Generalized Wannier Functions

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February 2, 2008

Abstract
We consider single particle Schrödinger operators with a gap in the energy spectrum. We construct a countable set of exponentially decaying functions, which form a complete, orthonormal basis set for the states below the spectral gap. Each such function is localized near a closed surface. Estimates on the exponential decay rate and a discussion of the geometry of these surfaces is included.

1 Introduction
The fast developing field of nano-science and the need for microscopic understanding of the biological processes are just two of the driving forces for the search of computationally efficient electronic structure algorithms. One important goal is to develop electronic structure algorithms that scale linearly with the number of particles. It seems that such algorithms will involve a localized, real-space description of the electronic structure [1] and, of course, Wannier functions will play a major role [2, 3].

The Wannier functions were originally defined for perfectly periodic crystals [4]. Their key property is the exponential localization, which has been proven for 1D periodic systems [5] and for simple bands in more than 1 dimension [6, 7, 8].

A natural and important question is if one can define the equivalent of the Wannier functions for systems that are not periodic. Examples of such generalized Wannier functions were given by Kohn and Onffroy [9] for crystals with one impurity and Rehr and Kohn [10] for crystals with surfaces. In a relatively recent paper [11], Nenciu conjectured that any system with a gap in the energy spectrum should posses exponentially localized Wannier functions and he proved the conjecture in one dimension. His proof is based on an idea introduced by Kivelson [12], who showed that, for 1D perfectly periodic systems, the eigenvectors of $P_0 x P_0$ provide a set of Wannier functions ($P_0 =$ the band projection operator). Moreover, it was later shown by Marzari and Vanderbilt [13] that these Wannier functions are maximally localized. Now, if one tries to extend Kivelson’s construction to more than one dimension, the problem is that, even for perfectly periodic systems, $P_0 x P_0$, $P_0 y P_0$ and $P_0 z P_0$ do not commute, and any of these three operators have, in general, continuum spectrum and, consequently, no localized eigenvectors.

In this paper, we propose an alternative way of looking into the problem. Let us first state our main result. Consider a $\nabla^2$-bounded potential $v$ over $\mathbb{R}^d$ ($d = 1, 2, \ldots$), with relative
bound less than one. We consider only potentials that are bounded from below. Measuring the energy from the bottom of the potential, it is equivalent to say that the potentials are positive. Other than this, the only assumption on \( v \) is that the self-adjoint Hamiltonian,

\[
H : \mathcal{D}(-\nabla^2) \to L^2(\mathbb{R}^d), \quad H = -\nabla^2 + v,
\]

has a gap in the energy spectrum. Let \( \mathcal{K} \) be the space of all the states below the gap. Our goal is to construct a countable set of orthonormal functions, all decaying exponentially and forming a complete basis set for \( \mathcal{K} \). The solution is given in the following theorem.

**Theorem 1.** For \( q > 0 \), let \( W_q \) be the following bounded, self-adjoint operator:

\[
W_q : \mathcal{K} \to \mathcal{K}, \quad W_q \equiv P_0 e^{-q\rho} P_0,
\]

where \( \rho = [1 + r^2]^{1/2} \). Then the following are true.

i) The spectrum of \( W_q \), \( \sigma(W_q) \), is discrete.

ii) All eigenvectors decay exponentially (with the same rate) as \( |\vec{r}| \to \infty \).

Since \( W_q \) is self-adjoint and \( \sigma(W_q) \) is discrete, its eigenvectors form a complete and orthonormal basis for \( \mathcal{K} \). Thus, simply by solving for the eigenvalues of \( W_q \), one can construct a complete (in \( \mathcal{K} \)), orthonormal and exponentially decaying set of functions. These functions will not have all the localization properties listed in Ref. [11]. Instead we can prove that the eigenvector corresponding to the eigenvalue \( \lambda_i \) is exponentially localized around the sphere of radius

\[
r_i = \sqrt{\left(\frac{\ln \lambda_i}{q}\right)^2 - 1},
\]

and centered at the origin. We believe that such an eigenvector is localized around one or more points on the sphere and, in general, the localization in the direction normal to the sphere is exponential while the localization parallel to the sphere is not. However, these functions can be as useful as the usual Wannier functions. For example, the matrix element of the Hamiltonian, between a state localized around the sphere of radius \( r_{i-m} \) and a state localized around the sphere of radius \( r_{i+n} \), decays exponentially with \( m \) and \( n \).

