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In the Classroom

The Kronig-Penney Model: A Single Lecture Illustrating the Band Structure of Solids

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A simple model of a crystalline solid that leads to an electronic band structure is presented. The development requires no quantum mechanics beyond that taught in most physical chemistry courses and can be taught in a single one-hour lecture.

In spite of the ever increasing importance of solid-state chemistry, little solid-state theory is taught in most physical chemistry courses. In this paper we present a relatively simple quantum-mechanical model of the solid state that requires no more quantum theory than is taught in any standard physical chemistry course and that yields directly the band electronic structure of crystalline lattices. Furthermore, the material here can easily be presented in one lecture. The model that we shall present was first formulated in 1930 by R. de L. Kronig and W. G. Penney [1] and is called the Kronig-Penney model. Although the Kronig-Penney model is discussed in a number of solid-state physics texts [2],

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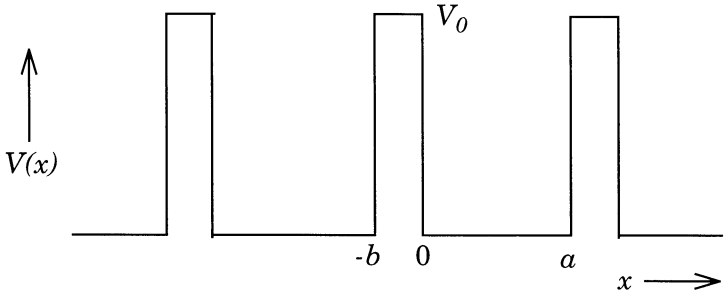

FIGURE 1. THE KRONIG-PENNEY POTENTIAL.

it is usually developed in a way that makes it fairly abstruse to most chemistry undergraduate students.

The Kronig-Penney model is represented by the one-dimensional periodic potential shown in Figure 1.

Even though the model is one-dimensional, it is the periodicity of the potential that is the crucial property that yields electronic band structure. The mathematical form of the repeating unit of the potential is

$$\begin{aligned} V(x) &= V_0 \qquad -b < x < 0 \\ &= 0 \qquad\quad 0 < x < a \end{aligned} \tag{1}$$

As shown in Figure 1, the potential has a period of $c = a + b$. The Schrödinger equation for this model is

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \qquad 0 < x < a \tag{2a}$$

$$\frac{d^2\psi}{dx^2} + \frac{2m(E - V_0)}{\hbar^2}\psi = 0 \qquad -b < x < 0 \tag{2b}$$

The coefficients in both of these equations are constants, so the solutions are similar to that of a particle in a box. The solutions to Equations 2 are

$$\psi_1 = A^{i\alpha x} + Be^{-i\alpha x} \qquad 0 < x < a \tag{3a}$$

and

$$\psi_2 = Ce^{\beta x} + De^{-\beta x} \qquad -b < x < 0 \tag{3b}$$

where

$$\alpha = \frac{(2mE)^{1/2}}{\hbar} \tag{4}$$

and

$$\beta = \frac{[2m(V_0 - E)]^{1/2}}{\hbar} \tag{5}$$

are real quantities if we assume for the time being that $E < V_0$.

The fact that the potential is periodic imposes a restriction on the form of the wave function $y(x)$. Define an operator $\hat{T}$ that shifts $y(x)$ by a distance c. The resulting wave function $y(x + c)$ must be a multiple of $y(x)$, and so we write

$$\hat{T}\mathrm{y}(x) = t\mathrm{y}(x) = \mathrm{y}(x + c) \tag{6}$$

where t is a constant that is of magnitude unity. We can apply this translation operator repeatedly to obtain

$$\hat{T}^n\mathrm{y}(x) = t^n\mathrm{y}(x) = \mathrm{y}(x + nc) \tag{7}$$

At this point we shall apply a periodic boundary condition that pictures the one-dimensional lattice to be a ring of N atoms, so that $y(x) = y(x + Nc)$. Clearly if N is large, this condition has no physical consequence. This (standard) boundary condition is called the Born-von Karmen boundary condition [3]. If we apply this boundary condition to Equation 7, then we have

$$\hat{T}^N\mathrm{y}(x) = t^N\mathrm{y}(x) = \mathrm{y}(x + Nc) = \mathrm{y}(x) \tag{8}$$

