2 N}{\partial p_i \partial q_j}\frac{\partial^2 O}{\partial q_i \partial p_j} + \frac{\partial^2 N}{\partial q_i \partial q_j}\frac{\partial^2 O}{\partial p_i \partial p_j}\right) + \cdots . \end{aligned} \tag{38}$$

Here the subscript PB means Poisson bracket:

$$\{N,O\}_{PB} = \frac{\partial N}{\partial q_i}\frac{\partial O}{\partial p_i} - \frac{\partial N}{\partial p_i}\frac{\partial O}{\partial q_i} . \tag{39}$$

The applied magnetic field changes the commutation relation between physical momenta, so the original Bloch wavefunction does not generate the correct energy band any more. However, if the magnetic field is small, one can imagine that the deviation is also small. The general idea to solve this perturbed system is to design a unitary transformation which can diagonalize the Hamiltonian, however this purpose seems to be too hard to achieve in one step. A more realistic goal is to block diagonolize the Hamiltonian operator with respect to the band index n. Yet even this is difficult to accomplish exactly. Fortunately, there is a recursive procejure to do this order by order.

In general, for a Hilbert space operator $\hat{O}$, suppose one can find a unitary matrix $U^{(0)}(\boldsymbol{q},\boldsymbol{p})$ in the phase space, such that it can diagonalize $O(\boldsymbol{q},\boldsymbol{p})$ according to the usual matrix product. The substitution by the star

product would change this simple result in two ways: (1) $U^{(0)}(\boldsymbol{p},\boldsymbol{q})$ is not unitary with respect to the star product, although it is with respect to the usual product; (2) generally, $U^{(0)}(\boldsymbol{q},\boldsymbol{p})$ cannot diagonalize $O(\boldsymbol{p},\boldsymbol{q})$. But the deviation is determined from the asymptotic expansion Eq.(38).

Formally, one can correct the original transformation U by a series of prefactors:

$$U = \prod_{i}^{\infty}(1+U^{(i)})U^{(0)} \tag{40}$$

$$U_{(n)} = \prod_{i}^{n}(1+U^{(i)})U^{(0)}\,. \tag{41}$$

The Hermitian part of $U^{(1)}$ is dertermined as follows:

$$U^{(1)} + U^{(1)\dagger} + \frac{i}{2}\{U^{(0)}, U^{(0)\dagger}\}_{PB} = 0\,. \tag{42}$$

For the nth order one will obtain

$$U_{(n)} \star U^{\dagger}_{(n)} = 1 + \Delta^{(n+1)} + \Delta_R\,, \tag{43}$$

where $\Delta^{(n+1)}$ is of the order $(n+1)$ and Δ_R is of higher order. Then $U^{(n+1)}$ is so chosen that

$$U^{(n+1)} + U^{(n+1)\dagger} + \Delta^{(n+1)} = 0\,. \tag{44}$$

So the Hermitian part is all about making the transformation unitary.

One still have another constraint to fix the antihermitian part, i.e. to diagonalize O with respect to the star product. At the beginning, one has

$$U^{(0)} \star O \star U^{(0)\dagger} = O^{(0)}_{D} + O^{(1)} + O_R\,, \tag{45}$$

where $O_D^{(0)}$ is diagonal, $O^{(1)}$ is the first order residue with possible off-diagonal elements, and O_R is of higher order. In general order,

$$U_{(n)} \star O \star U_{(n)}^{\dagger} = O_D^{(n)} + O^{(n+1)} + O_R \,. \tag{46}$$

So one should choose $U^{(n)}$ such that

$$U^{(n+1)} O_D^{(n)} + O_D^{(n)} U^{(n+1)\dagger} + O^{(n+1)} = O_D^{(n+1)} \,. \tag{47}$$

The off-diagonal element yields

$$\frac{1}{2}[(U^{(n+1)} - U^{(n+1)\dagger}), O_D^{(n)}] = -O^{(n+1)} - \frac{1}{2}\{\Delta^{(n+1)}, O_D^{(n)}\} \,. \tag{48}$$

This completes diagonalizing O with respect to the star product.