By simply modifying the function form of \( \rho \), we can obtain generalized Wannier functions that are localized around more general closed surfaces (like ellipsoids, etc.).

## 2 Proof of the main statement

The proof of our main statement involves the analytic continuation technique, first used by des Cloizeaux [6, 7] in the context of band calculations. Let \( P_0 \) denote the projection operator onto the states below the gap. Let \( E_{\pm} \) denote the upper respectively the lower edge of the gap \( \Delta \) and consider the unitary transformation \( e^{-iq\rho} \), with \( q \) real. We define the following unitarily equivalent representations of the band projector operator:

\[
P_0(q) = e^{-iq\rho} P_0 e^{iq\rho}.
\]
We will show later that we can analytically extend this family to complex $q$. More precisely:

**Lemma 1.** $P_0(q)$ extends to an analytic family of bounded operators,

$$\|P_0(q)\| < \infty, \quad (5)$$

for any $q$ in a complex strip $|\text{Im}q| < q_M$ ($\|A\| = \sup_{\|\psi\|=1} \sqrt{\langle A\psi, A\psi \rangle}$, for any operator $A$). Moreover, $q_M$ is always larger than

$$q_c = q_0 \left( \sqrt{1 + \Delta/q_0^2} - 1 \right), \quad (6)$$

where $q_0 = \sqrt{E_-} + \sqrt{E_+}$.

We start the proof of Theorem 1. i). We write $W_q$ as

$$W_q = P_0 \int_{\Gamma} e^{-q\rho}(z-H)^{-1} \frac{dz}{2\pi i}, \quad (7)$$

with $\Gamma$ a contour surrounding the lower band. Since $e^{-q\rho}(p^2 + a)^{-1}$ is Hilbert-Schmidt [14] and $(p^2 + a)(z-H)^{-1}$ is bounded, it follows that $W_q$ is Hilbert-Schmidt. As a consequence, $\sigma(W_q)$ is discrete. Moreover, the eigenvalues accumulate at zero and only at zero.

ii) Let $\psi$ be a normalized eigenvector, $W_q \psi = \lambda \psi$ (of course, $P_0 \psi = \psi$). Since

$$\lambda = \int e^{-q\rho} |\psi(\vec{r})|^2 d\vec{r}, \quad (8)$$

and $\rho \geq 1$, all eigenvalues are strictly positive and smaller than $e^{-q}$.

Let us consider first the case when $q$ is smaller than the $q_M$ of Lemma 1. In this situation we can prove

$$\int e^{2q\rho} |\psi(\vec{r})|^2 d\vec{r} < \infty, \quad (9)$$

which clearly shows that $|\psi(\vec{r})|$ decays faster than $e^{-q\rho}$ as $|\vec{r}| \to \infty$. Indeed, observing that $e^{q\rho}W_q = P_0(iq)P_0$, we find

$$\left[ \int e^{2q\rho} |\psi(\vec{r})|^2 d\vec{r} \right]^{1/2} = \|e^{q\rho} \psi\| = \lambda^{-1}\|e^{q\rho}W_q \psi\| = \lambda^{-1}\|P_0(iq)\psi\| \leq \lambda^{-1}\|P_0(iq)\|, \quad (10)$$

and, by definition, $q_M$ is the maximum value of $q$ for which $\|P_0(iq)\| < \infty$.

For the case when $q \geq q_M$, one can show that

$$\int e^{2q\rho} |\psi(\vec{r})|^2 d\vec{r} < \infty, \quad (11)$$

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for any $k < q_M$. Indeed,

$$
\|e^{ik\rho}\psi\| = \lambda^{-1} \|P_0(ik)e^{-(q-k)\rho}\psi\| \leq \lambda^{-1} \|P_0(ik)\| < \infty
$$

and this completes the proof of Theorem 1.

Thus, any $W_q$ with $q > 0$ provide a complete and orthonormal set of exponentially decaying functions. The exponential decay rate is larger or equal to the minimum between $q$ and $q_M$.

