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Wannier functions in one-dimensional disordered systems: Application to fractionally charged solitons

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Wannier functions can be defined as the eigenstates of the position operator projected onto a given band. Though this definition is equivalent to the usual definition of Wannier functions in a crystal, the present definition is useful in disordered systems as well. It is shown that if a band is separated from all other bands by a finite energy gap, the Wannier functions are spatially localized. Although the Wannier functions are typically too complicated to compute explicitly, they are a useful conceptual tool. As an example of their usefulness, they are here used to study the charge fluctuations associated with a fractionally charged topological defect or soliton. It is shown that fractional charge is a sharp quantum observable, thus confirming the results of previous continuum-model calculations [S. Kivelson and J. R. Schrieffer, Phys. Rev. B 25, 6447 (1982)].

I. INTRODUCTION

The one-electron energy eigenvalues of solids, especially in one dimension, often form isolated bands; that is to say, bands of allowed energies separated from all other bands by a finite energy gap. The states in a given isolated band α define a subspace S_α. Where possible, it is often useful, at least conceptually, to express states in this subspace in terms of a spatially localized basis set, which we will call in general Wannier functions (WF). It is well known that in a one-dimensional crystal with a center of symmetry it is always possible[1] to construct exponentially localized WF's. Moreover, for many isolated bands in three-dimensional solids it is possible[2] to find WF's which are not only exponentially localized but which transform simply under the operations of the space group of the crystal as well. The standard proofs of these properties depend heavily on the analytic properties of Bloch states. However, Kohn and Onffroy[3] have shown that in a one-dimensional crystal with a point defect, WF's exist which have the same asymptotic properties as those in the corresponding perfect crystal. This result suggests that the exponential localization of the WF's is a direct consequence of the existence of an energy gap, and not of the existence of perfect crystalline order.

With this in mind, we generalize the notion of a WF so that no direct reference need be made to the underlying structure of the solid, crystalline, or otherwise. Let α be an isolated band in a one-dimensional solid and let $\hat{P}_\alpha$ be the projection operator onto the subspace of band α. Then the WF's of band α, $|R,\alpha\rangle$, are defined to be the eigenstates of the projected position operator $\hat{R}_\alpha$,

$$\hat{R}_\alpha |R,\alpha\rangle = R |R,\alpha\rangle , \tag{1.1}$$

where

$$\hat{R} = \hat{P}_\alpha \hat{r} \hat{P}_\alpha , \tag{1.2}$$

and $\hat{r}$ is the position operator.[4] This definition of the WF is intuitively appealing; the WF is the "best" approximation to an eigenstate of the position operator that can be made out of states in band α.

In this paper we explore some of the properties of these generalized WF's. In Sec. II we show that the WF's as usually defined in crystalline systems are indeed eigenstates of the projected position operator. In Sec. III we show that an immediate consequence of the existence of an energy gap is that the WF's are sufficiently well localized that at least the second spatial moment of the WF is bounded. This result is beneficial for some uses of WF's; in particular, it is a necessary condition for the existence of a well-defined electron effective mass.[5] In Sec. IV we prove that for a system which consists of two semi-infinite pieces of crystal, C_1 and C_2, connected by a finite region of noncrystalline material (see Fig. 1), the WF's are exponentially localized and become indistinguishable from the WF's of the corresponding perfect crystal exponentially fast as one moves away from

the noncrystalline region D. This result is more general that that of Kohn and Onffroy in that it is valid in the presence of topological disorder (in which C_1 and C_2 are different) in addition to the case of a point defect ($C_1=C_2$) already considered by them.

Finally, as an example of the usefulness of the generalized WF's, we consider the quantum-mechanical charge fluctuations of the fractional charge[6] associated with solitons in a commensurate Peierls system. It was shown in Ref. 1 that in a continuum model of the commensurability 2 system,[7] the charge fluctuations vanish in the long-wavelength limit. However, the continuum model contains an artificial cutoff to the fermion spectrum. In Sec. V, we use the properties of the WF's to study the fractionally charged solitons. As in Ref. 8, we show that the charge fluctuations associated with the soliton are exponentially localized to the vicinity of the soliton. We thus confirm the fact that in the long-wavelength limit, fractional charge is a sharp quantum observable.

II. WANNIER FUNCTIONS IN THE PERFECT CRYSTAL

In a one-dimensional crystal with inversion symmetry, it is easy to show that the normally defined WF's are indeed eigenstates of $\hat{R}_\alpha$. We will consider explicitly only the usual case in which the eigenvalues of $\hat{R}_\alpha$ are nondegenerate, but the generalization to the case of degenerate eigenvalues is straightforward.[4] Specifically, consider the usual WF's which we label according to band (α,β) and according to the expectation value of the position operator

$$\langle R\alpha\,|\,\hat{r}\,|\,R\alpha\rangle = R\ . \tag{2.1}$$

We will show that

$$\langle R\alpha\,|\,\hat{R}_\alpha\,|\,R'\beta\rangle = \delta_{\alpha\beta}\,\delta_{RR'}R\ . \tag{2.2}$$