Applying this scheme, one can find the effective Hamiltonian up to the second order

$$\begin{aligned} \mathcal{H} = {} & \varepsilon(\boldsymbol{\pi}) - (\boldsymbol{B} \times \boldsymbol{v}) \cdot \boldsymbol{a} - \boldsymbol{B} \cdot \boldsymbol{m} + \frac{3}{8}\{\mathcal{U}_i, \{\mathcal{U}_j, \alpha_{ij}\}\} + \mathcal{U}^2/2m \\ & + \frac{1}{2}\{v_j, \{\mathcal{U}_p, \partial_p \mathcal{U}_j\}\} + E_{VD} + \frac{1}{4}[[U_i, v_p], \partial_i U_p] \\ & - \frac{1}{2}\{\mathcal{U}_i, \partial_i(\boldsymbol{B} \cdot \mathcal{M})\} + \frac{1}{8}[\partial_p U_j, [\partial_j U_p, \varepsilon]] \,, \end{aligned} \tag{49}$$

where $\boldsymbol{\pi} = \boldsymbol{p} + \frac{1}{2}\boldsymbol{B} \times \boldsymbol{q}$ is the physical momentum before the transformation, $\alpha_{ij} = \partial_{ij}\varepsilon$ is the effective mass, $\mathcal{A} = \langle u_{n,\boldsymbol{p}} | i\partial \boldsymbol{p} | u_{n'\boldsymbol{p}'} \rangle$ is the Berry connection, $\mathcal{U} = \frac{1}{2}\boldsymbol{B} \times \mathcal{A}$ is the gauge momentum associated with the Berry connection, and $\mathcal{M}_k = -\epsilon_{ijk}\frac{1}{4}\{\mathcal{A}_i, V_j\}$ is the magnetic moment. Also, lower case letters $\boldsymbol{u}\,, \boldsymbol{a}\,, \boldsymbol{m}\,, \boldsymbol{v}$ are for the intraband part and upper case letters $\boldsymbol{U}\,, \boldsymbol{A}\,, \boldsymbol{M}\,, \boldsymbol{V}$

the interband part of $\mathcal{U}\,,\mathcal{A}\,,\mathcal{M}\,,\mathcal{V}$, respectively. The quantity E_{VD} is from the conventional perturbation theory:

$$E_{VD} = -\sum_{m\neq n} \frac{|\boldsymbol{B}\cdot\boldsymbol{M}_{nm} + (\boldsymbol{B}\times\boldsymbol{v})\cdot\boldsymbol{A}_{mn}|^2}{E_n - E_m}\,. \tag{50}$$

Position and momentum are the two fundamental observables in the semiclassical description. Hence it is useful to derive their appropriate forms in the single band representation as well. Applying the same transformation which digonalize the hamiltonian function, and one can find that the position operator $\hat{\boldsymbol{r}}$ and the mechanic momentum operator $\hat{\boldsymbol{\pi}} = (\hat{\boldsymbol{p}} + \frac{1}{2}\boldsymbol{B}\times\hat{\boldsymbol{r}})$ after transformation become

$$\boldsymbol{r} = \boldsymbol{q} + \boldsymbol{a}_{(n)} + \boldsymbol{\Omega}_{(n)}\times\frac{1}{2}(\boldsymbol{B}\times\boldsymbol{a}_{(n)}) + u_\ell\partial_\ell\boldsymbol{a}_{(n)} + [F,\boldsymbol{A}]_{(n)} + \frac{1}{2}\{D_\ell\boldsymbol{A}, U_\ell\}_{(n)}\,, \tag{51}$$

$$\begin{aligned}\boldsymbol{k} = \boldsymbol{p} &+ \frac{1}{2}\boldsymbol{B}\times\boldsymbol{q} + \boldsymbol{B}\times\boldsymbol{a}_{(n)} - \frac{1}{2}(\boldsymbol{B}\cdot\boldsymbol{\Omega}_{(n)})\boldsymbol{B}\times\boldsymbol{a}_{(n)} \\ &+ u_\ell\partial_\ell(\boldsymbol{B}\times\boldsymbol{a}_{(n)}) + \boldsymbol{B}\times[F,\boldsymbol{A}]_{(n)} + \frac{1}{2}\boldsymbol{B}\times\{D_\ell\boldsymbol{A}, U_\ell\}_{(n)}\,,\end{aligned} \tag{52}$$

where $\partial_\ell \equiv \frac{\partial}{\partial k_\ell}$, and n is the band index (hereafter I will drop the subscript n for simplicity). D_ℓ is defined to be the covariant derivative: $D_\ell X = \partial_\ell X - i[a_\ell, X]$ for some quantity X. And

$$F_{mm'} = \frac{\boldsymbol{E}\cdot\boldsymbol{A}_{mm'} - \frac{1}{2}\{\boldsymbol{B}\times\boldsymbol{v},\cdot\boldsymbol{A}\}_{mm'} + \frac{1}{4}\epsilon_{\ell ij}B_\ell\{A_i, V_j\}_{mm'}}{\varepsilon_m - \varepsilon_{m'}} \tag{53}$$

is a correction factor purely from interband interference effects. It should be noted that the expression of $\boldsymbol{r}$ is only valid up to the first order in external fields (see Eq.(51)), while the expression for $\boldsymbol{k}$ is valid to the second order.