We now discuss their localization. We will limit ourselves to the case $q \leq q_M$. Let us write the eigenvalues of $W_q$ as $\lambda_i = e^{-q\rho_i}$. Since $\lambda_i$ are positive and accumulate at zero, $\{\rho_i\}_i$ is a sequence of positive numbers which accumulate at infinity. If $\psi_i$ is an eigenvector corresponding to $\lambda_i$, then we have from Eq. (8),

$$
\int e^{q(\rho - \rho_i)}|\psi_i(\vec{r})|^2d\vec{r} = 1
$$

and from Eqs. (10),

$$
\int e^{2q(\rho - \rho_i)}|\psi_i(\vec{r})|^2d\vec{r} \leq \|P_0(iq)\|^2.
$$

Observing that the right side of the last two equations is independent of the index $i$, we can conclude that $\psi_i$ is exponentially localized (to annihilate the exponential factors) around the sphere defined by $\rho = \rho_i$, i.e. the sphere of radius $r_i$ given in Eq. (3). More precisely, $\psi_i$ falls off exponentially with a rate $q$ as $\rho - \rho_i \rightarrow \infty$ and with a rate $q/2$ as $\rho - \rho_i \rightarrow -\infty$. Of course, the maximum localization is obtained when $q = q_M$.

The rest of the paper contains the proof of Lemma 1, which provides a lower bound for $q_M$. This lower bound can be easily estimated from the band structure and we found, from numerical calculations, that $q_c$ is a very good approximation of $q_M$ for small gaps.

### 3 Proof of Lemma 1

The proof follows Barbaroux et al [15]. We will try to eliminate the unnecessary constants and optimize the technique.

**Proposition.** Consider $A$ and $B$, two bounded, self-adjoint operators. Assume that $A$ has a spectral gap located at 0,

$$
d_{\pm} \equiv \text{dist}(\sigma_{\pm}(A), 0) > 0,
$$

where $\sigma_{\pm}$ denote the parts of the spectrum located above and below zero. Let $P_{\pm}$ denote the spectral projector onto the states corresponding to $\sigma_{\pm}(A)$ and $C > 0$ be a bounded self-adjoint operator such that $s_+ \equiv d_+ - \|P_+CP_+\| > 0$. Then, for $q$ real,

$$
\|(A - C + iqB)^{-1}\| \leq \left(1 - \frac{|q|}{q}\right)^{-1} \max\left\{\frac{1}{s_+}, \frac{1}{d_-}\right\},
$$

(16)
where
\[ \tilde{q} = \frac{\sqrt{s_+d_-}}{\|P_+BP_-\|}. \] (17)

**Proof.** Let \( \varphi \) be a norm one but otherwise arbitrary vector, \( \varphi_{\pm} = P_{\pm}\varphi \) and \( B_{+-} = P_+BP_- \). We start from the observation
\[ \Re \langle \varphi_+ - \varphi_-, (A - C + iqB)\varphi \rangle \leq \|(A - C + iqB)\varphi\|. \] (18)
The left hand side is equal to,
\[ \langle \varphi_+, (A - C)\varphi_+ \rangle - \langle \varphi_-, (A - C)\varphi_- \rangle - 2q \text{Im} \langle \varphi_+, B\varphi_- \rangle, \] (19)
and we have successively:
\[ \|(A - C + iqB)\varphi\| \] (20)
\[ \geq s_+ \|
\begin{pmatrix} \varphi_+ \end{pmatrix}\|^2 + d_- \|
\begin{pmatrix} \varphi_- \end{pmatrix}\|^2 - 2|q| \|B_{+-}\| \|
\begin{pmatrix} \varphi_+ \end{pmatrix}\| \|
\begin{pmatrix} \varphi_- \end{pmatrix}\|
\]
\[ = (1 - |q|/\tilde{q}) (s_+ \|
\begin{pmatrix} \varphi_+ \end{pmatrix}\|^2 + d_- \|
\begin{pmatrix} \varphi_- \end{pmatrix}\|^2) \\
+ |q| \|B_{+-}\| \left( 4\sqrt{s_+} \|
\begin{pmatrix} \varphi_+ \end{pmatrix}\| - 4\sqrt{d_-} \|
\begin{pmatrix} \varphi_- \end{pmatrix}\| \right)^2, \]
\[ \geq (1 - |q|/\tilde{q}) \min\{s_+, d_-\} \] (21)
and the affirmation follows. \([\blacksquare]\)

