Title: Dynamics of electrons in crystalline solids: Wannier functions, Berry curvature and related issues

Name: Gianluca Panati

Affil./Addr.: La Sapienza University of Rome

Rome, 00185 Italy

E-mail: panati@mat.uniroma1.it

Dynamics of electrons in crystalline solids: Wannier functions, Berry curvature and related issues

Synonyms

Dynamics of Bloch electrons; theory of Bloch bands; semiclassical model of solid-state physics.

Related entries

Mathematical quantum theory for crystals [00262]. Born-Oppenheimer approximation, adiabatic limit and related mathematical issues [00260]. Beyond the Born-Oppenheimer approximation [00251].

Definition/abstract

Crystalline solids are solids in which the ionic cores of the atoms are arranged periodically. The dynamics of a test electron in a crystalline solid can be conveniently analyzed by using the *Bloch-Floquet transform*, while the localization properties of electrons are

better described by using *Wannier functions*. The latter can also be obtained by minimizing a suitable localization functional, yielding a convenient numerical algorithm.

Macroscopic transport properties of electrons in crystalline solids are derived, by using adiabatic theory, from the analysis of a perturbed Hamiltonian, which includes the effect of external macroscopic or slowly-varying electromagnetic potentials. The geometric *Berry phase* and its curvature play a prominent role in the corresponding effective dynamics.

The periodic Hamiltonian

In a crystalline solid, the ionic cores are arranged periodically, according to a periodicity lattice $\Gamma = \left\{\gamma \in \mathbb{R}^d : \gamma = \sum_{j=1}^d n_j\,\gamma_j \text{ for some } n_j \in \mathbb{Z}\right\} \simeq \mathbb{Z}^d$, where $\{\gamma_1, \dots, \gamma_d\}$ are fixed linearly independent vectors in $\mathbb{R}^d$.

The dynamics of a test electron in the potential generated by the ionic cores of the solid and, in a mean-field approximation, by the remaining electrons is described by the Schrödinger equation $\mathrm{i}\partial_t\psi = H_{\mathrm{per}}\psi$, where the Hamiltonian operator reads (in Rydberg units)

$$H_{\mathrm{per}} = -\Delta + V_\Gamma(x) \qquad \text{acting in } L^2(\mathbb{R}^d). \tag{1}$$

Here $\Delta = \nabla^2$ is the Laplace operator and the function $V_\Gamma : \mathbb{R}^d \to \mathbb{R}$ is periodic with respect to Γ, *i.e.* $V_\Gamma(x+\gamma) = V_\Gamma(x)$ for all $\gamma \in \Gamma$, $x \in \mathbb{R}^d$. A mathematical justification of such a model in the reduced Hartree-Fock approximation was obtained in [CLL; CDL], see [entry 00262] and references therein.

To assure that H_{per} is self-adjoint in $L^2(\mathbb{R}^d)$ on the Sobolev space $W^{2,2}(\mathbb{R}^d)$, we make an usual Kato-type assumption on the Γ-periodic potential:

$$V_\Gamma \in L^2_{\mathrm{loc}}(\mathbb{R}^d) \text{ for } d \le 3, \qquad V_\Gamma \in L^p_{\mathrm{loc}}(\mathbb{R}^d) \text{ with } p > d/2 \text{ for } d \ge 4. \tag{2}$$

Clearly, the case of a potential with Coulomb-like singularities is included.

The Bloch-Floquet tranform (Bloch representation)

Since $H_{\rm per}$ commutes with the lattice translations, it can be decomposed as a direct integral of simpler operators by the (modified) Bloch-Floquet transform. Preliminarily, we define the dual lattice as $\Gamma^* := \left\{k \in \mathbb{R}^d : \ k \cdot \gamma \in 2\pi\mathbb{Z} \text{ for all } \gamma \in \Gamma\right\}$. We denote by Y (resp. Y^*) the centered fundamental domain of Γ (resp. Γ^*), namely

$$Y^* = \left\{k \in \mathbb{R}^d : k = \textstyle\sum_{j=1}^d k'_j\, \gamma^*_j \ \text{ for } k'_j \in [-\frac{1}{2}, \frac{1}{2}]\right\},$$

where $\{\gamma^*_j\}$ is the dual basis to $\{\gamma_j\}$, *i.e.* $\gamma^*_j \cdot \gamma_i = 2\pi\delta_{j,i}$. When the opposite faces of Y^* are identified, one obtains the torus $\mathbb{T}^*_d := \mathbb{R}^d/\Gamma^*$.