That $\hat{R}_\alpha\,|\,R,\beta\rangle \propto \delta_{\alpha\beta}$ is immediately apparent from the definition of $\hat{R}_\alpha$. The translational invariance of the crystal and the orthogonality of the WF's imply that

$$\langle R,\alpha\,|\,\hat{R}_\alpha\,|\,R',\alpha\rangle = R\delta_{RR'} + \langle R-R',\alpha\,|\,\hat{R}_\alpha\,|\,0,\alpha\rangle\ . \tag{2.3}$$

To complete the proof, we note that the WF's can be chosen to be real and to be eigenstates of the inversion operator $\mathscr{I}$:

$$\mathscr{I}\,|\,R,\alpha\rangle = \lambda_\alpha\,|\,R,\alpha\rangle\ , \tag{2.4}$$

where $\lambda_\alpha=\pm1$. Thus,

$$\begin{aligned}\langle R,\alpha\,|\,\hat{R}_\alpha\,|\,0,\alpha\rangle &= \langle R,\alpha\,|\,\hat{r}\,|\,0,\alpha\rangle \\ &= -(\lambda_\alpha)^2\langle -R,\alpha\,|\,\hat{r}\,|\,0,\alpha\rangle \\ &= -\langle 0,\alpha\,|\,\hat{r}\,|\,-R,\alpha\rangle \\ &= -\langle R,\alpha\,|\,\hat{r}\,|\,0,\alpha\rangle = 0\ ,\end{aligned} \tag{2.5}$$

where in the latter three expressions, we have invoked inversion symmetry, translational symmetry, and reality, respectively.

III. SECOND MOMENT OF $|R\alpha\rangle$

As long as the solid under consideration is well described by a one-particle Hamiltonian with a velocity-independent potential,

$$H = \frac{-\hbar^2}{2M_e}\frac{\partial^2}{\partial x^2} + V(x)\ , \tag{3.1}$$

the position operator obeys the commutation relation

$$[[\hat{H},\hat{r}],\hat{r}] = \frac{\hbar^2}{2M_e}\ . \tag{3.2}$$

From this, it is possible to place an upper bound on the average second moment $[l_\alpha]^2$ of the WF's in band α,

$$[l_\alpha]^2 = \frac{1}{N}\sum_R \langle R\alpha\,|\,(\hat{r}-R)^2\,|\,R\alpha\rangle\ , \tag{3.3}$$

where N is the dimension of S_α. The derivation proceeds along lines similar to those of the usual proof of the f sum rule. A similar approach was used in Ref. 6 to obtain an estimate of the band-edge effective mass (which was found to be related to l_α). For simplicity, we will consider only the lowest band, α. We note that

$$P_\alpha = \sum_R |\,R,\alpha\rangle\langle R,\alpha\,| \tag{3.4}$$

and that

$$\langle\beta\,|\,(\hat{r}-R)\,|\,R,\alpha\rangle = \langle\beta\,|\,\hat{r}\,|\,R,\alpha\rangle\ , \tag{3.5}$$

where $|\,\beta\rangle$ is any state in $S_{\beta\neq\alpha}S_\alpha$. With the use of these relations, it is easy to show that

$$\begin{aligned}&\frac{1}{N}\sum_R \langle R,\alpha\,|\,[[H,\hat{r}-R],\hat{r}-R]\,|\,R,\alpha\rangle \\ &\quad = -\frac{\hbar^2}{M_e} \\ &\quad = \frac{2}{N}\sum_j\sum_{\beta\neq\alpha}\sum_k [E_\alpha(j)-E_\beta(k)]\,|\langle\alpha,j\,|\,\hat{r}\,|\,\beta,k\rangle|^2,\end{aligned} \tag{3.6}$$

where $|\alpha,j\rangle$ is an energy eigenstate in band α with energy $E_\alpha(j)$. Since, by assumption, band α is separated by a finite energy gap E_g from all other bands,

$$E_\beta(k)-E_\alpha(j)\geq E_g \ . \tag{3.7}$$

Thus,

$$\frac{1}{N}\sum_j \langle\alpha,j|\hat{r}(1-\hat{P}_\alpha)\hat{r}|\alpha,j\rangle \leq \frac{\hbar^2}{2M_eE_g} \ . \tag{3.8}$$

Since $(\hat{r}-R)|R,\alpha\rangle=(1-\hat{P}_\alpha)\hat{r}|R,\alpha\rangle$, it follows that

$$[l_\alpha]^2 \leq \frac{\hbar^2}{2M_eE_g} \ . \tag{3.9}$$

Equation (3.9) is suggestive of an electron bound state with binding energy E_g. It is, therefore, tempting to speculate that the existence of an energy gap implies that

$$\langle x|R,\alpha\rangle \sim \exp(-|x-R|/l_0) \ , \tag{3.10}$$

where $l_0=\hbar/\sqrt{2M_eE_g}$. We will derive a result of this sort for a specific class of model systems in the next section. However, a general demonstration that an energy gap implies exponential localization of the WF's has not yet been found.

