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Exponential localization of Wannier functions in insulators

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The exponential localization of Wannier functions is proved in dimensions 2 and 3, settling a long-standing conjecture. The proof relies on an equivalence between the nullity of the first Chern class defined by the Berry connection and the triviality of the Bloch bundle. The analytic quasi-Bloch functions are shown to satisfy an explicit equation and a condition for the reality of the Wannier functions is given. More generally, the vanishing of the Hall current or of the Chern numbers is equivalent to the exponential localization of the Wannier functions.

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The description of the band structure of an insulator with an orthonormal and exponentially localized basis is a crucial issue since it allows for the development of computational methods scaling linearly with the system size[1] and it yields a more familiar understanding of the physics in term of tight-binding Hamiltonians with short range parameters. Maximally localized Wannier functions[2] are an answer to the problem since they form an orthonormal basis, but they are not necessarily exponentially localized. Kohn showed [3] that in one dimensional insulators a basis of exponentially localized Wannier functions exists, however Kohn's demonstration cannot be extended to higher dimensions. Thus for realistic materials it is not known if exponentially localized Wannier functions exist.

In this work we demonstrate the existence of exponentially localized Wannier functions in two and three dimensions. We outline a practical method to obtain them and determine the conditions for their reality.

We consider a crystal with a Bravais lattice Γ and a unit cell C . The reciprocal lattice is denoted by Γ^* and the reciprocal unit cell by Ω . A function $f(\mathbf{r})$ is Γ -periodic if $f(\mathbf{r} + \mathbf{R}) = f(\mathbf{r})$ for any direct-lattice vector \mathbf{R} in Γ , while a function $f(\mathbf{k})$ is Γ^* -periodic if $f(\mathbf{k} + \mathbf{G}) = f(\mathbf{k})$ for any reciprocal-lattice vector \mathbf{G} in Γ^* . In addition, a function $f_{\mathbf{k}}(\mathbf{r})$ is called Γ^* -covariant if $f_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = e^{-i\mathbf{G}\cdot\mathbf{r}}f_{\mathbf{k}}(\mathbf{r})$. The dynamics of the electrons in the crystal is described by a Hamiltonian $H = -\Delta + V(\mathbf{r})$ (in Ry), where the potential V is real and Γ -periodic. According to Bloch's theorem, the eigenfunctions of H can be written as $\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$, where the Bloch states $u_{n\mathbf{k}}(\mathbf{r})$ are Γ -periodic and Γ^* -covariant. The Bloch states $u_{n\mathbf{k}}$ are eigenstates of the Hamiltonian $H(\mathbf{k}) = (-i\nabla + \mathbf{k})^2 + V(\mathbf{r})$ with energy $\epsilon_n(\mathbf{k})$.

Wannier functions are defined as

$$w_n(\mathbf{r} - \mathbf{R}) = \frac{1}{|\Omega|} \int_{\Omega} d\mathbf{k} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})} u_{n\mathbf{k}}(\mathbf{r}), \quad (1)$$

where $|\Omega|$ is the volume of Ω . The localization properties of the Wannier functions are related to the regularity of $u_{n\mathbf{k}}$ as a function of \mathbf{k} . In a nutshell, the more regular the states, the more localized the Wannier functions [3, 4, 5]. Exponential decay is obtained if and only if the functions are analytic [4].

In the simplest procedure, the energies $\epsilon_n(\mathbf{k})$ and the Bloch functions $u_{n\mathbf{k}}$ are determined as a function of \mathbf{k} by ordering the eigenvalues by increasing energies $\epsilon_1(\mathbf{k}) \leq \epsilon_2(\mathbf{k}) \leq \dots$. Although this procedure is standard in band-structure calculations, it gives Bloch states $u_{n\mathbf{k}}$ that are not regular in \mathbf{k} since the phase of $u_{n\mathbf{k}}$ is random. Moreover, at a crossing point the energy $\epsilon_n(\mathbf{k})$ has usually a kink. In one dimension, Kohn [3] showed that the phase and the ordering of the Bloch states can be chosen so that the Bloch states are analytic functions of \mathbf{k} . In three dimensions this is generally not possible [4].