One defines, initially for $\psi \in C_0(\mathbb{R}^d)$, the modified **Bloch-Floquet transform** as

$$(\tilde{\mathcal{U}}_{\rm BF}\psi)(k,y) := \frac{1}{|Y^*|^{\frac{1}{2}}} \sum_{\gamma\in\Gamma} \mathrm{e}^{-\mathrm{i}k\cdot(y+\gamma)}\, \psi(y+\gamma), \qquad y \in \mathbb{R}^d,\, k \in \mathbb{R}^d. \tag{3}$$

For any fixed $k \in \mathbb{R}^d$, $\big(\tilde{\mathcal{U}}_{\rm BF}\psi\big)(k,\cdot)$ is a Γ-periodic function and can thus be regarded as an element of $\mathcal{H}_{\rm f} := L^2(\mathbb{T}_Y)$, $\mathbb{T}_Y$ being the flat torus $\mathbb{R}^d/\Gamma$. The map defined by (3) extends to a unitary operator $\tilde{\mathcal{U}}_{\rm BF} : L^2(\mathbb{R}^d) \longrightarrow \int^{\oplus}_{Y^*} \mathcal{H}_{\rm f}\, dk$, with inverse given by

$$\left(\tilde{\mathcal{U}}^{-1}_{\rm BF}\varphi\right)(x) = \frac{1}{|Y^*|^{\frac{1}{2}}} \int_{Y^*} dk\ \mathrm{e}^{\mathrm{i}k\cdot x}\varphi(k,[x]),$$

where $[\,\cdot\,]$ refers to the decomposition $x = \gamma_x + [x]$, with $\gamma_x \in \Gamma$ and $[x] \in Y$.

The advantage of this construction is that the transformed Hamiltonian is a fibered operator over Y^*. Indeed, one checks that

$$\tilde{\mathcal{U}}_{\rm BF}\, H_{\rm per}\, \tilde{\mathcal{U}}^{-1}_{\rm BF} = \int^{\oplus}_{Y^*} dk\, H_{\rm per}(k)$$

with fiber operator

$$H_{\rm per}(k) = \big(-\mathrm{i}\nabla_y + k\big)^2 + V_\Gamma(y)\,, \qquad k \in \mathbb{R}^d, \tag{4}$$

acting on the k-independent domain $W^{2,2}(\mathbb{T}_Y) \subset L^2(\mathbb{T}_Y)$. The latter fact explains why is mathematically convenient to use the *modified* BF transform. Each fiber operator

$H_{\rm per}(k)$ is self-adjoint, has compact resolvent and thus pure point spectrum accumulating at infinity. We label the eigenvalue increasingly, *i. e.* $E_0(k) \leq E_1(k) \leq E_2(k) \leq \ldots$. With this choice, they are Γ^*-periodic, *i. e.* $E_n(k+\lambda) = E_n(k)$ for all $\lambda \in \Gamma^*$. The function $k \mapsto E_n(k)$ is called the nth **Bloch band**.