IV. IMPERFECT CRYSTALS

In this section we consider a system of the type pictured in Fig. 1 which consists of two semi-infinite crystals, C_1 and C_2, separated by a finite "defect" region D. Crystals C_1 and C_2 need not be the same, but there must be a finite energy gap in the combined spectrum of C_1 and C_2 separating the band of interest from all other bands. Such a situation can occur accidentally if two unrelated

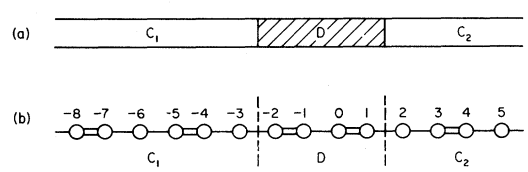

FIG. 1. (a) Schematic representation of the allowed type of defects. (b) Schematic representation of a topological defect or soliton in a charge-density-wave system with commensurability 3. The double bond represents a region of charge buildup and the single bond a region of charge depletion. C_1 and C_2 are related to each other by a one lattice constant shift of the double bond.

crystals happen to have coincident gaps. However, of more interest is the case in which C_1 and C_2 are topologically distinct versions of otherwise identical crystals [an example of such a system is shown schematically in Fig. 1(b)]. Therefore, we will confine our discussion to the cases in which C_1 and C_2 are either identical or only topologically distinct. The case of unrelated crystals can be treated by the same techniques, but it is considerably more complicated.

In order to determine the properties of the WF's, it is convenient first to establish the properties of the projection operators $\hat{P}_\alpha$. In this we reproduce in greater generality the results of Kohn and Onffroy.[3] The projection operator is most conveniently defined in terms of an energy integral

$$\hat{P}_\alpha=\int_{E_{\alpha-1}}^{E_\alpha} dE \sum_\psi |\psi\rangle\delta(E-E_\psi)\langle\psi| = -\frac{1}{\pi}\mathrm{Im}\int_{E_{\alpha-1}}^{E_\alpha} dE\,\hat{G}(E) \ , \tag{4.1}$$

where

$$\hat{G}(E)=(E+i\eta-\hat{H})^{-1} \tag{4.2}$$

and $\{|\psi\rangle\}$ are a complete set of eigenvectors of the Hamiltonian $\hat{H}$. In a perfect crystal the exact choice of the cutoff energies, E_α, is unimportant so long as E_α lies in the band gap between band α and band $\alpha+1$. However, in an imperfect system there are often localized states in the forbidden gap. The choice of E_α then determines which localized states are to be associated with band α and which with band $\alpha+1$. As we shall see, there is a unique optimal choice of E_α which makes the projection operators P_α as short range as possible. It was shown in Ref. 2 that in a perfect crystal the energy $E_\alpha(K)$ of an electron in band α with wave vector K satisfies the equation

$$\cos(Ka)=\mu(E) \ , \tag{4.3}$$

where $E_\alpha(K)=E$ and $\mu(E)$, considered as a function of complex E, is an entire function of E. Equation (4.3) can be taken either to define the multivalued function $E(K)$, which, for real K, is equal to $E_\alpha(K)$ [each α corresponds to a different branch of the function $E(K)$] or to define the complex wave number as a function of the energy $K(E)$. We will see that the optimal choice of limits to the integral in Eq. (4.1) are the energies E_α at which $d\mu/dE$ vanishes,

$$\left[\frac{d\mu}{dE}\right]_{E=E_\alpha}=0 \ . \tag{4.4}$$

In Ref. 2, it is shown that E_α, which lies in the forbidden gap, is the value of $E(K)$ at the branch point, $K=K_\alpha$, which connects the branch of $E(K)$ corresponding to band α with that corresponding to band $\alpha+1$. Note that since $K(E)$ is a multivalued function of E,

$$K_\alpha = g_\alpha + 2n\pi/a \pm i h_\alpha \ , \tag{4.5}$$

where $g_\alpha=\pi/a$ for α even and 0 for α odd. It is easy to show (see Appendix A and Ref. 4) that for the perfect crystal, the behavior of the projection operator $\hat{P}_\alpha^{(C)}$ is determined by the position of the branch points K_α,

$$\langle x \mid P_\alpha^{(C)} \mid x' \rangle \sim \exp(-\kappa_\alpha \mid x-x' \mid) \ , \tag{4.6}$$

where

$$\kappa_\alpha = \min(h_{\alpha-1}, h_\alpha) \ . \tag{4.7}$$

Here, by the expression

$$f(x) \sim \exp(-\kappa_0 \mid x \mid) \ ,$$

we mean that for any $\kappa < \kappa_0$

$$\lim_{\mid x \mid \to \infty} f(x)\exp(\kappa \mid x \mid) = 0 \ .$$

The principal mathematical result of this section (which is actually proven in Appendix A) is that by choosing E_α according to Eq. (4.4) we ensure that $\hat{P}_\alpha$ is equally localized in the imperfect system as in the crystalline system,

$$\langle x \mid \hat{P}_\alpha \mid x' \rangle \equiv P_\alpha(x,x') \sim \exp(-\kappa_\alpha \mid x-x' \mid) \ , \tag{4.8}$$

and that the projection operator approaches that of the perfect crystal exponentially rapidly with distance from the defect,

$$\mid P_\alpha(x,x') - P_\alpha^{(C)}(x,x') \mid \sim \exp[-\kappa_\alpha(\mid x \mid + \mid x' \mid)] \ , \tag{4.9}$$

where $P_\alpha^{(C)}(x,x')$ is the projection operator of the corresponding crystal defined by the relation

$$P_\alpha^{(C)}(x,x') \equiv \begin{cases} \langle \mid P_\alpha^{(C_1)} \mid x' \rangle & \text{for } x,x'<0 \\ \langle x \mid P_\alpha^{(C_2)} \mid x' & \text{for } x,x'>0 \\ 0 & \text{otherwise} \ . \end{cases} \tag{4.10}$$

It is clearly impossible for the projection operator to be more localized in the imperfect system than in the perfect crystal. Thus, Eqs. (4.8) and (4.9) show that our choice of the limits of integration in defining $\hat{P}_\alpha$ were, indeed, optimal. It should be stressed that Eqs. (4.8) and (4.9) hold regardless of the nature of the defect region. In particular, even if the electronic spectrum includes states in the gap which are localized in a region large compared to κ_α^{-1} (for instance, a state with energy very near the band edge), the projection operators still satisfy these equations.

