Physics Letters A 380 (2016) 3430–3433

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Energy bands and gaps near an impurity

E. Mihóková [a,*], L.S. Schulman [b]

[a] Institute of Physics, Acad. of Sciences of the Czech Rep., Cukrovarnická 10, 162 53 Prague 6, Czech Republic
[b] Physics Department, Clarkson University, Potsdam, NY 13699-5820, USA

ARTICLE INFO

Article history:
Received 11 April 2016
Received in revised form 9 August 2016
Accepted 11 August 2016
Available online 18 August 2016
Communicated by V.A. Markel

Keywords:
Crystal structure
Impurity
Modeling
Energy bands

ABSTRACT

It has been suggested that in the neighborhood of a certain kind of defect in a crystal there is a bend in the electronic band. We confirm that this is indeed possible using the Kronig–Penney model. Our calculations also have implications for photonic crystals.

Band gaps occur for waves in any non-trivial periodic structure. Current interest, however, focuses on two particular manifestations: electrons and photons. The present work, although focused on electrons, does have material relevant to photonic crystals.

In Baran et al. [1] the authors deal with electron states in crystals and explain the luminescence spectra of β-Ca_2SiO_4:Eu^{2+}, Eu^{3+}. They have the interesting suggestion that in the neighborhood of an impurity there is a bend in the conduction band; namely in that region there are fewer electron states and they are of higher energy.

There are other experimental observations that could be explained by considering local changes in the conduction or valence bands. As an example, consider irregularities that have been seen in the low temperature dependence of scintillator delayed-recombination signals. For many substances this signal is approximately temperature independent. This phenomenon has been explained as due to quantum tunneling between a recombination center and a nearby trap, and has been seen in a number of scintillating materials [2–6]. In particular, a constant low temperature delayed recombination signal was observed up to at least about 150–200 K. However, there is at least one important case that does not fit this picture. The intense peak in the delayed recombination signal in Ce^{3+}-doped $Gd_3Ga_3Al_2O_{12}$ (GGAG) [4] at around 100 K has so far not been satisfactorily explained. But if the conduction band does bend near the Ce^{3+} impurity things can change dramatically. The Ce^{3+} ion and the nearby resonant trap could then have different energy separations from the conduction band and unlike the Ce^{3+} excited state, the trap can be very shallow. The temperature independent quantum tunneling between Ce^{3+} and the trap would be accompanied by the transfer of excitation energy from the shallow trap to Ce^{3+} via the conduction band at very low temperatures. The latter temperature dependent process would produce the observed bump in the delayed recombination signal.

We have explored this idea of the conduction band bending using the simplest of one-dimensional models, the Kronig–Penney model with δ-functions.

A great deal of work along these lines has already been done, since impurities play an important role in almost-periodic systems. Early literature that employs the Kronig–Penney model includes Stęślicka and Sengupta [7], Kasamanyan [8] and many others. For photonic crystals, where the one-dimensional feature can be directly relevant, the Kronig–Penney model has also provided a framework; see Luna-Acosta et al. [9,10]. The emphasis in these works has been on the impurity state itself or on transmission properties. In many cases the techniques are similar [11], however, our primary concern is electronic states that respond to a single impurity. This seems close to the work of Baran et al. [1].

What we find is that a lone defect has a profound effect on the eigenstates, and besides shifting the location of the gap it can also change the nature of the eigenfunctions throughout the crystal. The Bloch theorem does not apply [12] and many familiar features show radical differences. We cannot be sure of the extent to which these properties persist in three dimensions, although [1] suggests its relevance.

