Reply to "Comment on 'Existence of Wannier-Stark localization' "

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The argument of Emin and Hart is not that the staircase potential does not couple Bloch states of different energy bands; it does. Rather, the net effect of such interband terms on Wannier-Stark localization is argued to vanish. A new proof of a relationship disputed by Page and Brown is presented. The contradiction that Page and Brown claim results from this relationship is shown to be an artifact of their use of an incomplete set of basis states.

The application of a spatially constant electric field has two effects on the periodic potential of a carrier of charge q in a one-dimensional periodic solid. First, the electric field equivalently alters the shape of each potential well. Second, the electric field shifts the energies of the potential wells of different primative cells relative to one another. The first effect maintains the translational degeneracy of the solid while the second does not. Thus the second effect can give rise to (Wannier-Stark) localization.[1-4]

To take account of these two distinct effects, Emin and Hart[4] express the potential energy of the electric field $-qEx$ as the sum of a (periodic) sawtooth function and a (nonperiodic) staircase function, with both functions having characteristic lengths equal to the fundamental lattice constant a. By incorporating the periodic sawtooth component into the periodic potential, Emin and Hart reduce the problem of Wannier-Stark localization to a study of the effect of the staircase potential on the eigenstates of an electron in a periodic (albeit, electric-field-dependent) potential. An electronic eigenstate is then expressed as a superposition of electric-field-dependent Bloch states $|E;n,k\rangle=\exp(ikx)u_{n,k}(E,x)$ of energy $\varepsilon(E;n,k)$ arising from the periodic potential composed of the solid's periodic potential plus the electric-field-dependent sawtooth periodic potential. Here n is the band index and k is the wave vector. In terms of the expansion coefficients $A_i(E;n,k)$ the ith electronic eigenstate, with energy ε_i, is the solution of[4]

$$[\varepsilon(E;n,k)-\varepsilon_i]A_i(E;n,k) =(qEa)\sum_{n',k'}\langle E;n,k|S(x,a)|E;n',k'\rangle A_i(E;n',k') \ , \tag{1}$$

where $S(x,a)$ is the staircase function with step length equal to the lattice constant a and step height equal to unity. In the single-band approximation, interband matrix elements $(n\neq n')$ are discarded on the right-hand side of Eq. (1).[2,4] Then the solution of Eq. (1) yields the Wannier-Stark eigenstates.[2,4] More generally, Emin and Hart argue[4] that the interband terms make no net contribution to the right-hand side of Eq. (1). Here another argument is presented to show that the interband terms of Eq. (1) vanish.

The matrix elements of the staircase potential between Bloch states may be readily evaluated:[4]

$$\langle n,k|S(x,a)|n',k'\rangle = \left[a\sum_{m=0}^{N-1} m\exp[i(k'-k)ma]\right]I(n,k;n',k') \ , \tag{2}$$

where

$$I(n,k;n',k')=\int_0^a dx\,\exp[i(k'-k)x]u^*_{n,k}(x)u_{n',k'}(x) \ . \tag{3}$$

The prefactor of $I(n,k;n',k')$ in Eq. (2) is an oscillatory function of $k'-k$ that diverges as $1/(k'-k)$ when $(k'-k)\to 0$. However, the k and k' dependences of the matrix elements of the staircase potential arise from $I(n,k;n',k')$ as well as from the m summation. Indeed, it is $I(n,k;n',k')$ that involves Bloch states and the coherence effects that provide for the orthogonality of Bloch states of different bands: $I(n,k;n',k)=\delta_{n,n'}/N$. Thus, to proceed, the right-hand side of Eq. (2) must be manipulated to a more useful form:

$$\begin{aligned}\langle n,k|S(x,a)|n',k'\rangle &= \left[-i\partial\left[\sum_{m=0}^{N-1}\exp[i(k'-k)ma]\right]\Big/\partial k'\right]I(n,k;n',k') \\ &= i\left[-\frac{\partial\langle n,k|n',k'\rangle}{\partial k'}+N\delta_{k,k'}\frac{\partial I(n,k;n',k')}{\partial k'}\right] \ ,\end{aligned} \tag{4}$$