We define the following analytic family,
\[ H_q = e^{-iq\rho}He^{iq\rho} = H + q^2|\nabla\rho|^2 + q \left( \nabla\rho \cdot \vec{p} + \vec{p} \cdot \nabla\rho \right), \] (22)
where we notice that \( |\nabla\rho| \leq 1 \). Since \( \nabla\rho \cdot \vec{p} + \vec{p} \cdot \nabla\rho \) is relatively \( H \)-bounded, \( H_q \) extends to an analytic family of type A over the entire complex plane [16]. Then, according to Combes and Thomas [17],
\[ P_0(q) = \int_{\Gamma} (z - H_q)^{-1} \frac{dz}{2\pi i}, \] (23)
where \( \Gamma \) surrounds the lower band. One can see that \( P_0(q) \) belongs to an analytic family of bounded operators as long as \( \Gamma \) belongs to the resolvent set of \( H_q \). As we will argue later, we have to worry only about the point where \( \Gamma \) crosses the real axis. We consider then an energy \( E \) in the spectral gap and calculate for which values of \( q \) the resolvent \( (H_q - E)^{-1} \) remains a bounded operator. It is enough to consider only purely imaginary \( q \). In the above Proposition, we take
\[ A = \|H - E\|^{-1/2}(H - E)|H - E|^{-1/2}, \] (24)
\[ B = |H - E|^{-1/2}(\nabla\rho \cdot \vec{p} + \vec{p} \cdot \nabla\rho)|H - E|^{-1/2} \] (25)
\[ C = q^2 |H - E|^{-1/2} |\nabla \rho|^2 |H - E|^{-1/2}. \] (26)

Then we have \( d_- = 1 \) and \( s_+ = 1 - q^2/(E_+ - E) \), and we evaluate \( \| B_{+\pm} \| \) from,

\[
\| B_{+\pm} \| = \sup_{\varphi_+, \varphi_-} \left| \left\langle |H - E|^{-1/2} \varphi_+, \nabla \rho \cdot \vec{p} |H - E|^{-1/2} \varphi_- \right\rangle \right|
+ \left\langle \nabla \rho \cdot \vec{p} |H - E|^{-1/2} \varphi_+, |H - E|^{-1/2} \varphi_- \right\rangle ,
\] (27)

where the supremum goes over all norm one \( \varphi_+ \) and \( \varphi_- \) in the upper respectively lower band. If

\[
\psi_\pm = (H + a)^{1/2} |E - H|^{-1/2} \varphi_\pm, \] (28)

for some positive \( a \), then we find

\[
\| B_{+\pm} \| \leq \left\| p(H + a)^{-1/2} \right\| \left( \sqrt{\| \psi_- \|} + \sqrt{\| \psi_+ \|} \right). \] (29)

Since the potential is positive, \( \| p(H + a)^{-1/2} \| \leq 1 \) for all \( a > 0 \). We take the limit \( a = 0 \) and use the spectral theorem to evaluate \( \| \psi_\pm \| \) and finally find

\[
\| B_{+\pm} \| \leq \frac{\sqrt{E_-} + \sqrt{E_+}}{\sqrt{(E_+ - E)(E - E_-)}}. \] (30)

From Eq. (16), we can conclude

\[
\left\| |H - E|^{1/2} (H_{iq} - E)^{-1} |H - E|^{1/2} \right\| \leq \frac{1}{s_+ (1 - |q|/\tilde{q})}, \] (31)

where

\[
\tilde{q} = \frac{\sqrt{(E - E_-) (E_+ - E - q^2)}}{\sqrt{E_-} + \sqrt{E_+}}. \] (32)

The optimal position of the energy \( E \) in the spectral gap for \( \tilde{q} \) to become maximum is \( E_c = (E_- + E_+ - q^2)/2 \) which leads to \( \tilde{q} = (\Delta - q^2)/2q_0 \). Then from Eq. (31),

\[
\| (H_{iq} - E_c)^{-1} \| \leq \frac{\Delta + q^2}{\Delta - q^2} \frac{2}{\Delta - q^2 - 2q_0 |q|}, \] (33)

and the right side is finite as long as

\[
q < q_0 \left( \sqrt{1 + \Delta/q_0^2} - 1 \right). \] (34)

As one can easily see, adding an imaginary part to \( E_c \) will not affect the real part in Eq. (18) and the immediate consequence of this is that \( (H_{iq} - E_c + i\varepsilon)^{-1} \) is bounded as long as \( (H_{iq} - E_c)^{-1} \) is bounded. Consequently, for \( |\text{Im} q| < q_c \), we can always find a curve \( \Gamma \) surrounding the lower band and lying in the resolvent set of \( H_{iq} \).
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