This is because the second order terms in r would give contributions that are higher than second order in the equations of motion, hence they can be neglected in this treatment. This situation is analogous to the first order case, there we only need a zeroth order r for constructing the first order equations of motion.

Up to now, the expressions of the physical position and mechanical momentum projected into the n-th band are obtained, and so is the effective Hamiltonian function which governs the dynamic evolution. It is possible to build a semiclassical effective theory based on this information. The dynamics of the canonical variables is governed by the Hamiltonian equations of motion:

$$\begin{pmatrix} \dot{\boldsymbol{q}} \\ \dot{\boldsymbol{p}} \end{pmatrix} = \begin{pmatrix} \mathbf{0}_{3\times 3} & \boldsymbol{I}_{3\times 3} \\ -\boldsymbol{I}_{3\times 3} & \mathbf{0}_{3\times 3} \end{pmatrix} \begin{pmatrix} \frac{\partial H}{\partial \boldsymbol{q}} \\ \frac{\partial H}{\partial \boldsymbol{p}} \end{pmatrix} . \tag{54}$$

Eqs.(51)-(52) give non-canonical transformations from $(\boldsymbol{q}, \boldsymbol{p})$ to $(\boldsymbol{r}, \boldsymbol{k})$. They should also induce a change in the Hamiltonian function:

$$\mathcal{H}(\boldsymbol{r}(\boldsymbol{q}, \boldsymbol{p}), \boldsymbol{k}(\boldsymbol{q}, \boldsymbol{p})) = H(\boldsymbol{q}, \boldsymbol{p}) \tag{55}$$

In analogy with the classical equations of motion, the dynamics of the physical phase space variables reads:

$$\begin{pmatrix} \dot{\boldsymbol{r}} \\ \dot{\boldsymbol{k}} \end{pmatrix} = \begin{pmatrix} \{\boldsymbol{r}, \boldsymbol{r}\}_{PB} & \{\boldsymbol{r}, \boldsymbol{k}\}_{PB} \\ \{\boldsymbol{k}, \boldsymbol{r}\}_{PB} & \{\boldsymbol{k}, \boldsymbol{k}\}_{PB} \end{pmatrix} \begin{pmatrix} \frac{\partial \mathcal{H}}{\partial \boldsymbol{r}} \\ \frac{\partial \mathcal{H}}{\partial \boldsymbol{k}} \end{pmatrix} . \tag{56}$$

From Eqs.(51) and (52), one can find that:

$$\{r_i, r_j\}_{PB} = \frac{\epsilon_{\ell ij}\tilde{\Omega}_\ell}{1 + \boldsymbol{B}\cdot\tilde{\boldsymbol{\Omega}}} \tag{57}$$

$$\{r_i, p_j\}_{PB} = \frac{\delta_{ij} + B_i\tilde{\Omega}_j}{1 + \boldsymbol{B}\cdot\tilde{\boldsymbol{\Omega}}}\,, \tag{58}$$

$$\{p_i, p_j\}_{PB} = -\frac{\epsilon_{ij\ell}B_\ell}{1 + \boldsymbol{B}\cdot\tilde{\boldsymbol{\Omega}}}\,, \tag{59}$$

which are determined by two quantities: the magnetic field $\boldsymbol{B}$ and the modified Berry curvature $\tilde{\boldsymbol{\Omega}}$ with

$$\tilde{\boldsymbol{\Omega}}(\boldsymbol{k}) = \boldsymbol{\Omega}(\boldsymbol{k}) + \frac{1}{2}\nabla\times\{D_\ell\boldsymbol{A}, U_\ell\} + \nabla\times[F, \boldsymbol{A}]\,. \tag{60}$$

$\tilde{\boldsymbol{\Omega}}$ is the usual Berry curvature plus corrections that are first order in field. Substituting Eqs.(57)-(59) into Eq.(56), we finally obtain the equations of motion as

$$\dot{\boldsymbol{r}} = \frac{\partial\mathcal{H}}{\partial\boldsymbol{k}} - \dot{\boldsymbol{k}}\times\tilde{\boldsymbol{\Omega}}, \tag{61}$$

$$\dot{\boldsymbol{k}} = -\frac{\partial\mathcal{H}}{\partial\boldsymbol{r}} - \dot{\boldsymbol{r}}\times\boldsymbol{B}\,. \tag{62}$$