This problem can be partially solved for a *composite band*, i.e. a set of eigenstates (take $\epsilon_1(\mathbf{k}), \dots, \epsilon_M(\mathbf{k})$ for definiteness) which are isolated from the others. More precisely, there is a $a > 0$ such that $|\epsilon_n(\mathbf{k}) - \epsilon_m(\mathbf{k}')| > a$ for any \mathbf{k} and \mathbf{k}' in Ω , $1 \leq n \leq M$ and $m > M$. In insulators it is always possible to isolate a composite band since gaps exist between valence and conduction bands and between valence bands and core states. This is not necessarily the case in metals. An example of a composite band is given in fig.1 for Silicon. Exponentially localized Wannier functions are obtained if we can find M analytic functions $v_{n\mathbf{k}}$ (called *quasi-Bloch* states) that span the same vector space as the M Bloch states of the composite band. The problem of the existence of analytic quasi-Bloch states was solved for a single isolated band (i.e. $M = 1$) in 3D by des Cloizeaux[4] and Nenciu[6]. In this work we show that analytic quasi-Bloch functions exist for any composite band 2D and 3D. For definiteness, we consider in detail the 3D case.

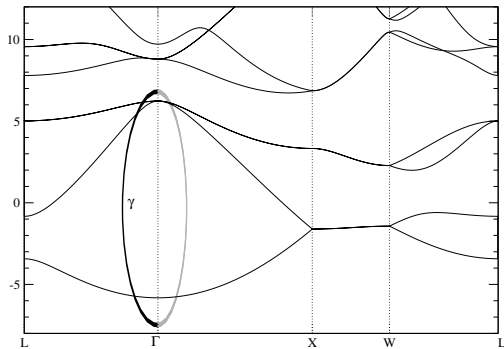


FIG. 1: Band structure of silicon. The contour γ encloses the energies of the composite band.

The quasi-Bloch functions $v_{n\mathbf{k}}$ can be expressed as $v_{n\mathbf{k}} = \sum_m u_{m\mathbf{k}}(\mathbf{r})U_{mn}^{(\mathbf{k})}$, where $U(\mathbf{k})$ is a unitary matrix. The corresponding Wannier functions are

$$w_n(\mathbf{r}) = \frac{1}{|\Omega|} \int_{\Omega} d\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}} \sum_m u_{m\mathbf{k}}(\mathbf{r})U_{mn}^{(\mathbf{k})}. \quad (2)$$

To study the analytic properties of $\epsilon_n(\mathbf{k})$ and $u_{n\mathbf{k}}$ we perform the analytic continuation of these functions in the complex plane, namely $\mathbf{k} = \mathbf{k}' + i\mathbf{k}''$. The branch points of $\epsilon_n(\mathbf{k})$ determine the points of non-analyticity of the function $u_{n\mathbf{k}}$ [3, 7]. Even very simple crystals, such as silicon, exhibit such branch points [8].

We define the norm of a function u by $\|u\| = \int_C |u(\mathbf{r})|^2 d\mathbf{r}$ and we denote by $L^2(C)$ the set of Γ -periodic functions $u(\mathbf{r})$ such that $\|u\| < +\infty$. The (Sobolev) space $W^2(C)$ is the set of functions that are in $L^2(C)$ together with their first and second derivatives. We assume that the potential $V(\mathbf{r})$ is real and in $L^2(C)$. This condition encompasses potentials with Coulomb singularities and the potentials used in LDA and GGA calculations.

The Hamiltonian $H(\mathbf{k})$ is polynomial in \mathbf{k} , its domain is $W^2(C)$. Thus, $H(\mathbf{k})$ is an analytic family of type (A) [9, 10]. The reality of $V(\mathbf{r})$ implies that $H^\dagger(\mathbf{k}) = H(\mathbf{k}^*)$ and $H^*(\mathbf{k}) = H(-\mathbf{k}^*)$. When \mathbf{k} is complex, $H(\mathbf{k})$ is not Hermitian but there still are eigenvalues $\epsilon_n(\mathbf{k})$ and eigenstates $u_{n\mathbf{k}}$ in $W^2(C)$ such that $H(\mathbf{k})u_{n\mathbf{k}} = \epsilon_n(\mathbf{k})u_{n\mathbf{k}}$. The calculation of band structures in the complex plane is available in some standard band-structure packages [11].