From the properties of P_α, it is easy to derive the properties of the WF's by perturbation theory. Because the difference between the projection operators in the imperfect system and crystal are exponentially small away from the defect region, so is the difference between the projected position operators $\hat{R}_\alpha$ and $\hat{R}_\alpha^{(C_j)}$. Thus, we can construct the WF's by perturbation theory in $\delta\hat{R}_\alpha^{(j)} = \hat{R}_\alpha - \hat{R}_\alpha^{(C_j)}$ starting with the crystalline WF's, $\mid R,\alpha \rangle^{(C_j)}$ as the zeroth-order wave functions. It has been shown by Kohn[1] that

$$\langle x \mid R,\alpha \rangle^{(C_j)} \sim \exp(-\kappa_\alpha \mid x-R \mid) \ . \tag{4.11}$$

It follows then from Eqs. (4.8) and (4.9) that

$$\langle x \mid \delta\hat{R}_\alpha^{(j)} \mid R,\alpha \rangle^{(C_j)} \sim \exp(-\kappa_\alpha \mid x-R \mid) \tag{4.12}$$

and that

$$\langle x \mid \delta\hat{R}_\alpha^{(j)} \mid R,\alpha \rangle^{(C_j)} \sim \exp(-2\kappa_\alpha \mid R \mid) \ , \tag{4.13a}$$

where we take $C_j=C_1$ for $R<0$ and $C_j=C_2$ for $R>0$. Since the perturbation itself is exponentially localized it follows to any finite order in perturbation theory that

$$\langle x \mid R,\alpha \rangle \sim \exp(-\kappa_\alpha \mid x-R \mid) \tag{4.13b}$$

and that

$$(\langle x \mid R,\alpha \rangle - \langle x \mid R,\alpha \rangle^{(C_j)}) \sim \exp(-2\kappa_\alpha \mid R \mid) \ . \tag{4.13c}$$

Like the projection operator itself, the WF's in the imperfect solid are exponentially localized with the same fall-off distance κ_α^{-1}, as in the appropriate perfect crystal, and they approach the WF's of the perfect crystal exponentially fast away from the defect.

V. APPLICATION TO FRACTIONAL CHARGE

There has recently been considerable interest in the observation that the soliton excitations in com-

mensurate charge-density-wave systems can have fractional expectation value of the charge associated with them. The question naturally arises: What is the meaning of this fractional charge? Is it a sharp quantum observable? After all, fractional expectation value of the charge shows up all the time in quantum mechanical systems such as, for example, the H_2^+ molecule where each hydrogen has an average of $\frac{1}{2}$ electron in the ground state. However, this is not a particularly interesting type of fractional charge; any experiment that measures the charge on one H atom will find charge equal to $+1$ half the time and charge equal to 0 the other half. In other words, the charge fluctuations

$$[\delta Q]=(\langle \hat{Q}^2\rangle-\langle \hat{Q}\rangle^2)^{1/2}=\tfrac{1}{2} \tag{5.1}$$

are the same magnitude as the charge itself

$$\langle \hat{Q}\rangle=\tfrac{1}{2}\ . \tag{5.2}$$

In this section we will consider the WF's of a commensurate charge-density-wave (CDW) system in the presence of a soliton. As shown schematically in Fig. 2 for the case of commensurability 2, the soliton is a domain wall between regions of two different, energetically equivalent ground-state configurations of the CDW. The WF's for the valence band are also shown schematically in the same figure.

There are two technicalities involved in applying the analysis of the preceding section to the present system. The first is that, although the one-electron problem should properly be expressed in terms of the Schrödinger equation [Eq. (3.1)], the most popular models, for instance the Su, Schrieffer, and Heeger[9] (SSH) model that we will consider explicitly in Appendix B, are tight-binding models. Thus, the analytic structure of $E(K)$ is somewhat different in the model systems than in the case we have considered. Nonetheless, in Appendix B, we show that the analytic structure $E(K)$ in the tight-binding model is sufficiently similar to the

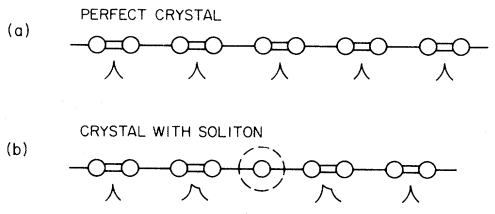

FIG. 2. Schematic representation of the lattice and the valence-band WF's of a CDW with commensurability 2. The double bonds represent regions of charge accumulation. The WF's in the perfect crystal are symmetric (bonding) about the bond centers.

itinerant case that all the same theorems stated in Sec. IV hold for the tight-binding model as well. The second point is that a rather interesting ambiguity can arise for the special case of commensurability 2 in defining the spaces $S_{\rm vb}$ and $S_{\rm cb}$, corresponding to the valence and conduction bands, respectively. So long as the model has charge conjugation symmetry (as, for instance, the SSH model), there will always be a bound state at exactly midgap associated with the soliton. The same symmetry implies that the cutoff energy E_α, separating the valence-band states from the conduction-band states, lies at exactly midgap [see Eq. (4.1)]. Thus, it is ambiguous whether this bound state should be associated with the valence band or the conduction band. Hence, rather than arbitrarily associate it with either band, we have kept it separate, defining it to constitute a one-state midgap band S_0. For this reason there is no valence band WF associated with atom 0 in Fig. 2.