where it has been noted that

$$\sum_{m=0}^{N-1} \exp[i(k'-k)ma]I(n,k;n',k')=\langle n,k|n',k'\rangle \tag{5}$$

and

$$\sum_{m=0}^{N-1} \exp[i(k'-k)ma]=N\delta_{k,k'} \; . \tag{6}$$

Using Eq. (4), Eq. (1) becomes

$$\begin{aligned}[\varepsilon(E;n,k)-\varepsilon_i]A_i(E;n,k) &= i(qEa)\sum_{n',k'}\left[-\frac{\partial\langle n,k|n',k'\rangle}{\partial k'}+N\delta_{k,k'}\frac{\partial I(n,k;n',k')}{\partial k'}\right]A_i(E;n',k') \\ &= i(qEa)\sum_{n',k'}\left[\langle n,k|n',k'\rangle\frac{\partial A_i(E;n',k')}{\partial k'}+N\delta_{k,k'}\frac{\partial I(n,k;n',k')}{\partial k'}A_i(E;n',k')\right] \\ &= i(qEa)\left[\frac{\partial A_i(E;n,k)}{\partial k}+\sum_{n',k'}N\delta_{k,k'}\frac{\partial I(n,k;n',k')}{\partial k'}A_i(E;n',k')\right] ,\end{aligned} \tag{7}$$

where the orthonormality of Bloch functions has been noted, $\langle n,k|n',k'\rangle=\delta_{n,n'}\delta_{k,k'}$.

In the absence of an interband contribution, $n'\neq n$, to the right-hand side of Eq. (7), the solutions of Eq. (7) are Wannier-Stark states.[2,4] The first term in the large parentheses on the right-hand side of Eq. (7) involves a derivative with respect to k, $\partial A_i(E;n,k)/\partial k$. This feature indicates that this term is the net contribution from values of k' that are not equal to k but are centered at k. Thus, while the first term in the large parentheses after the first equality of Eq. (7) links terms of different bands, the net contribution, given by the first term in the large parentheses after the final equality of Eq. (7), does not.

To establish Wannier-Stark localization, it is now shown that the second term on the right-hand side of Eq. (7) vanishes for $n\neq n$ since then $\partial I(n,k;n',k')/\partial k'|_{k'=k}=0$. To prove that $\partial I(n,k;n',k')/\partial k'|_{k'=k}$ vanishes for $n\neq n$, the equivalence of the $u_{n,k}(x)$ in each primitive cell is exploited to write

$$\begin{aligned} iN\frac{\partial I(n,k;n',k')}{\partial k'}\bigg|_{k'=k} &= N\int_0^a dx\, u_{n,k}^*(x)\left[\frac{i\partial}{\partial k}-x\right]u_{n',k}(x) \\ &= \sum_{p=0}^{N-1}\int_{pa}^{(p+1)a}dx\, u_{n,k}^*(x)\left[\frac{i\partial}{\partial k}-(x-pa)\right]u_{n',k}(x) \\ &= \int_0^{Na}dx\, u_{n,k}^*(x)\left[\frac{i\partial}{\partial k}-x\right]u_{n',k}(x)+a\delta_{n,n'}\sum_{p=0}^{N-1}\frac{p}{N} ,\end{aligned} \tag{8}$$

where it has been noted that the orthogonality of Bloch states ensures that

$$\int_{pa}^{(p+1)a}dx\, u_{n,k}^*(x)u_{n',k}(x)=\delta_{n,n'}/N \; . \tag{9}$$

The integral of the final equality of Eq. (8) depends on the arbitrary phase factors of the cellular component of a Bloch function, the $\phi_n(k)$'s, through the integral's proportionality to $\exp\{i[\phi_{n'}(k)-\phi_n(k)]\}$. In addition, the arbitrary phase factor contributes $-N^{-1}\partial\phi_n(k)/\partial k$ to the final integral of Eq. (8) when $n'=n$. Because of this arbitrariness, the integral of Eq. (8) is generally nonzero when $n'=n$. Since Wannier-Stark localization only hinges on the vanishing of the integral of Eq. (8) when $n'\neq n$, the presence of the arbitrary phase factors may be ignored.