For a given \mathbf{k} , $P(\mathbf{k}) = \sum_{n=1}^M |u_{n\mathbf{k}}\rangle\langle u_{n\mathbf{k}^*}|$ defines a projector [7]. The space $F(\mathbf{k})$ is the M -dimensional vector space generated by the Bloch states $u_{n\mathbf{k}}$, i.e. the image of $P(\mathbf{k})$. The Riesz formula for the projector is

$$P(\mathbf{k}) = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z - H(\mathbf{k})}.$$

where γ is a contour enclosing all the eigenvalues $\epsilon_{n\mathbf{k}}$ of the composite band (see fig.1). $P(\mathbf{k})$ is analytic in \mathbf{k} on a strip $\Omega_C = \{\mathbf{k} = \mathbf{k}' + i\mathbf{k}'', \mathbf{k}' \in \Omega, |\mathbf{k}''_j| < A, j = 1, 2, 3\}$

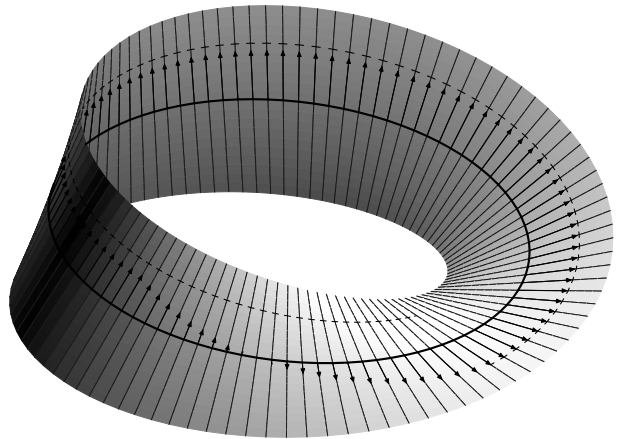


FIG. 2: Möbius bundle. The solid circle is the base B and the thin straight lines are the fibers $F(x)$. The dashed line represents the continuous but not periodic basis vector field $\mathbf{e}(x)$. The arrows represent the continuous and periodic vector field $\mathbf{v}(x)$. It is clear that $\mathbf{v}(x)$ has to be zero for some x .

with $A > 0$ even if the states $|u_{n\mathbf{k}}\rangle$ are not analytic in \mathbf{k} [4]. An example of this contour for Si is given in Fig. 1. The quasi-Bloch states $v_{n\mathbf{k}}$ are a basis of $F(\mathbf{k})$ where each $v_{n\mathbf{k}}$ is analytic in \mathbf{k} , Γ -periodic and Γ^* -covariant.

As noted by several authors [4, 6, 12], the existence of quasi-Bloch states is directly connected to the topology of a *vector bundle* [13]. We illustrate first with a simple example how the topology of a vector bundle is related to the existence of an analytic and periodic basis.

A vector bundle is essentially a space E comprised of a manifold B (the base) and a vector space $F(x)$ (the fiber) attached to each point x of B . In the simplest example, B is a circle and $F(x)$ is a one-dimensional real vector space. This is visualized in Fig. 2. To each point x of the circle $0 \leq x \leq 2\pi$ we can attach a vector $\mathbf{v}(x)$ which is an element of $F(x)$. Topology intervenes when we determine how the fiber at $x = 0$ is related to the fiber at $x = 2\pi$: we can use periodic boundary conditions $\mathbf{v}(2\pi) = \mathbf{v}(0)$ or antiperiodic boundary conditions $\mathbf{v}(2\pi) = -\mathbf{v}(0)$. In the first case the bundle is a cylinder, in the second it is a Möbius strip.

We want to define a vector $\mathbf{v}(x)$ that is regular, (anti)periodic and such that $\mathbf{v}(x)$ generates the fiber $F(x)$. On the bundle we define a basis $\mathbf{e}(x)$ of $F(x)$ that is regular and of constant length 1, so that $\mathbf{e}(2\pi) = \mathbf{e}(0)$. Thus, we are looking for a real function $y(x)$ such that $\mathbf{v}(x) = y(x)\mathbf{e}(x)$ satisfies the boundary conditions. If the bundle is a cylinder, one can take $y(x) = 1$ for all x . There is no topological obstruction and the vector bundle is said to be trivial. If the bundle is a Möbius strip, $y(2\pi) = -y(0)$; since the function $y(x)$ is regular, by the intermediate value theorem there needs to be a point x between 0 and 2π such that $y(x) = 0$, as shown in Fig. 2. At this x , $\mathbf{v}(x)$ is zero and thus cannot be a basis of $F(x)$.