We are interested in the ground-state properties of the system, that is the state in which all the states in $S_{\rm vb}$ are occupied and all other states are empty. Equivalently, this is the state in which all the valence band WF's, $|R,\text{vb}\rangle$, are occupied. Following Ref. 8, we define an operator $\hat{Q}_s$ which measures the charge of the soliton

$$\hat{Q}_s=\int dx\, f(x)[\hat{\rho}(x)-\langle c\,|\,\hat{\rho}(x)\,|\,c\rangle]\ , \tag{5.3}$$

where $\hat{\rho}(x)$ is the charge-density operator, $\langle c\,|\,\hat{\rho}(x)\,|\,c\rangle$ is the expectation value of the charge-density operator in the perfect crystalline (soliton-free) case, and $f(x)$ is a slowly varying envelope function of much larger spatial extent than the soliton. It has been shown[9] previously that the expectation value of the charge that should be associated with the soliton is

$$Q=e[(N/M)+n]\ .$$

N is the number of allowed spin polarizations, M is the order of commensurability, and n is a small integer. Thus, the charge associated with the soliton in Fig. 2 is $\frac{1}{2}e$ for spinless electrons ($N=1$). In the language of WF's, it is apparent from the figure that, whereas in the perfect crystal there is one WF associated with every two sites in the presence of the soliton, one site has no WF associated with it. Since the WF's approach those of the crystal exponentially fast and are themselves exponentially localized, it is clear that

$$\begin{aligned}\langle s\,|\,\hat{Q}_s\,|\,s\rangle&=N\sum_R\langle R,\text{vb}\,|\,\hat{Q}_s\,|\,R,\text{vb}\rangle\\&=(e/M)m+O(e^{-\kappa L})\ ,\end{aligned} \tag{5.4}$$

where $|s\rangle$ is the electronic ground state of the soliton-bearing system, κ^{-1} is the decay length of the WF's, and L is the spatial extent of the envelope function $f(x)$. (In Appendix B the WF, and in particular κ, are calculated explicitly for the SSH model with commensurability 2.)

Now, we wish to calculate the charge fluctuations in the presence of the soliton δQ to determine whether the fractional charge is meaningful. We define the charge fluctuations in the usual way,

$$\begin{aligned}[\delta Q]^2 &= \langle s|[\hat{Q}_s]^2|s\rangle - \langle s|\hat{Q}_s|s\rangle^2 \\ &= N\sum_R \langle R,\mathrm{vb}|\hat{Q}_s[1-\hat{P}_{\mathrm{vb}}]\hat{Q}_s|R,\mathrm{vb}\rangle \\ &= N\sum_R \int dx\,dx' f(x)f(x')\phi_R^*(x-R)\phi_R(x'-R)[\delta(x-x')-P_{\mathrm{vb}}(x,x')]\,, \end{aligned} \tag{5.5}$$

where $\langle x|R,\mathrm{vb}\rangle = \phi_R(x-R)$. Note that there is no contribution to δQ from regions in which $f(x)$ is a constant since

$$\int dx\,\phi_R(x-R)[\delta(x-x')-P_{\mathrm{vb}}(x',x)] = 0\,. \tag{5.6}$$

To best illustrate the behavior of δQ, we will consider an envelope function which is constant over a region of width $2L$ about the soliton, $f(x)=1$ for $|x|<L$, and then drops to zero over a region of width l. δQ can be expanded in powers of $df(x)/dx$ to yield the expression

$$\begin{aligned}[\delta Q]^2 &= N^2e^2\sum_R \{[f'(R)]^2\kappa^{-2}A_{11} + \tfrac{1}{2}f''(R)f'(R)\kappa^{-3}A_{21} + \cdots\} \\ &= N^2e^2[A_{11}B(\kappa a)^{-1}(\kappa l)^{-1} + O((\kappa l)^{-2})]\,, \end{aligned} \tag{5.7}$$

where a is a lattice constant and A_{nm} and B are the pure numbers

$$A_{nm} = \int dx\,dx'[\kappa(x-R)]^n[\kappa(x'-R)]^m\phi_R^*(x-R)\phi_R(x'-R)[\delta(x-x')-P_{\mathrm{vb}}(x,x')] \tag{5.8}$$

and

$$B = \left[\frac{a}{l}\right]\sum_R [f'(R)]^2\,. \tag{5.9}$$

Since $\phi_R(x-R)$ is localized in a region of width κ^{-1} about $x=R$, A_{nm} is of the order 1 and likewise, since $f'(R)$ is nonzero only in a region of width l, B is also of order 1.