For fixed $k \in Y^*$, one considers the eigenvalue problem

$$H_{\rm per}(k)\, u_n(k,y) = E_n(k)\, u_n(k,y), \qquad \|u_n(k,\cdot)\|_{L^2(\mathbb{T}_Y)} = 1. \tag{5}$$

A solution to the previous eigenvalue equation (*e. g.* by numerical simulations) provides a complete solution to the dynamical equation induced by (1). Indeed, if the initial datum ψ_0 satisfies

$$(\tilde{\mathcal{U}}_{\rm BF}\, \psi_0)(k,y) = \varphi(k)\, u_n(k,y) \quad \text{ for some } \varphi \in L^2(Y^*),$$

(one says in jargon that "ψ_0 is concentrated on the nth band") then the solution $\psi(t)$ to the Schrödinger equation with initial datum ψ_0 is characterized by

$$(\tilde{\mathcal{U}}_{\rm BF}\, \psi(t))(k,y) = \left(\mathrm{e}^{-\mathrm{i}E_n(k)t}\varphi(k)\right) u_n(k,y).$$

In particular, the solution is exactly concentrated on the nth band at any time. By linearity, one recovers the solution for any initial datum. Below, we will discuss to which extent this dynamical description survives when macroscopic perturbations of the operator (1) are considered.

Wannier functions and charge localization

While the Bloch representation is a useful tool to deal with dynamical and energetic problems, it is not convenient to study the localization of electrons in solids. A related crucial problem is the construction of a basis of generalized eigenfunctions of the operator $H_{\rm per}$ which are exponentially localized in space. Indeed, such a basis allows to develop computational methods which scale linearly with the system size [Go], makes

possible the description of the dynamics by *tight-binding* effective Hamiltonians, and plays a prominent role in the modern theories of macroscopic polarization [KSV; Re] and of orbital magnetization[TCVR].

A convenient system of localized generalized eigenfunctions has been proposed by Wannier [Wa]. By definition, a **Bloch function** corresponding to the n^{th} Bloch band is any u satisfying (5). Clearly, if u is a Bloch function then $\tilde{u}$, defined by $\tilde{u}(k,y) = \mathrm{e}^{\mathrm{i}\vartheta(k)}\, u(k,y)$ for any Γ^*-periodic function ϑ, is also a Bloch function. The latter invariance is often called *Bloch gauge invariance*.

Definition 1. *The* ***Wannier function*** $w_n \in L^2(\mathbb{R}^d)$ *corresponding to a Bloch function* u_n *for the Bloch band* E_n *is the preimage of* u_n *with respect to the Bloch-Floquet transform, namely*

$$w_n(x) := \left(\tilde{\mathcal{U}}_{\text{BF}}^{-1} u_n\right)(x) = \frac{1}{|Y^*|^{\frac{1}{2}}} \int_{Y^*} dk\ \mathrm{e}^{\mathrm{i}k\cdot x} u_n(k,[x]).$$

The translated Wannier functions are

$$w_{n,\gamma}(x) := w_n(x-\gamma) = \frac{1}{|Y^*|^{\frac{1}{2}}} \int_{Y^*} dk\ \mathrm{e}^{-\mathrm{i}k\cdot\gamma}\ \mathrm{e}^{\mathrm{i}k\cdot x} u_n(k,[x]), \qquad \gamma \in \Gamma.$$

Thus, in view of the orthogonality of the trigonometric polynomials and the fact that $\tilde{\mathcal{U}}_{\text{BF}}$ is an isometry, the functions $\{w_{n,\gamma}\}_{\gamma\in\Gamma}$ are mutually orthogonal in $L^2(\mathbb{R}^d)$. Moreover, the family $\{w_{n,\gamma}\}_{\gamma\in\Gamma}$ is a complete orthonormal basis of $\tilde{\mathcal{U}}_{\text{BF}}^{-1}\,\text{Ran}\,P_*$, where $P_*(k)$ is the spectral projection of $H_{\text{per}}(k)$ corresponding to the eigenvalue $E_n(k)$ and $P_* = \int_{Y^*}^{\oplus} P_*(k)\, dk$.