For a composite band the base of the bundle is Ω_C and

for each point \mathbf{k} the fiber is $F(\mathbf{k})$. The boundary conditions are: if \mathbf{k} and $\mathbf{k} + \mathbf{G}$ are in $\Omega_{\mathbb{C}}$ for some $\mathbf{G} \in \Gamma^*$, we require that $v_{n\mathbf{k}+\mathbf{G}}(\mathbf{r}) = e^{-i\mathbf{G}\cdot\mathbf{r}}v_{n\mathbf{k}}(\mathbf{r})$ for $n = 1, \dots, M$. This vector bundle is called a Bloch bundle [14]. A bundle for which analytic quasi-Bloch states exist is called a trivial bundle [13]. The manifold $\Omega_{\mathbb{C}}$ is a kind of three-dimensional complex manifold called a Stein manifold. As a consequence, Oka's principle [14], shows that the triviality of the analytic bundle is equivalent to the triviality of the differentiable bundle over the six dimensional real manifold made of Ω (corresponding to the real part of \mathbf{k} in $\Omega_{\mathbb{C}}$) times the three dimensional cube $] -A, A[$ ³ (corresponding to the imaginary part of \mathbf{k} in $\Omega_{\mathbb{C}}$). The cube is contractible (i.e. it can continuously be shrunk to a point). Thus, a bundle over $\Omega_{\mathbb{C}}$ is trivial if and only if it is trivial over Ω (see [15], p. 450 for a precise statement). For general manifolds, the Chern classes are not sufficient to classify vector bundles [16]. But it can be proved [14] that in the case of a Bloch bundle over Ω , the nullity of the first Chern class of the m -dimensional unitary principal bundle over Ω is equivalent, in one, two or three dimensions, to having a trivial vector bundle. In other words, quasi-Bloch states exist if and only if the first Chern class of the bundle is zero.

The triviality of the Bloch bundle is also equivalent to the existence of an analytic family of bounded invertible operators $\mathcal{U}(\mathbf{k})$ such that $P(\mathbf{k}) = \mathcal{U}(\mathbf{k})P(0)\mathcal{U}^{-1}(\mathbf{k})$ and $\mathcal{U}(\mathbf{k})^\dagger = \mathcal{U}(\mathbf{k}^*)^{-1}$, so that $\mathcal{U}(\mathbf{k})$ is unitary for real \mathbf{k} [14]. A local explicit expression for $\mathcal{U}(\mathbf{k})$ is provided by the Nagy-Kato formula [9]

$$\mathcal{U}(\mathbf{k}) = \left(1 - (P(\mathbf{k}) - P(0))^2\right)^{-1/2} \left(P(\mathbf{k})P(0) + (1 - P(\mathbf{k}))(1 - P(0))\right).$$

However, it is valid only if $\|P(\mathbf{k}) - P(0)\| < 1$. If we choose an orthonormal basis v_n of $F(0)$, then the vectors $v_{n\mathbf{k}} = \mathcal{U}(\mathbf{k})v_n$ are quasi-Bloch states.

It remains to prove that the first Chern class of the bundle over Ω is zero. For that purpose, we introduce the Berry connection corresponding to a basis $v_{n\mathbf{k}}$ of $F(\mathbf{k})$, defined as the vector of matrix functions $\mathbf{A}(\mathbf{k}) = (A^1(\mathbf{k}), A^2(\mathbf{k}), A^3(\mathbf{k}))$ with matrix elements

$$\mathbf{A}_{mn}(\mathbf{k}) = \int_{\mathcal{C}} v_{m\mathbf{k}}^*(\mathbf{r}) \nabla_{\mathbf{k}} v_{n\mathbf{k}}(\mathbf{r}) d\mathbf{r}.$$

The curvature of this connection is [2, 14]

$$\begin{aligned} B^{ij}(\mathbf{k}) &= \text{tr} \left(\frac{\partial A^j}{\partial k_i} - \frac{\partial A^i}{\partial k_j} + [A^i, A^j] \right) \\ &= \text{Tr} \left(P(\mathbf{k}) \left[\frac{\partial P(\mathbf{k})}{\partial k_i}, \frac{\partial P(\mathbf{k})}{\partial k_j} \right] \right), \end{aligned}$$

where tr is the matrix trace and Tr the operator trace. The time-reversal symmetry $P(\mathbf{k}) = (P(-\mathbf{k}))^*$ implies that $B^{ij}(-\mathbf{k}) = -B^{ij}(\mathbf{k})$.