We have thus shown that if $f(x)$ is a sufficiently slowly varying function of x, $[\delta Q]^2$ tends to zero, $[\delta Q]^2 \sim (\kappa l)^{-1}$. Since charge is typically defined only in the long-wavelength limit, this shows that the fractional charge is in fact a sharp quantum observable. However, we expect a stronger result to hold, since the disturbance in the electronic structure due to the presence of the soliton decays exponentially with distance from the soliton. We would expect the portion of the charge fluctuations that are due to the presence of the soliton to be exponentially small. Thus, we are led to examine the dependence of $[\delta Q]^2$ on L, $[\delta Q]^2_L$. Since the contributions to the integrals in Eq. (5.5) come only from the regions in which $f(x)$ is varying, it is clear that for $L_1 > L_2 \gg \kappa^{-1}$,

$$[\delta Q]^2_{L_1} - [\delta Q]^2_{L_2} \sim e^{-2\kappa L_2}\,.$$

All but an exponentially small portion of the charge fluctuations have nothing to do with the soliton. They are the charge fluctuations associated with a finite gap semiconductor. The ease with which we established these results demonstrates the usefulness of WF's as a conceptual tool.

Note added in proof. The proof of the sharpness of the fractional charge in Ref. 8 has recently been extended to include a general commensurability m continuum model by Y. Frishman and B. Horovitz (unpublished).

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I would like to thank Professor J. R. Schrieffer for giving me fractional charge and Professor W. Kohn for lending me a Wannier function.

APPENDIX A: THE PROPERTIES OF $P_\alpha(x,x')$

In this appendix we will show that for any one-dimensional system with a defect (topological or

not), such as that shown in Fig. 1(a), the projection operator onto band α satisfies Eqs. (4.8) and (4.9). The proof is in three parts.

The first step is to show that the Green's function of the imperfect system [see Eq. (4.2)] can be expressed in terms of the Green's function of the crystal according to the expression

$$\begin{aligned} G_{x,x'}(E) &= \langle x \mid \hat{G}(E) \mid x' \rangle \\ &= G^{(C)}_{x,x'}(E) \\ &\quad + \int_{x_1 \in D} dx_1 \int_{x_2 \in D} dx_2 G^{(C)}_{x,x_1}(E) \\ &\quad \times T_{x_1,x_2}(E) G^{(C)}_{x_2,x'}(E) , \end{aligned} \tag{A1}$$

where

$$G^{(C)}_{xx'}(E) = \begin{cases} \langle x \mid (E + i\eta - H^{(C_1)})^{-1} \mid x' \rangle \\ \qquad \text{for } x,x' < 0 \\ \langle x \mid (E + i\eta - H^{(C_2)})^{-1} \mid x' \rangle \\ \qquad \text{for } x,x' > 0 \\ 0 \quad \text{otherwise.} \end{cases} \tag{A2}$$

The T matrix is an analytic function of E in the upper-half E plane, and the x_1 and x_2 integrals are confined to the defect region [D in Fig. 1(a)]. Equation (A1) defines the usual T matrix of scattering theory if D is a nontopological defect.

That Eq. (A1) applies to the case of a topological defect is easily shown. First we consider the Green's function for a system that consists of perfect crystal C_1 for $x < 0$ and C_2 for $x > 0$, with an infinite barrier between them. The Green's function $\tilde{G}$ for this system can easily be shown to be

$$\begin{aligned} \tilde{G}_{xx'}(E) &= G^{(C)}_{xx'}(E) \\ &\quad - G^{(C)}_{x0}(E)[G^{(C)}_{00}(E)]^{-1} G^{(C)}_{0x'}(E) , \end{aligned} \tag{A3}$$

where $\tilde{G}_{xx'} = 0$ if $x > 0$ and $x' < 0$ or if $x < 0$ and $x' > 0$. Now, the difference between the artificial system and the system with the desired topological defect D can be treated as a scattering potential with the result that $G(E)$ can be expressed as in Eq. (A1) in terms of $\tilde{G}$ (instead of $G^{(C)}$) and an effective T matrix $\tilde{T}$ (instead of T). However, with the aid of Eq. (A3), an expression for G in terms of $G^{(C)}$ of the form of Eq. (A1) can be obtained. That $T(E)$ is analytic in the upper half E plane follows from the fact the retarded Green's function G is analytic in the upper half plane.

The second part of the proof is to show that if $f(E)$ is any function which is analytic in the upper half plane (and does not blow up as $E \to \infty$), then

$$\begin{aligned} I_{xx} &= \int_{E_{\alpha-1}}^{E_\alpha} G^{(C)}_{xx'}(E) f(E) dE \\ &\sim \exp(-\kappa_\alpha \mid x - x' \mid) . \end{aligned} \tag{A4}$$

To do this, consider the E integral. Since both G and f are analytic in the upper half plane we can deform the contour of integration as shown in Fig. 3(a) so that

$$\begin{aligned} I_{xx'} &= \int_{E_{\alpha-1}}^{E_{\alpha-1}+i\infty} dE\, G^{(C)}_{xx'}(E) f(E) \\ &\quad - \int_{E_\alpha}^{E_\alpha + i\infty} G^{(C)}_{xx'}(E) f(E) . \end{aligned} \tag{A5}$$