In view of the properties of the Bloch-Floquet transform, the existence of an exponentially localized Wannier function for the Bloch band E_n is equivalent to the existence of an analytic and Γ^*-pseudoperiodic Bloch function (recall that (3) implies that the Bloch function must satisfy $u(k+\lambda,y) = \mathrm{e}^{-\mathrm{i}\lambda\cdot y}\, u(k,y)$ for all $\lambda \in \Gamma^*$). A local argument assures that there is always a choice of the Bloch gauge such that the Bloch

function is analytic around a given point. However, as several authors noticed [Cl; Ne2], there might be topological obstruction to obtain a global analytic Bloch function, in view of the competition between the analyticity and the pseudoperiodicity.

Hereafter, we denote by $\sigma_*(k)$ the set $\{E_i(k) : n \leq i \leq n+m-1\}$, corresponding to a physically relevant family of m Bloch bands, and we assume the following *gap condition*:

$$\inf_{k\in\mathbb{T}_d^*} \operatorname{dist}\left(\sigma_*(k), \sigma(H(k)) \setminus \sigma_*(k)\right) > 0. \tag{6}$$

If a Bloch band E_n satisfies (6) for $m = 1$ we say that it is an single isolated Bloch band. For $m > 1$, we refer to a composite family of Bloch bands.

Single isolated Bloch band

In the case of a single isolated Bloch band, the problem of proving the existence of exponentially localized Wannier functions was raised in 1959 by W. Kohn [Ko], who solved it in dimension $d = 1$. In higher dimension, the problem has been solved, always in the case of a single isolated Bloch band, by J. des Cloizeaux [Cl] (under the non generic hypothesis that V_Γ has a center of inversion) and finally by G. Nenciu under general hypothesis [Ne1], see also [HS] for an alternative proof. Notice, however, that in real solids it might happen that the interesting Bloch band (*e. g.* the conduction band in graphene) is not isolated from the rest of the spectrum and that $k \mapsto P_*(k)$ is not smooth at the degeneracy point. In such a case, the corresponding Wannier function decreases only polynomially.

Composite family of Bloch bands

It is well-known that, in dimension $d > 1$, the Bloch bands of crystalline solids are not, in general, isolated. Thus the interesting problem, in view of real applications, concerns the case of composite families of bands, *i. e.* $m > 1$ in (6), and in this context

the more general notion of *composite Wannier functions* is relevant [Bl], [Cl]. Physically, condition (6) is always satisfied in semiconductors and insulators, by considering the family of all the Bloch bands up to the Fermi energy.

Given a composite family of Bloch bands, we consider the orthogonal projector (in Dirac's notation)

$$P_*(k) := \sum_{i=n}^{n+m-1} |u_i(k)\rangle \langle u_i(k)| ,$$

which is independent from the Bloch gauge, and we pose $P_* = \int_{Y^*}^{\oplus} P_*(k)\, dk$. A function χ is called a **quasi-Bloch function** if

$$P_*(k)\chi(k,\cdot) = \chi(k,\cdot) \quad \text{and} \quad \chi(k,\cdot) \neq 0 \qquad \forall k \in Y^*. \tag{7}$$

Although the terminology is not standard, we call **Bloch frame** a set $\{\chi_a\}_{a=1,\dots,m}$ of quasi-Bloch functions such that $\{\chi_1(k), \dots, \chi_m(k)\}$ is an orthonormal basis of $\operatorname{Ran} P_*(k)$ at (almost-)every $k \in Y^*$. As in the previous case, there is a gauge ambiguity: a Bloch frame is fixed only up to a k-dependent unitary matrix $U(k) \in \mathcal{U}(m)$, *i. e.* if $\{\chi_a\}_{a=1,\dots,m}$ is a Bloch frame then the functions $\widetilde{\chi}_a(k) = \sum_{b=1}^m \chi_b(k) U_{b,a}(k)$ also define a Bloch frame.