To evaluate the integral of Eq. (8), the cellular functions are represented as a superposition of Wannier functions of site index m of the nth band, $a_n(x-am)$:

$$u_{n',k}(x)=N^{-1/2}\sum_{m=0}^{N-1}\exp[ik(am-x)]a_{n'}(x-am) \; . \tag{10}$$

With this representation

$$\left[\frac{i\partial}{\partial k}-x\right]u_{n',k}(x)=N^{-1/2}\sum_{m=0}^{N-1}\left[\frac{i\partial}{\partial k}-x\right]\exp[ik(am-x)]a_{n'}(x-am)$$
$$=N^{-1/2}\sum_{m=0}^{N-1}(-am)\exp[ik(am-x)]a_{n'}(x-am)\ . \tag{11}$$

Thus, with Eqs. (10) and (11),

$$\int_0^{Na}dx\, u_{n,k}^*(x)\left[\frac{i\partial}{\partial k}-x\right]u_{n',k}(x)=N^{-1}\sum_{m=0}^{N-1}\sum_{m'=0}^{N-1}(-am)\exp[ika(m-m')]\int_0^{Na}dx\, a_n^*(x-am')a_{n'}(x-am)$$
$$=N^{-1}\sum_{m=0}^{N-1}\sum_{m'=0}^{N-1}(-am)\exp[ika(m-m')]\delta_{n,n'}\delta_{m,m'}$$
$$=-a\delta_{n,n'}\sum_{m=0}^{N-1}m/N\ , \tag{12}$$

where the orthogonality of the Wannier functions has been utilized. Combining Eqs. (8) and (12), for $n\neq n$, yields

$$iN\frac{\partial I(n,k;n',k')}{\partial k'}\bigg|_{k'=k}=N\int_0^a dx\, u_{n,k}^*(x)\left[\frac{i\partial}{\partial k}-x\right]u_{n',k}(x)=0\ . \tag{13}$$

Thus the second term on the right-hand side of Eq. (7) vanishes for $n'\neq n$ and Wannier-Stark localization is established. In essence our discussion only restates the theorems that $i\partial/\partial k$ operating on $u_{n,k}(x)$ gives x minus the cellular location, while $-i\partial/\partial k$ operating on $\exp(ikx)$ gives x and $-i\partial/\partial k$ operating on a Bloch state gives the cellular location.[3]

Here, and in the crystal momentum representation,[2-6] derivatives are written with respect to k and k'. However, k and k' represent discrete points with the minimum separation between successive values being $2\pi/Na$. As a result, one cannot always carry out the limiting procedure associated with differentiation, $\partial f(k)/\partial k=\lim_{\Delta k\to 0}\{[f(k+\Delta k)-f(k)]/\Delta k\}$, even though Δk bcomes arbitrarily small as $N\to\infty$. For example, if $f(k)=\exp(ikx)$, one has that $[f(k+\Delta k)-f(k)]/\Delta k=f(k)[\exp(i\Delta kx)-1]/\Delta k$ is only equal to $ixf(k)$ if $x\Delta k\ll 1$. This requirement is not always met because x is unbounded and can reach a value approximately equal to Na for which $x\Delta k$ is not much less than 1. Since the Wannier-Stark states are localized this difficulty should not arise here.