It is remarkable that the second order equations of motion retains a simple elegant structure. Compared with Eqs.(9)-(10), the only difference is that we need to work with the modified (more accurate) Hamiltonian and Berry curvature. The non-canonicality from these Poission brackets induces the correction to the density of states. Denote the Jacobian matrix from the canonical variables to physical variables by $\mathcal{J}$. Then the density of states is determined by the determinant of $\mathcal{J}$ [15]: $\mathcal{D} = \det(\mathcal{J})$. The result is

$$\mathcal{D} = 1 + \boldsymbol{B}\cdot\tilde{\boldsymbol{\Omega}}\,. \tag{63}$$

4 Electromagnetic Polarizability

In the first application, I would like to discuss the magnetoelectric polarizability. The corresponding response function is predicted to contain a Chern-Simons form, which should be quantized to integer multipliers of $e^2/2h$ by symmetry arguments. The semiclassical approach for the Chern-Simons form is examined by Xiao Di *et al.* [23] by using the non-Abelian electronic dynamics and modern theory of polarization. However, his method is not rigorous due to the first order accuracy of the semiclassical theory. Our theory can serve as part of the theoretical ground for his method.

This problem is now revisited from the modern theory of polarization. According to King-Smith and Vanderbilt [13], under an appropriate gauge choice for the Berry connection, the polarization for solids is:

$$\boldsymbol{P} = \int_{BZ} \frac{d^3k}{(2\pi)^3} \boldsymbol{a} \,. \tag{64}$$

This is the formula without external fields. The presence of a magnetic field $\boldsymbol{B}$ modifies it in two ways: (1) the density of states is altered by an amount of $\boldsymbol{B} \cdot \boldsymbol{\Omega}$; (2) the physical position obtains additional corrections: comparing with the zero field expression $\boldsymbol{r} = \boldsymbol{q} + \boldsymbol{a}$, the Berry connection is field shifted by the last four terms of Eq.(51). We take account of all these variations, collect terms of first order in external field and rewrite them in terms of the physical momentum $\boldsymbol{k}$. It is the trace part of the response function that should have

the Chern-Simons form, so finally we have:

$$\begin{aligned}\alpha &= \frac{1}{3}Tr\left(\frac{\partial P_i}{\partial B_j}\right) \\ &= -\int_{BZ}\frac{d^3k}{(2\pi)^3}\left(\frac{1}{2}\Omega\cdot\boldsymbol{a}+\frac{1}{3}[\frac{\partial F}{\partial B_i},A_i]\right. \\ &\qquad \left.+\frac{1}{6}\{\epsilon_{\ell im}D_\ell A_i,A_m\}\right). \end{aligned} \tag{65}$$

By using density operator perturbation technique and adiabatic pumping, Essin et al [11, 12] has obtained the general Chern-Simons 3-form for the electromagnetic polarizability. Note that the first term in Eq.(65) only involves single band quantities, and is exactly the same expression as obtained by A.M.Essin *et al.* [12] for the Abelian case. The other two terms correspond to the perturbative contributions stemming from the change of basis in previous papers [17, 23].

5 Magnetic Susceptibility

In the second application, I would like to examine the magnetization and its response to external fields. Start from the standard definition of the magnetization in statistical mechanics:

$$\boldsymbol{M} = -\frac{1}{V}\left(\frac{\partial G}{\partial \boldsymbol{B}}\right)_{\mu,T,V}, \tag{66}$$

where $G = U - TS - N\mu$ is the thermodynamics grand potential, and V the system volume. G can also be obtained from the partition function $G = Tr[g(\hat{\mathrm{H}})]$, with $g(\varepsilon) = -k_B T \ln\{1 + \exp[(\mu - \varepsilon)/k_B T]\}$.

For a single band semiclassical theory, the trace reduces to integration of the physical momentum over the Brillouin zone:

$$G = \int_{BZ} \mathcal{D} g_{PS} \frac{d^3k}{8\pi^3}, \tag{67}$$

where g_{PS} is the single state grand potential in the phase space. It contains two parts: $g_{PS} = g_{Landau} + g_{quasi}$. g_{Landau} is the Landau diamagnetic free energy, and its contribution to G is:

$$G_{Landau} = -\frac{1}{48} B_\lambda B_\nu \epsilon_{\lambda\ell k} \epsilon_{\mu\nu\rho} \int_{BZ} \frac{d^3k}{8\pi^3} \frac{\partial f_0(\varepsilon_n)}{\partial \varepsilon_n} \alpha_{\ell\nu} \alpha_{k\rho}, \tag{68}$$

where ε_n is the n-th band dispersion, f_0 the Fermi distribution function, and $\alpha_{k\rho} = \partial^2 \varepsilon_n / \partial \pi_k \partial \pi_\rho$ the effective mass tensor. For a simple metal, the effective mass tensor takes a diagonal form under principal axes, rendering a simplification of G_{Landau} to its standard form.