Definition 2. *The* ***composite Wannier functions*** *corresponding to a Bloch frame* $\{\chi_a\}_{a=1,\dots,m}$ *are the functions*

$$w_a(x) := \left(\tilde{\mathcal{U}}_{\mathrm{BF}}^{-1}\chi_a\right)(x), \qquad a \in \{1, \dots, m\} .$$

As in the case of a single Bloch band, the exponential localization of the composite Wannier functions is equivalent to the analyticity of the corresponding Bloch frame (which, in addition, must be Γ^*-pseudoperiodic). As before, there might be topological obstruction to the existence of such a Bloch frame. As far as the operator (1) is concerned, the existence of exponentially localized composite Wannier functions has been proved in [Ne1] in dimension $d = 1$; as for $d > 1$, the problem remained unsolved

for more than two decades, until recently [Pa; BPCM]. Notice that for *magnetic* periodic Schrödinger operators the existence of exponentially localized Wannier functions is generically false.

The Marzari-Vanderbilt localization functional

To circumvent the long-standing controversy about the existence of exponentially localized composite Wannier functions, and in view of the application to numerical simulations, the solid-state physics community preferred to introduce the alternative notion of *maximally localized Wannier functions* [MaVa]. The latter are defined as the minimizers of a suitable localization functional, known as the Marzari-Vanderbilt (MV) functional. For a single-band normalized Wannier function $w \in L^2(\mathbb{R}^d)$, the localization functional is

$$F_{MV}(w) = \int_{\mathbb{R}^d} |x|^2 |w(x)|^2 dx - \sum_{j=1}^{d} \left(\int_{\mathbb{R}^d} x_j |w(x)|^2 dx \right)^2, \tag{8}$$

which is well-defined at least whenever $\int_{\mathbb{R}^d} |x|^2 |w(x)|^2 dx < +\infty$. More generally, for a system of L^2-normalized composite Wannier functions $w = \{w_1, \dots, w_m\} \subset L^2(\mathbb{R}^d)$ the **Marzari-Vanderbilt localization functional** is

$$F_{MV}(w) = \sum_{a=1}^{m} F_{MV}(w_a) = \sum_{a=1}^{m} \int_{\mathbb{R}^d} |x|^2 |w_a(x)|^2 dx - \sum_{a=1}^{m} \sum_{j=1}^{d} \left(\int_{\mathbb{R}^d} x_j |w_a(x)|^2 dx \right)^2. \tag{9}$$

We emphasize that the above definition includes the crucial constraint that the corresponding Bloch functions $\varphi_a(k, \cdot) = (\tilde{\mathcal{U}}_{\mathrm{BF}}\, w_a)(k, \cdot)$, for $a \in \{1, \dots, m\}$, are a Bloch frame.

While such approach provided excellent results from the numerical viewpoint, the existence and exponential localization of the minimizers have been investigated only recently [PaPi].

Dynamics in macroscopic electromagnetic potentials

To model the transport properties of electrons in solids, one modifies the operator (1) to include the effect of the external electromagnetic potentials. Since the latter vary at the laboratory scale, it is natural to assume that the ratio ε between the lattice constant $a = |Y|^{1/d}$ and the length-scale of variation of the external potentials is small, *i. e.* $\varepsilon \ll 1$. The original problem is replaced by

$$\mathrm{i}\,\varepsilon\,\partial_\tau \psi(\tau, x) = \left(\frac{1}{2} \left(-\mathrm{i}\nabla_x - A(\varepsilon x) \right)^2 + V_\Gamma(x) + V(\varepsilon x) \right) \psi(\tau, x) \equiv H_\varepsilon \psi(\tau, x) \tag{10}$$

where $\tau = \varepsilon t$ is the macroscopic time, and $V \in C^\infty_{\mathrm{b}}(\mathbb{R}^d, \mathbb{R})$ and $A_j \in C^\infty_{\mathrm{b}}(\mathbb{R}^d, \mathbb{R})$, $j \in \{1, \ldots, d\}$, are respectively the external electrostatic and magnetic potential. Hereafter, for the sake of a simpler notation, we consider only $d = 3$.