* Corresponding author.
E-mail addresses: mihokova@fzu.cz (E. Mihóková), schulman@clarkson.edu (L.S. Schulman).

http://dx.doi.org/10.1016/j.physleta.2016.08.017
0375-9601/

Without an impurity and in a simple form, the Kronig–Penney model has Hamiltonian

$$H_0 = \frac{p^2}{2m} + \lambda \sum_{n=0}^{N-1} \delta(x - na)\,,$$

where a is the lattice spacing, N the number of cells, m the mass, and λ the strength of the potential. Note that we immediately use a δ function potential, since for the matters of principle that we seek the details of the periodic potential should not matter. In keeping with this viewpoint we also set $m = 1$ and $\hbar = 1$. To make comparisons to physical systems we will derive our energy scale from typical values for crystal systems.

We shall generally take λ to be negative, mimicking the attraction experienced by electrons at atomic locations. And finally, for the electronic case we insist (as is usual in these models) that the state at $x = Na$ differ from that at $x = 0$ *only* by a phase, that phase being Nka with k the wave vector entering the Bloch theorem.

With these assumptions, the wave function in cell n (such that $na < x < (n+1)a$) can be taken to be $\psi_n = A_n e^{iK(x-na)} + B_n e^{-iK(x-na)}$ with energy $E = K^2/2$. The condition at na imposed by the δ-function is $\Delta\psi' = 2\lambda\psi$ with $\Delta\psi'$ being the change in ψ's derivative. Note that the K appearing here is not the k of the Bloch theorem. It follows that

$$\begin{bmatrix} A_n \\ B_n \end{bmatrix} = M \begin{bmatrix} A_{n-1} \\ B_{n-1} \end{bmatrix}, \text{ with } M = \begin{bmatrix} \Omega(1+z) & \Omega^* z \\ -\Omega z & \Omega^*(1-z) \end{bmatrix},$$

$z = \lambda/(2iK)$, and $\Omega = e^{iKa}$ ($\Omega^* = e^{-iKa}$). The requirement that the eigenvalues of M^N be of magnitude 1 fixes the allowable bands and the gaps. Letting $\phi = Ka$, this condition is $|\cos\phi + (\lambda/2K)\sin\phi| < 1$. For bound states one can do an analytic continuation and the spectral condition is $\left|\cosh\bar{\phi} - (|\lambda|/2\overline{K})\sinh\bar{\phi}\right| < 1$, where $\overline{K}$ and $\bar{\phi}$ are the analytic continuations, $E = -\overline{K}^2/2$ and λ is assumed negative. We will later use the numerical value of the top of the "valence band" (the bound states) and the bottom of the conduction band to relate our energy to the physical scales. The matrix M is known as the transfer matrix; it conserves current ($\propto K(|A_n|^2 - |B_n|^2)$) and is an element of the group SU(1, 1) [13].

We assume that our impurity is at site L with $1 \le L \le N$. We do *not* seek a value for the impurity level—as some of the articles cited earlier do. Rather we assume it is there and its associated defect provides a force—different from the usual—on nearby electrons. This is in keeping with the physical situation in [1], where the presence of Eu^{3+} (an impurity) causes an additional charge compensating defect to appear in the vicinity of the europium to maintain the lattice charge neutrality. To keep things simple we assume that in cell-L, as a consequence, there is an additional positive, constant, repulsive potential throughout the interval $La < x < (L+1)a$ [14]. To provide a framework for solution we further assume that this situation repeats, so that, as for the system without impurities, we require that the associated full transfer matrix (presented below) has eigenvalues of magnitude unity. (In this our method could be thought of as involving a supercell. For photons one calculates instead transmission probability.)