g_{quasi} is due to the modification of the quasi-particle energy $\mathcal{H}$. Applying an electric field may induce a current, driving the system away from

equilibrium. To avoid this, I assume that the n-th band is fully occupied. In this case one would also throw away $\boldsymbol{E}\cdot\boldsymbol{q}$ term in the electric potential energy. Then one rewrites the other second order Hamiltonian function in terms of physical variables, plugs it in $g(\varepsilon)$ and carrys on the Taylor series expansion to second order. Combining g_{PS} with Eqs. (16)-(17), one obtains:

$$\begin{aligned}\boldsymbol{M} = &\int_{BZ}\frac{d^3k}{8\pi^3}(\boldsymbol{m}f_0 - \boldsymbol{\Omega}g) - \int_{BZ}\frac{d^3k}{8\pi^3}\left(\frac{1}{2}\boldsymbol{a}\times(\boldsymbol{E}\times\boldsymbol{\Omega})f_0 + \boldsymbol{\Omega}(\boldsymbol{E}\cdot\boldsymbol{a})f_0\right.\\ &-\boldsymbol{m}(\boldsymbol{E}\cdot\boldsymbol{a})f_0' - \boldsymbol{a}\times\nabla(\boldsymbol{E}\cdot\boldsymbol{a})f_0 + \left[\frac{\partial F}{\partial\boldsymbol{B}}, \boldsymbol{E}\cdot\boldsymbol{A}\right]f_0\\ &\left.+\frac{1}{2}\hat{e}_i[D_\ell(\boldsymbol{E}\cdot\boldsymbol{A}), \epsilon_{ij\ell}A_j]f_0\right) - \frac{\partial}{\partial\boldsymbol{B}}(G_{Landau} + G_{quasi} + G_{orb-geo} + G_{geo})\,.\end{aligned} \tag{69}$$

The magnetization falls into three groups. The first group reproduces the magnetization obtained by Junren Shi *et al.* [18], and is an intrinsic contribution. The second group describes how the electric field would induce the magnetization. Taking its derivative with respect to the electric field would lead to the same result as Eq. (65) (assume zero temperature). The magnetic moment $\boldsymbol{m}$ is defined as: $\boldsymbol{m} = -1/4\epsilon_{ijk}\{r_j, \dot{r}_k\}$. So the electric field modifies the magnetic moment through altering the position or the velocity. Among the first four terms in the second group, the first one comes from the anomalous velocity, and it amounts to the surface Hall effect mentioned by A.M. Essin *et al.* [12]. The second and third term corresponds to the electric dipole shifted Fermi energy. For an insulator, the Fermi surface lies within the band gap, so the third term vanishes. The fourth term is due to the electric dipole modified velocity. They together yield the Chern-Simons form.

The third group would give rise to the magnetic susceptibility. G_{quasi} is the system grand potential soly due to the quasi-particle energy. It can be further divided into two parts: the Pauli paramagnetism contribution

$$G_{Pauli} = \int_{BZ} \frac{d^3k}{8\pi^3} f_0'(\boldsymbol{B}\cdot\boldsymbol{m})^2/2\,, \tag{70}$$

and the Van Vleck-like contribution

$$G_{VV} = \int_{BZ} \frac{d^3k}{8\pi^3} f_0 H^{(2)}\,. \tag{71}$$

Note that the Pauli contribution is not in the usual sense and may contain the magnetic moment due to the orbital motion. $G_{orb-geo}$ is characterized by the coupling between the orbital moment and density of states:

$$G_{orb-geo} = -\int_{BZ} \frac{d^3k}{8\pi^3} (\boldsymbol{B}\cdot\boldsymbol{\Omega})(\boldsymbol{B}\cdot\boldsymbol{m}) f_0\,. \tag{72}$$

Di Xiao *et al.* [25] have find a good realization of this term in graphene, when the inversion symmetry is broken by applying a staggered potential. G_{geo} is of purely geometric origin:

$$\begin{aligned} G_{geo} = \int_{BZ} \frac{d^3k}{8\pi^3} \Big(& \frac{1}{2}\boldsymbol{B}\cdot\nabla\times\{D_\ell \boldsymbol{A}, U_\ell\} \\ & + \boldsymbol{B}\cdot\nabla\times[F,\boldsymbol{A}]\Big)\, g\,. \end{aligned} \tag{73}$$

In a two band model, it will pick up the detailed geometric information of the band curve near the band bottom.

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Vita

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