While the dynamical equation (10) is quantum mechanical, physicists argued [Bl] that for suitable wavepackets, which are localized on the n^{th} Bloch band and spread over many lattice spacings, the main effect of the periodic potential V_Γ is the modification of the relation between the momentum and the kinetic energy of the electron, from the free relation $E_{\text{free}}(k) = \frac{1}{2}k^2$ to the function $k \mapsto E_n(k)$ given by the n^{th} Bloch band. Therefore the semiclassical equations of motion are

$$\begin{cases} \dot{r} = \nabla E_n(\kappa) \\ \dot{\kappa} = -\nabla V(r) + \dot{r} \times B(r) \end{cases} \tag{11}$$

where $r \in \mathbb{R}^3$ is the macroscopic position of the electron, $\kappa = k - A(r)$ is the kinetic momentum with $k \in \mathbb{T}^*_d$ the Bloch momentum, $-\nabla V$ the external electric field and $B = \nabla \times A$ the external magnetic field.

In fact, one can derive also the first-order correction to (11). At this higher accuracy, the electron acquires an effective k-dependent electric moment $\mathcal{A}_n(k)$ and

magnetic moment $\mathcal{M}_n(k)$. If the n^{th} Bloch band is non-degenerate (hence isolated), the former is given by the **Berry connection**

$$\mathcal{A}_n(k) = \mathrm{i}\,\langle u_n(k)\,,\,\nabla_k u_n(k)\rangle_{\mathcal{H}_{\mathrm{f}}} = \mathrm{i}\int_Y u_n(k,y)^*\,\nabla_k u_n(k,y)\,dy,$$

and the latter reads $\mathcal{M}_n(k) = \frac{\mathrm{i}}{2}\,\langle \nabla_k u_n(k)\,,\,\times(H_{\mathrm{per}}(k) - E_n(k))\nabla_k u_n(k)\rangle_{\mathcal{H}_{\mathrm{f}}}$, *i. e.* explicitly

$$\big[\mathcal{M}_n(k)\big]_i = \frac{\mathrm{i}}{2}\sum_{1\leq j,\,l\leq 3}\epsilon_{ij\,l}\,\big\langle \partial_{k_j} u_n(k)\,,\,(H_{\mathrm{per}}(k) - E_n(k))\partial_{k_l} u_n(k)\big\rangle_{\mathcal{H}_{\mathrm{f}}}$$

where $\epsilon_{ij\,l}$ is the totally antisymmetric symbol. The refined semiclassical equations read

$$\begin{cases} \dot{r} = \nabla_\kappa\,(E_n(\kappa) - \varepsilon B(r)\cdot\mathcal{M}_n(\kappa)) - \varepsilon\dot{\kappa}\times\Omega_n(\kappa) \\ \dot{\kappa} = -\nabla_r\,(V(r) - \varepsilon B(r)\cdot\mathcal{M}_n(\kappa)) + \dot{r}\times B(r) \end{cases} \tag{12}$$

where $\Omega_n(k) = \nabla\times\mathcal{A}_n(k)$ corresponds to the curvature of the Berry connection. The previous equations have a hidden Hamiltonian structure [PSpT]. Indeed, by introducing the semiclassical Hamiltonian function $H_{\mathrm{sc}}(r,\kappa) = E_n(\kappa) + V(r) - \varepsilon B(r)\cdot\mathcal{M}_n(\kappa)$, equations (12) become

$$\begin{pmatrix} \mathbb{B}(r) & -\mathbb{I} \\ \mathbb{I} & \varepsilon\,\mathbb{A}_n(\kappa) \end{pmatrix}\begin{pmatrix} \dot{r} \\ \dot{\kappa} \end{pmatrix} = \begin{pmatrix} \nabla_r H_{\mathrm{sc}}(r,\kappa) \\ \nabla_\kappa H_{\mathrm{sc}}(r,\kappa) \end{pmatrix} \tag{13}$$

where $\mathbb{I}$ is the identity matrix and $\mathbb{B}$ (resp. $\mathbb{A}_n$) is the 3×3 matrix corresponding to the vector field B (resp. Ω_n), *i. e.* $\mathbb{B}_{l,m}(r) = \sum_{1\leq j\leq 3}\epsilon_{lmj}B_j(r) = (\partial_l A_m - \partial_m A_l)(r)$. Since the matrix appearing on the l.h.s corresponds to a symplectic form $\Theta_{B,\varepsilon}$ (*i. e.* a non-degenerate closed 2-form) on $\mathbb{R}^6$, equations (13) have Hamiltonian form with respect to $\Theta_{B,\varepsilon}$.