Page and Brown[7] offer two criticisms of the proof of Emin and Hart.[4] First, Page and Brown incorrectly claim that Ref. 4 states that "Bloch states of different field-dependent energy bands are not coupled by the step-like component of the electric-field potential."[7] In particular, they argue that the right-hand side of Eq. (2) of this paper does not vanish for $k'\neq k$ and $n\neq n'$. However, this is not the claim of Ref. 4 or the present paper. Rather, the argument of Ref. 4 and of this paper [indicated here in Eq. (7)] is that the net interband contribution of the first term on the right-hand side of Eq. (7) vanishes upon summing over k'. In effect, the right-hand side of Eq. (2) is $[\partial\delta(k'-k)/\partial k']I(n,k;n',k')$, where $I(n,k;n',k)\propto\delta_{n,n'}$. The right-hand side of Eq. (2) does not vanish for $k'\neq k$. However, when the right-hand side of Eq. (2) is a factor in an integral over k', the surviving contribution to the integral is restricted to the immediate vicinity of $k'=k$. This is the meaning of the derivative of a δ function.

Second, Page and Brown question the correctness of Eq. (13). In particular, they obtain a formula for $\partial\xi_{n,n}(k)/\partial k$ [where $\xi_{N,n}(k)=\int_0^a dx\,|u_{n,k}(x)|^2x$] that vanishes when Eq. (13) is fulfilled. Since $\partial\xi_{n,n}(k)/\partial k$ is generally nonzero, they challenge Eq. (13). Here another proof of Eq. (13) is offered [cf. Eqs. (8)–(13)]. In addition, $\xi_{n,n}(k)$ is calculated in the Appendix of this paper. It is confirmed that $\xi_{n,n}(k)$ is generally k dependent. In the Appendix a method similar to that of Page and Brown is used to obtain formulas for $\partial\xi_{n,n}(k)/\partial k$, Eqs. (A7) and (A13), that differ from the result of Page and Brown. Furthermore, the formulas for $\partial\xi_{n,n}(k)/\partial k$ obtained in the Appendix of this paper are shown, via Eq. (A15), to agree with explicit differentiation of $\xi_{n,n}(k)$ with respect to k. Finally, the Page-Brown finding that $\partial\xi_{n,n}(k)/\partial k=0$ is shown [below Eq. (A13)] to arise from using only Bloch functions of a single wave vector (excluding $k'\neq k$) as a basis to describe functions that mix states of different wave vector [see Eq. (B3) of Ref. (7)]. Thus the general relationship, Eq. (13), does not imply that $\partial\xi_{n,n}(k)/\partial k=0$. The contradiction that Page and Brown claim is only an artifact of their use of an incomplete set of basis states.

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APPENDIX: EVALUATION OF $\partial\xi_{n,n}(k)/\partial k$

To obtain $\zeta_{n,n}(k)$, note that the periodicity of $u_{nk}(x)$ implies that

$$N\xi_{n,n}(k)=N\int_0^a dx\,|u_{n,k}(x)|^2x$$
$$=\sum_{p=0}^{N-1}\int_{pa}^{(p+1)a}dx\,|u_{n,k}(x)|^2(x-pa)$$
$$=\int_0^{Na}dx\,|\psi_{n,k}(x)|^2x-(N-1)a/2\ . \qquad \text{(A1)}$$

In the Wannier representation

$$\psi^*_{n',k'}(x)\psi_{n,k}(x)=N^{-1}\sum_{m'}\sum_{m=0}^{N-1}\exp[ia(km-k'm')]\times a^*_{n'}(x-m'a)a_n(x-ma) \qquad \text{(A2)}$$

and the $n'=n$ matrix element of x between Wannier states, with $y=x-m'a$, is

$$\int dx\; a^*_n(x-m'a)a_n(x-ma)x$$
$$=\int dy\; a^*_n(y)a_n(y+m'a-ma)y+(ma)\delta_{m',m}$$
$$=\langle 0|x|m-m'\rangle+(ma)\delta_{m',m'} \qquad \text{(A3)}$$