Thus, we are interested in the behavior of $G^{(C)}$ for argument $E_\alpha + i\epsilon$. Let $\varphi_{\alpha K}(x) e^{ikx}$ be the Bloch state with energy eigenvalue $E_\alpha(K)$ [$\varphi_{\alpha K}$ is a periodic function $\varphi_{\alpha K}(x) = \varphi_{\alpha K}(x + a)$]. Kohn[1] has shown that as a function of complex K, there exists a function $\varphi_K(x)$ which is a multivalued function of K such that for real K, $\varphi_K(x) = \pm \varphi_{\alpha K}(x)$. $\varphi_K(x)$ has a similar analytic structure as $E(\kappa)$; it has branch points at the points $K = K_\alpha$ defined in Eq. (4.5), and is analytic everywhere else. The only difference is that where $E(K)$ has first-order branch points, $\varphi_K(x)$ has third-order branch points. With this in mind, it is easy to see that

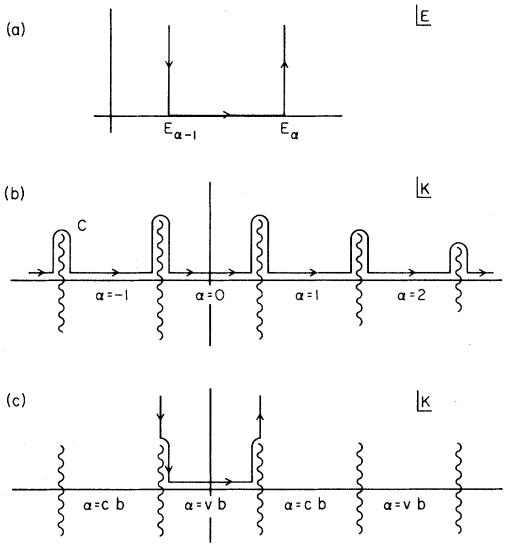

FIG. 3. Contours of integration in the complex E and K planes.

$$G^{C}_{xx'}(E_\beta+i\epsilon)=\sum_\alpha \int_{-\pi/a}^{\pi/a}\frac{dK}{2\pi}\frac{\varphi^*_{\alpha K}(x)\varphi_{\alpha K}(x')\exp[iK(x-x')]}{E_\beta+i\epsilon-E_\alpha(K)} \tag{A6}$$

$$=\int_C \frac{dK}{2\pi}\frac{\varphi^*_K(x)\varphi_K(x')\exp[iK(x-x')]}{E_\beta+i\epsilon-E(K)}\ , \tag{A7}$$

where the contour of integration is shown in Fig. 3(b). Note that $\varphi_\kappa(x)$ and $E(K)$ have values $\varphi_{\alpha K}(x)$ and $E_\alpha(K)$ along the segment of the real K axis labeled α. The portion of the integral around the branch cuts cancel due to the $\kappa\rightarrow-\kappa$ symmetry (ensured by Kramer's theorem). This integral can be evaluated simply by closing the contour at ∞. The result is

$$G^{(C)}_{xx'}(E_\beta+i\epsilon)=i\exp[ig_\beta(x-x')-\kappa_\beta(\epsilon)\,|\,x-x'\,|\,]\varphi_{K(E^*_\beta+i\epsilon)}(x)\varphi_{K(E_\beta+i\epsilon)}(x')\mathcal{F}\ , \tag{A8}$$

where $K(E)$ is defined in Eq. (4.3), $i\kappa_\beta(\epsilon)\equiv K(E_\beta+i\epsilon)-g_\beta$, and g_β is defined in Eq. (4.5). The terms represented schematically by $\mathcal{F}$ are slowly varying functions of E and are independent of x and x'. Note that $\kappa_\beta(0)=\kappa_\beta$ [defined in Eq. (4.5)], and that $\kappa_\beta(\epsilon)$ is a monotonically increasing function of ϵ. Substituting this expression into Eq. (A5) we obtain

$$I_{xx'}=\int_0^\infty d\epsilon\mathcal{F}f(E_{\alpha-1}+i\epsilon)\times\exp[-\kappa_{\alpha-1}(\epsilon)\,|\,x-x'\,|\,]-\int_0^\infty\mathcal{F}f(E_\alpha+i\epsilon)\times\exp[-\kappa_\alpha(\epsilon)\,|\,x-x'\,|\,]\ , \tag{A9}$$

where $\mathcal{F}$ again represents unimportant factors that are periodic in x and x'. From Eq. (A5) is is clear that

$$I_{xx'}\sim\exp(-\kappa_\alpha\,|\,x-x'\,|\,)\ , \tag{A10}$$

where κ_α is defined in Eq. (4.5).

The final step in the proof consists of joining the two previous pieces. Since

$$P_\alpha(xx')=\int_{E_{\alpha-1}}^{E_\alpha}dE\,G_{xx'}(E)\ , \tag{A11}$$

it is clear that from Eqs. (A1) and (A4) that

$$P_\alpha(xx')-P^{(C)}_\alpha(xx')\sim\exp(-\kappa_\alpha\,|\,x\,|-\kappa_\alpha\,|\,x'\,|\,)\ .$$

Equations (4.8) and (4.9) follow directly from this.