The first Chern class is the cohomology class of $(i/2\pi)\text{tr}B(\mathbf{k})$ in the second cohomology group $H^2(\Omega)$ [13]. To determine it, we use the pairing between cohomology and homology groups. The manifold Ω is isomorphic to a 3-torus, so that its second homology group is $H_2(\Omega) = \mathbb{R}^3$ [13]. A basis of $H_2(\Omega)$ is provided by the 2-cycles $\Theta_\ell = \{\mathbf{k} \in \Omega, k_\ell = 0\}$, for $\ell = 1, 2, 3$. Thus, the coupling between the curvature and $H_2(\Omega)$ is given by the three Chern numbers (in 2D there is only one Chern number)

$$C_\ell = \frac{i}{2\pi} \sum_{ij} \int_{\Theta_\ell} B^{ij}(\mathbf{k}) dk_i \wedge dk_j.$$

$B^{ij}(-\mathbf{k}) = -B^{ij}(\mathbf{k})$ implies that $C_\ell = 0$. We know by de Rham's theorem, that the pairing is non-degenerate [13]. Thus, the vanishing of the three Chern numbers C_1, C_2 and C_3 implies that the first Chern class is zero. As a corollary, we deduce that no exponentially localized Wannier functions exist for Chern insulators (i.e. insulators with non-zero Chern numbers [17]) and that Chern insulators cannot exist if the Hamiltonian and the ground state are time-reversal symmetric (this was noticed by Haldane [18] for the case $M = 1$).

With this result in hand, two forms of the exponential localization of the Wannier functions are obtained: (i) by using a version of the Paley-Wiener theorem (Theorem IX.13 of ref. [19]), we find that $e^{b|\mathbf{r}|}w_n(\mathbf{r})$ is square integrable over \mathbb{R}^3 for any $b < A$; (ii) by repeating the reasoning of des Cloizeaux (section III.B of ref.4), we see that $\lim_{|R| \rightarrow \infty} e^{b|R|}w_n(\mathbf{r} - \mathbf{R}) = 0$ for any $b < A$.

The condition that $V(\mathbf{r})$ is square integrable is satisfied by potentials with Coulomb singularity. However, for some applications, relativistic perturbations (e.g. spin-orbit or Darwin terms) are added to $H(\mathbf{k})$. These perturbations contain terms involving $\nabla V(\mathbf{r})$ which are not square integrable for potentials with Coulomb singularities and the exponential localization of the Wannier function is no longer ensured. Further terms of the relativistic expansion would be still more singular. This problem was noticed a long time ago by chemists [20] and various methods were proposed to solve it [21]. The technically simplest solution is to define relativistic Wannier functions. The Hamiltonian $H(\mathbf{k})$ is derived from the Dirac equation [22] $H(\mathbf{k}) = -ic\boldsymbol{\alpha} \cdot (\nabla + i\mathbf{k}) + \beta c^2/2 + V(\mathbf{r})$. As for the case of the Schrödinger equation, if the real periodic potential $V(\mathbf{r})$ is square integrable, then there exist exponentially localized relativistic Wannier functions for a composite band. The main difficulty is again the triviality of the Bloch-Dirac bundle, proved in ref. 14.

Given the existence of analytic quasi-Bloch functions $v_{n\mathbf{k}}$, we need a practical method to determine the unitary matrix $U(\mathbf{k})$ such that $v_{n\mathbf{k}}(\mathbf{r}) = \sum_m U_{mn}^{(\mathbf{k})} u_{m\mathbf{k}}(\mathbf{r})$. Being analytic, the quasi-Bloch functions satisfy the Cauchy-Riemann equation $\bar{\partial} v_{n\mathbf{k}} = 0$, where $\bar{\partial} = (\bar{\partial}_x, \bar{\partial}_y, \bar{\partial}_z)$ and, if $\mathbf{k} = \mathbf{k}' + i\mathbf{k}''$, $\bar{\partial}_j = (1/2)(\partial_{k'_j} + i\partial_{k''_j})$. If we de-