since $\langle 0|m-m'\rangle=\delta_{m',m}$. Combining Eqs. (A1)–(A3) and defining $h=m-m'$:

$$N\xi_{n,n}(k)=N^{-1}\sum_{m=0}^{N-1}\sum_{h=-m}^{(N-m-1)}\exp(ikah)[\langle 0|x|h\rangle+(ma)\delta_{h,0}]-(N-1)a/2$$
$$=N^{-1}\sum_{m=0}^{N-1}\sum_{h=-m}^{(N-m-1)}\exp(ikah)\langle 0|x|h\rangle$$
$$=\langle 0|x|0\rangle+\sum_{h=1}^{N-1}[(N-h)/N][\exp(ikah)\langle 0|x|h\rangle+\exp(-ikah)\langle 0|x|-h\rangle]$$
$$=\langle 0|x|0\rangle+\sum_{h=1}^{N-1}[(N-h)/N][\exp(ikah)\langle 0|x|h\rangle+\text{c.c.}]\ . \qquad \text{(A4)}$$

In obtaining the second equality of Eq. (A4), the summation involving $\delta_{h,0}$ was performed and two equal and oppositely signed contributions were canceled. The third equality is obtained by combining terms of the double summation that have the same value of h. The final equality results from the observation, proved with the procedure of Eq. (A3), that $\langle 0|x|-h\rangle=\langle h|0|0\rangle=\langle 0|x|h\rangle^*$. Thus $\xi_{n,n}(k)$ is generally dependent on k. The neglect of the effect of the edges of the periodic potential, appropriate in treating the potential as truly periodic, is accomplished by replacing $(N-h)/N$ by unity in Eq. (A4).

The derivative of $\xi_{n,n}(k)$ with respect to k may be expressed in terms of matrix elements of the operators related to electronic position between Bloch states. To begin, Eq. (A1) is used to write

$$N\frac{\partial\xi_{n,n}(k)}{\partial k}=\partial\left[\int_0^{Na}dx\,|\psi_{n,k}(x)|^2x\right]\Big/\partial k$$
$$=\int_0^{Na}dx\;x\left[\psi^*_{n,k}(x)\frac{\partial\psi_{n,k}(x)}{\partial k}+\text{c.c.}\right]\ . \qquad \text{(A5)}$$

With the completeness relation,

$$\delta(x-y)=\sum_{n',k'}\psi_{n',k'}(x)\psi^*_{n',k'}(y)\ , \qquad \text{(A6)}$$

and its complex conjugate, we have

$$N\frac{\partial\xi_{n,n}(k)}{\partial k}=i\sum_{n',k'}[X(n,k;n',k')M(n',k';n,k)-\text{c.c.}]\ , \qquad \text{(A7)}$$

where

$$X(n,k;n',k')=\int_0^{Na}dx\;\psi^*_{n,k}(x)x\psi_{n',k'}(x) \qquad \text{(A8)}$$

and

$$M(n',k';n,k)=-i\int_0^{Na}dx\;\psi^*_{n',k'}(x)\frac{\partial\psi_{n,k}(x)}{\partial k}\ . \qquad \text{(A9)}$$

Here $X(n,k;n',k')$ and $M(n',k';n,k)$ are matrix elements of the operators associated with the carrier's position and cellular location, respectively. Using Eqs. (A2) and (A3), the expression for the matrix elements of x between Wannier states, in Eqs. (A8) and (A9), yields

$$X(n,k;n',k')=M(n,k;n',k')+P(n,k;n',k') \qquad \text{(A10)}$$

and

$$M(n',k';n,k)$$
$$=aN^{-1}\sum_{m'}\sum_{m=0}^{N-1}m\exp[ia(km-k'm')]\delta_{m',m}\delta_{n',n}$$
$$=aN^{-1}\sum_{m=0}^{N-1}m\exp[ia(k-k')m]\delta_{n',n'}\ , \qquad \text{(A11)}$$

where

$$P(n,k;n',k')=N^{-1}\sum_{m'}\sum_{m=0}^{N-1}\exp[ia(k'm-km')]\times\langle 0|x|m-m'\rangle\ . \qquad \text{(A12)}$$