The mathematical derivation of the semiclassical equations (12) from (10) as $\varepsilon\to 0$ has been accomplished in [PSpT]. The first order correction to the semiclassical equations (11) was previously investigated in [SuNi], but the heuristic derivation in the latter paper does not yield the term of order ε in the second equation. Without such a

term, is not clear if the equations have a Hamiltonian structure.

As for mathematically related problems, both the semiclassical asymptotic of the spectrum of H_ε and the corresponding scattering problem have been studied in detail (see [GMS] and references therein). The effective quantum Hamiltonians corresponding to (10) for $\varepsilon \to 0$ have also been deeply investigated [Ne2].

The connection between (10) and (12) can be expressed either by an Egorov-type theorem involving quantum observables, or by using Wigner functions. Here we focus on the second approach.

Fist we define the Wigner function. We consider the space $\mathcal{C} = C_{\rm b}^\infty(\mathbb{R}^{2d})$ equipped with the standard distance $d_{\mathcal{C}}$, and the subspace of Γ^*-periodic observables

$$\mathcal{C}_{\rm per} = \{a \in \mathcal{C} : a(r, k+\lambda) = a(r,k) \;\forall\, \lambda \in \Gamma^*\}.$$

Recall that according to the Calderon-Vaillancourt theorem there is a constant C such that for $a \in \mathcal{C}$ its Weyl quantization $\widehat{a} \in \mathcal{B}(L^2(\mathbb{R}^3))$ satisfies

$$|\,\langle\psi,\, \widehat{a}\,\psi\rangle_{L^2(\mathbb{R}^3)}\,| \,\leq\, C\, d_{\mathcal{C}}(a,0)\,\|\psi\|^2\,.$$

Hence, the map $\mathcal{C} \ni a \mapsto \langle\psi,\, \widehat{a}\,\psi\rangle \in \mathbb{C}$ is linear continuous and thus defines an element W_ε^ψ of the dual space $\mathcal{C}'$, the Wigner function of ψ. Writing

$$\langle\psi,\, \widehat{a}\,\psi\rangle =: \langle W_\varepsilon^\psi,\, a\rangle_{\mathcal{C}',\mathcal{C}} =: \int_{\mathbb{R}^{2d}} a(q,p)\, W_\varepsilon^\psi(q,p)\, dq\, dp$$

and inserting the definition of the Weyl quantization for a one arrives at the formula

$$W_\varepsilon^\psi(q,p) = \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} d\xi\, \mathrm{e}^{\mathrm{i}\xi\cdot p}\, \psi^*(q+\varepsilon\xi/2)\, \psi(q-\varepsilon\xi/2), \tag{14}$$

which yields $W_\varepsilon^\psi \in L^2(\mathbb{R}^{2d})$. Although W_ε^ψ is real-valued, it attains also negative values in general, so it does not define a probability distribution on phase space.

After this preparation, we can vaguely state the link between (10) and (12), see [TePa] for the precise formulation. Let E_n be an isolated, non-degenerate Bloch band. Denote

by $\overline{\Phi}_\varepsilon^\tau(r,k)$ the flow of the dynamical system (12) in canonical coordinates $(r,k) = (r,\kappa + A(r))$ (recall that the Weyl quantization, and hence the definition of Wigner function, is not invariant under non-linear changes of canonical coordinates). Then for each finite time-interval $I \subset \mathbb{R}$ there is a constant C such that for $\tau \in I$, $a \in \mathcal{C}_{\rm per}$ and for ψ_0 "well-concentrated on the $n^{\rm th}$ Bloch band" one has

$$\left| \int_{\mathbb{R}^{2d}} a(q,p) \left(W_\varepsilon^{\psi(\tau)}(q,p) - W_\varepsilon^{\psi_0} \circ \overline{\Phi}_\varepsilon^{-\tau}(q,p) \right) dq\, dp \right| \leq \varepsilon^2\, C\, d_{\mathcal{C}}(a,0)\, \|\psi_0\|^2 \,,$$

where $\psi(t)$ is the solution to the Schrödinger equation (10) with initial datum ψ_0.