note by $\mathbf{u}(\mathbf{k})$ and $\mathbf{v}(\mathbf{k})$ the vectors with components $u_{n\mathbf{k}}$ and $v_{n\mathbf{k}}$, the Cauchy-Riemann equation gives us $\bar{\partial}\mathbf{v} = (\bar{\partial}\mathbf{u})U + \mathbf{u}(\bar{\partial}U) = 0$. Multiplying by the conjugate of \mathbf{u} , we find $\bar{\partial}U = XU$, where $X_{mn}(\mathbf{k}) = -\langle u_{m-\mathbf{k}}^* | \bar{\partial}u_{n\mathbf{k}} \rangle$. Note that, on regions where $u_{n\mathbf{k}}$ is analytic, $X_{mn}(\mathbf{k}) = 0$. The equation $\bar{\partial}U = XU$ should be solved in the space of Γ^* -periodic matrices $U(\mathbf{k})$ such that $U(\mathbf{k})^\dagger = U(\mathbf{k}^*)^{-1}$. This condition ensures the orthogonality of the quasi-Bloch functions on the real axis. Explicit integral expressions are available to solve the Cauchy-Riemann equation $\bar{\partial}f = g$ [23]. They turn $\bar{\partial}U = XU$ into an integral equation that can be solved numerically.

Note that, if U is a particular solution of $\bar{\partial}U = XU$, the general solution can be written UA , where A is any Γ^* -periodic analytic matrix satisfying $A(\mathbf{k})^\dagger = A(\mathbf{k}^*)^{-1}$. For instance, $A(\mathbf{k})$ can be any matrix of the form $A(\mathbf{k}) = \exp(\sum_{\mathbf{R}} a_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}})$, where the sum is over a finite number of sites of Γ and the matrices $a_{\mathbf{R}}$ satisfy $a_{\mathbf{R}}^\dagger = -a_{-\mathbf{R}}$. This very large set of solutions corresponds to the fact that exponential decay is a long-range property: any finite linear combination of exponentially decaying Wannier functions centered on various sites is still exponentially decaying. Therefore, once analytic $v_{n\mathbf{k}}$ are found, it is still necessary to search for Wannier functions that are localized on atoms [2] by properly choosing $A(\mathbf{k})$. This would provide Wannier functions that are localized on the short and long range.

It is convenient to determine under which condition the Wannier functions are real. In eq. (2), we take the complex conjugate and change the variable $\mathbf{k} \rightarrow -\mathbf{k}$

$$w_n^*(\mathbf{r}) = \frac{1}{|\Omega|} \sum_m \int_{\Omega} d\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}} u_{m-\mathbf{k}}^*(\mathbf{r}) (U_{mn}^{(-\mathbf{k})})^*.$$

The reality of $V(\mathbf{r})$ implies that we can choose $u_{m-\mathbf{k}}^*(\mathbf{r}) = u_{m\mathbf{k}}(\mathbf{r})$. Thus, the Wannier functions are real if $(U_{mn}^{(-\mathbf{k})})^* = U_{mn}^{(\mathbf{k})}$ for real \mathbf{k} . This property is satisfied if U has the symmetry $U(-\mathbf{k}^*) = U(\mathbf{k})^*$ for complex \mathbf{k} .

Wannier functions are often obtained by minimizing a functional $\Omega(U)$ [2]. The time-reversal symmetry I acts as $(IU)_{mn}^{(\mathbf{k})} = (U_{mn}^{(-\mathbf{k})})^*$ for real \mathbf{k} . If the functional Ω satisfies the symmetry $\Omega(IU) = \Omega(U)$ and if Ω has a unique minimum (up to a possible overall phase), then $U = IU$ and the Wannier functions are real. The spread functional Ω defined by Marzari and Vanderbilt [2] satisfies the symmetry $\Omega(IU) = \Omega(U)$. Thus, when the spread functional has a unique minimum U , the corresponding Wannier functions are real. This solves the so-called Marzari-Vanderbilt conjecture [2].

In this paper, we assumed that the system is time-reversal symmetric. If this is not the case (e.g. in the presence of an external magnetic field), the present approach implies that exponentially localized Wannier functions exist when the Chern numbers of the Bloch bundle are zero or, equivalently, when the Hall current is zero. Thus, the vanishing of the Hall current is a measure of the

exponential localization of the Wannier functions. This confirms rigorously Thouless' observation [24].

Electron localization is related to many fundamental problems in solid state physics: electric polarization[25], piezoelectricity, orbital magnetization[26] and the nature of the insulating state. A satisfactory description of these phenomena uses geometrical concepts such as (Berry) connections and Chern numbers. Here we have shown that geometrical methods solve the old problem of the existence of exponentially localized Wannier functions in two and three dimensions.

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