In cell L (i.e., $La < x < (L+1)a$) the momentum is reduced and we have $K' = \sqrt{K^2 - 2V}$, with V the value of the potential in that interval. As the wave function in that interval we take $\psi_L = A_L e^{iK'(x-La)} + B_L e^{-iK'(x-La)}$ (with analytic continuation if necessary). There are now two transfer matrices, from $L-1$ to L and from L to $L+1$. These are designated $M_{K\to K'}$ and $M_{K'\to K}$, respectively. A straightforward calculation gives

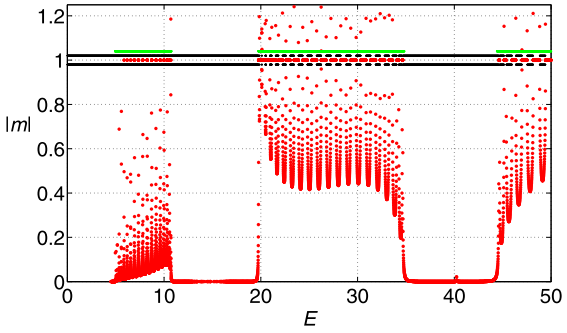

Fig. 1. Absolute values of eigenvalues of M_{all} ($|m|$) are shown as red points (some of which are excluded because of a cutoff in the axes). In addition, when an eigenvalue does not have magnitude 1, a pair of black dots are displayed at 1 ± 0.02. Finally to better judge the effect of the impurity, the normal, i.e., $V = 0$, energy band is shown in green at a height of 1.04 (although these are magnitude unity eigenvalues of M^N) [15]. Parameter values: $\lambda = -10$, $a = 1$, $V = 15$, $N = 20$, $L = 9$. The energy, E, in this figure is roughly twice the actual energy in eV. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article. See also [15].)

$$M_{K_1\to K_2} = \begin{bmatrix} \Omega_1\left(\frac{K_1+K_2}{2K_2} + z_2\right) & \Omega_1^*\left(\frac{K_2-K_1}{2K_2} + z_2\right) \\ \Omega_1\left(\frac{K_2-K_1}{2K_2} - z_2\right) & \Omega_1^*\left(\frac{K_1+K_2}{2K_2} - z_2\right) \end{bmatrix},$$

where $z_2 = \frac{\lambda}{2iK_2}$, $\Omega_1 = e^{iK_1 a}$, and K_1 and K_2 are either K and K' or the reverse. With the impurity at L the total transfer matrix for all L cells is $M_{\text{all}} \equiv M^{N-L} M_{K'\to K} M_{K\to K'} M^{L-2}$.

To see whether the spectrum of M_{all} fulfills the expectations of [1] we display Fig. 1. The red dots, which are slightly larger than the others, are the eigenvalues of M_{all}; when they have magnitude one indefinite ring propagation is possible. Superimposed on this image are green dots at height 1.04, which are located at energy values for which magnitude 1 eigenvalues exist for $V = 0$. These would be the bands (and in their absence, the gaps) without the impurity. To make clear that many energy values *within* the non-defect bands are also eliminated we have put a pair of black dots displaced by 0.02 from 1 for each eigenvalue of M_{all} that is *not* of magnitude 1 [15]. In principle this can also be seen from the red dots at small magnitude values [16]. A number of observations can be made from this image. First, many states that were formerly ($V = 0$) in the conduction band no longer appear there. Moreover, the first conduction band ($5 \lesssim E \lesssim 10$ in our units) has increased its energy, as suggested in [1]. That there is little or no increase for the next band is to be expected since the energies are larger and the potential may be expected to have less influence. And then there is what we do not see. No new states emerge in the gap, although the impurity can increase transmission, a kind of resonance phenomenon in photonic crystals. (Confusion may arise since the red dot at the top of the first conduction band might be taken to be to the right of the green dot above it. But this is an artifact of the dot size, which is larger for the $V \neq 0$ band.) No points appear below about $E = 4.5$ because of issues of numerical accuracy [17]. Even for transmission data, the values of the small-K matrix M_{all} are so large that a cutoff at 10^{-10} in the graph would lose these numbers as well.

It is interesting to focus on the first (left-most) E value in the conduction band. Although it is to the right of the beginning of the $V = 0$ band (confirming the "bend in the band") even this is not the full story. For more information we turn to another graph, shown in Fig. 2. First note that when $V = 0$ the wave functions