Slowly-varying deformations and piezoelectricity

To investigate the contribution of the electrons to the macroscopic polarization and to the piezoelectric effect, it is crucial to know how the electrons move in a crystal which is strained at the macroscopic scale. Assuming the usual *fixed-lattice approximation*, the problem can be reduced to study the solutions to

$$\mathrm{i}\, \partial_t \psi(t,x) = \left(-\frac{1}{2}\Delta + V_\Gamma(x,\varepsilon t) \right) \psi(t,x) \tag{15}$$

for $\varepsilon \ll 1$, where $V_\Gamma(\cdot,t)$ is Γ-periodic for every $t \in \mathbb{R}$, *i. e.* the periodicity lattice does not depend on time. While a model with a fixed lattice might seem unrealistic at first glance, we refer to [Re][KSV] for its physical justification. The analysis of the Hamiltonian $H(t) = -\frac{1}{2}\Delta + V_\Gamma(x,t)$ yields a family of time-dependent Bloch functions $\{u_n(k,t)\}_{n\in\mathbb{N}}$ and Bloch bands $\{E_n(k,t)\}_{n\in\mathbb{N}}$.

Assuming that the relevant Bloch band is isolated from the rest of the spectrum, so that (6) holds true at every time, and that the initial datum is well-concentrated on the $n^{\rm th}$ Bloch band, one obtains a semiclassical description of the dynamics analogous to (12). In this case, the semiclassical equations read

$$\begin{cases} \dot{r} = \nabla_k E_n(k,t) - \varepsilon\, \Theta_n(k,t) \\ \dot{\kappa} = 0 \end{cases} \tag{16}$$

where

$$\Theta_n(k,t) = -\partial_t \mathcal{A}_n(k,t) - \nabla_k \phi_n(k,t)$$

with

$$\mathcal{A}_n(k,t) = \mathrm{i}\,\langle u_n(k,t)\,,\, \nabla_k u_n(k,t)\rangle_{\mathcal{H}_\mathrm{f}} \qquad \phi_n(k,t) = -\mathrm{i}\,\langle u_n(k,t)\,,\, \partial_t u_n(k,t)\rangle_{\mathcal{H}_\mathrm{f}}\,.$$

The notation emphasizes the analogy with the electromagnetism: if $\mathcal{A}_n(k,t)$ and $\phi_n(k,t)$ are interpreted as the geometric analogous of the vector potential and of the electrostatic scalar potential, then $\Theta_n(k,t)$ and $\Omega_n(k,t)$ correspond, respectively, to the electric and to the magnetic field.

One can rigorously connect (15) and the semiclassical equations (16), in the spirit of the result stated at the end of the previous section, see [PSbT]. From (16) one obtains the **King-Smith and Vanderbilt formula** [KSV], which approximately predicts the contribution ΔP of the electrons to the macroscopic polarization of a crystalline insulator strained in the time interval $[0,T]$, namely

$$\Delta P = \frac{1}{(2\pi)^d} \sum_{n\in N_\mathrm{occ}} \int_{Y*} (\mathcal{A}_n(k,T) - \mathcal{A}_n(k,0))\, dk\,, \tag{17}$$

where the sum runs over all the occupied Bloch bands, *i. e.* $N_\mathrm{occ} = \{n \in \mathbb{N} \ : E_n(k,t) \leq E_F\}$ with E_F the Fermi energy. Notice that (17) requires the computation of the Bloch functions only at the initial and at the final time; in view of that, the previous formula is the starting point of any *state-of-the-art* numerical simulation of macroscopic polarization in insulators.

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