One final remark concerns the projection operators in tight-binding models. The analytic structure of $E(K)$ and $\varphi_K(n)$ is somewhat different for a tight-binding model than for the Schrödinger equation. For example, there are only a finite number of bands, not an infinite number as in Fig. 3(b). Thus, a different contour of integration must be employed than the one in Fig. 3(b). Nonetheless, the analytic structure of $E(K)$ for the various m-merized versions of the SSH model is quite similar to that of the Schrödinger equation. In particular, there are a series of branch points in complex K space which connect band α to band $\alpha+1$. For instance, in the dimerized SSH model (discussed in Appendix B), there are two bands with energies

$$E_\pm(K)/2t_0=\pm[\cos^2(Ka)+y^2\sin^2(Ka)]^{1/2}\ . \tag{A12}$$

Clearly the branch points for this model occur at

$$K=(n\pi/a)+\pi/a\pm(i/a)\tanh^{-1}(y)\ . \tag{A13}$$

The appropriate K-space contour of integration to use to evaluate the projection operator for this model is shown in Fig. 3(c).

APPENDIX B: WF IN THE SSH MODEL FOR $M=2$

In this section, as an example of WF's in a tight-binding model, we derive the WF for the dimerized SSH model

$$H=-\sum_n[t_0+(-1)^n\Delta_0/2](C^\dagger_nC^\dagger_{n+1}+\text{H.c.})\ . \tag{B1}$$

This is instructive since the simplicity of Eq. (B1) allows us to construct the WF's explicitly. The dimerization doubles the unit cell, so we define a new Bravais lattice

$$R_n=(2n+\tfrac{1}{2})a\ , \tag{B2}$$

where a is the original lattice constant. The lattice sites thus lie at the middle of the short bonds as shown in Fig. 2(a). There are two WF's associated with each site, the valence band WF, $\langle n\,|\,R,+\rangle=\varphi_+(na-R)$, which has bonding symmetry and the conduction band WF, $\varphi_-(na-R)$, which has antibonding symmetry:

$$\varphi_{\pm}(na-R)=\pm\varphi(R-na)\ . \tag{B3}$$

To construct these WF's we first must find the eigenstates of H, $|\kappa,\pm\rangle$, with the energy

$$E_{\pm}(K)=\pm\sqrt{[2t_0\cos(\kappa a)]^2+[\Delta_0\sin(\kappa a)]^2}\ .$$

This is easily done as in SSH. We then take the linear combination

$$\varphi_{\pm}(na-R)=\frac{1}{N}\sum_{\kappa}\exp[-\kappa(na-R)+\alpha_{\kappa}]\times\langle n\,|\,\kappa,\pm\rangle\ , \tag{B4}$$

where α_{κ} is a phase factor that we choose to satisfy Eq. (B3). The resulting expression for φ is

$$\varphi_{\pm}(na)=\begin{cases}\displaystyle\int_{-\pi/2}^{\pi/2}\frac{d\kappa}{2\pi}e^{i\kappa na}\left[\frac{\cos(\kappa)+iy\sin(\kappa)}{\cos(\kappa)-iy\sin(\kappa)}\right]^{1/4} & \text{for } Z=2n-\frac{1}{2}\\ \displaystyle\pm\int_{-\pi/2}^{\pi/2}\frac{d\kappa}{2\pi}e^{i\kappa na}\left[\frac{\cos(\kappa)-iy\sin(\kappa)}{\cos(\kappa)+iy\sin(\kappa)}\right]^{1/4} & \text{for } Z=2n+\frac{1}{2}\end{cases} \tag{B5}$$

where $y=(\Delta_0/2t_0)$. The branch points in the κ plane which determine the asymptotic properties of φ occur at $\kappa=\frac{1}{2}\pi(2n+1)\pm iK_0$ where the inverse decay length K_0 is defined by

$$K_0=\tanh^{-1}(y)\ . \tag{B6}$$

Notice that K_0 vanishes as the gap goes to zero. Thus, after some manipulations in the complex plane, φ can be written in a form which makes its asymptotic properties apparent:

$$\varphi_{\pm}(za)=\frac{\sqrt{2}}{2\pi}(-1)^n\times\begin{cases}\displaystyle\int_{K_0}^{\infty}d\kappa\,e^{-|z|\kappa|}\left[\frac{\sinh(\kappa)+y\cosh(\kappa)}{\sinh(\kappa)-y\cosh(\kappa)}\right]^{1/4} & \text{for } Z=2n-\frac{1}{2}\\ \displaystyle(\pm1)\int_{K_0}^{\infty}d\kappa\,e^{-|z|\kappa}\left[\frac{\sinh(\kappa)-y\cosh(\kappa)}{\sinh(\kappa)+y\cosh(\kappa)}\right]^{1/4} & \text{for } Z=2n+\frac{1}{2}\end{cases} \tag{B7}$$

or, at large distances,

$$\varphi_{\pm}(za)=\frac{\sqrt{2}}{2\pi}(-1)^n\frac{e^{-\kappa_0|z|}}{|z|}\times\begin{cases}(-\frac{1}{4})!(y\,|\,z\,|\,)^{1/4} & \text{for } Z=2n-\frac{1}{2}\\ (\frac{1}{4})!(y\,|\,z\,|\,)^{1/4} & \text{for } Z=2n+\frac{1}{2}.\end{cases} \tag{B8}$$

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