$P(n,k;n',k')$ is a matrix element of the operator associated with electronic polarization:

$P(n,k;n,k) = N\xi_{n,n}(k)$ of Eq. (A4). Furthermore, since $M(n,k;n',k') = M^*(n',k';n,k)$ and $M(n,k;n',k')$ vanishes when $n \neq n'$, Eq. (A7) may be transformed [using Eq. (A10)] to

$$N\frac{\partial \xi_{n,n}(k)}{\partial k} = i\sum_{k'} [P(n,k;n,k')M(n,k';n,k) - \text{c.c.}] \ . \tag{A13}$$

Since $P(n,k;n,k)$ and $M(n,k;n,k)$ are both real for $k'=k$, the $k'=k$ term of the summation of Eq. (A13) vanishes. Since Page and Brown ignore the $k' \neq k$ terms [cf. Eqs. (B3), (B5), (B6), and (B8) of Ref. 7], they find that $\partial \xi_{n,n}(k)/\partial k = 0$. However, it is the $k' \neq k$ terms that provide the contribution to the right-hand side of Eq. (A13).

To determine the contribution of the $k' \neq k$ terms to $\partial \xi_{n,n}(k)/\partial k$, Eq. (A11) is first rewritten as

$$M(n,k';n,k) = i\partial \left[N^{-1} \sum_{m=0}^{N-1} \exp[ia(k-k')m] \right] \Big/ \partial k' \ . \tag{A14}$$

Then, inserting Eq. (A14) into Eq. (A13) and integrating by parts yields

$$\begin{aligned} N\frac{\partial \xi_{n,n}(k)}{\partial k} &= \sum_{k'} \delta_{k',k} \left[\frac{\partial P(n,k;n,k')}{\partial k'} + \frac{\partial P^*(n,k;n,k')}{\partial k'} \right] \\ &= \sum_{k'} \delta_{k',k} \left[\frac{\partial P(n,k;n,k')}{\partial k'} + \frac{\partial P(n,k';n,k)}{\partial k'} \right], \end{aligned} \tag{A15}$$

since $P^*(n,k;n,k') = P(n,k';n,k)$ and

$$N^{-1} \sum_{m=0}^{N-1} \exp[ia(k-k')m] = \delta_{k',k} \ . \tag{A16}$$

Because $P(n,k;n,k) = N\xi_{n,n}(k)$ [given by Eq. (A4)], the right-hand side of the last equality of Eq. (A15) confirms that $N\partial \xi_{n,n}(k)/\partial k$ is simply the derivative of the right-hand side of Eq. (A4) with respect to k.

In summary, in this appendix it has first been shown that $\xi_{n,n}(k)$ is generally a function of k, given by Eq. (A4). Second, it has been confirmed that expressing $\partial \xi_{n,n}(k)/\partial k$ in terms of matrix elements of x and $-i\partial/\partial k$ between Bloch states, Eqs. (A8) and (A9), yields the same result for $\partial \xi_{n,n}(k)/\partial k$ as is obtained by explicit differentiation of $\xi_{n,n}(k)$, given by Eq. (A4), with respect to k. Finally, it is shown that the Page-Brown result that $\partial \xi_{n,n}(k)/\partial k = 0$ follows from the suppression of the $k' \neq k$ states from the summation involved in the completeness relation, Eq. (A6) [for comparison, see Eq. (B3) of Ref. 7]. It is not surprising that the $k' \neq k$ terms determine $\partial \xi_{n,n}(k)/\partial k$, since the act of differentiation involves states of different k: $\partial f(k)/\partial k = \lim_{k' \to k} [f(k') - f(k)]/(k'-k)$.

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