or that $t^N = 1$. Thus we find that t must be one of the N roots of unity, or that

$$t = e^{2\pi i l/N} \qquad l = 0, 1, 2, \ldots, N - 1 \tag{9}$$

Defining k by $k = 2\pi l/Nc$, t becomes $t = e^{ikc}$ and so we can write

$$\psi(x + c) = e^{ikc}\psi(x) \tag{10}$$

Now, any function $y(x)$ satisfying this equation can be written in the form

$$\psi(x) = u(x)e^{ikc} \tag{11}$$

where $u(x)$ is a periodic function with period c ($u(x + c) = u(x)$). To see that this must be so, we write

$$\begin{aligned}\psi(x + c) = u(x + c)e^{ik(x+c)} &= e^{ikc}u(x + c)e^{ikx} \\ &= e^{ikc}u(x)e^{ikx} \\ &= e^{ikc}\psi(x) \end{aligned} \tag{12}$$

as in Equation 10. Equation 11 is a fundamental result of solid-state physics and is known as Bloch's theorem [4]. Any wave function for a periodic potential of period c must necessarily have that form.

The solutions to Equations 2 yield four integration constants, and so we require four boundary conditions to determine them. Two of these boundary conditions can be taken to be that $y(x)$ and its first derivative must be continuous across any discontinuity in the potential, and we shall impose this condition at the point $x = 0$. If $\psi_1(x)$ denotes $\psi(x)$ for $-b < x < 0$ and $\psi_2(x)$ denotes $\psi_2(x)$ for $0 < x < a$, then these two boundary conditions read

$$\psi_1(0) = \psi_2(0) \qquad \text{and} \qquad \psi_1(0) = \psi_2(0) \tag{13}$$

where the prime denotes the first derivative. Furthermore, from Bloch's theorem, $u(x) = u(x + a)$ and so not only is $u(x)$ periodic, but its first derivative must also be periodic. Therefore, we have the two conditions

$$u(-b) = u(a) \qquad \text{and} \qquad u'(-b) = u'(a) \tag{14}$$

These four boundary conditions are sufficient to determine $y(x)$ completely. Equations 13 give the two equations

$$\begin{aligned}&A + B = C + D \\ &\beta C - \beta D = i\alpha A - i\alpha B\end{aligned} \tag{15}$$

and Equations 14 give

$$\begin{aligned} &Ae^{i(\alpha-k)a} + Be^{-i(\alpha+k)a} = Ce^{-(\beta-ik)b} + De^{(\beta+ik)b} \\ &i(\alpha-k)Ae^{i(\alpha-k)a} - i(\alpha+k)Be^{-i(\alpha+k)a} \\ &\qquad = (\beta-ik)Ce^{-(\beta-ik)b} - (\beta+ik)De^{(\beta+ik)b} \end{aligned} \tag{16}$$

In order for there to be a nontrivial solution to the above four equations for A, B, C, and D, the determinant of their coefficients must vanish. This gives us the determinantal equation

$$\begin{vmatrix} 1 & 1 & 1 & 1 \\ \beta & -\beta & i\alpha & -i\alpha \\ e^{(ik-\beta)b} & e^{(ik+\beta)b} & e^{i\alpha(\alpha-k)} & e^{i\alpha(\alpha+k)} \\ (\beta-ik)e^{(ik-\beta)b} & -(\beta+ik)e^{(ik+\beta)b} & i(\alpha-k)e^{ia(\alpha-k)} & -i(\alpha+k)e^{ia(\alpha+k)} \end{vmatrix} = 0 \tag{17}$$

It is straightforward, albeit lengthy, to show that Equation 17 is equivalent to

$$\frac{\beta^2-\alpha^2}{2\alpha\beta}\sinh(\beta b)\sin(\alpha a) - \cosh(\beta b)\cos(\alpha a) = \cos(a+b)k \tag{18}$$

(The step-by-step procedure is outlined in the Appendix for completeness, although it is certainly not really necessary to carry it out in class, or anywhere else for that matter.) Equation 18 may appear to be hopeless, but it can be cast into a more transparent form. From Equations 4 and 5 we have

$$\alpha^2 = \frac{2mV_0}{\hbar^2}\frac{E}{V_0} = \frac{2mV_0}{\hbar^2}\varepsilon \tag{19}$$

and

$$\beta^2 = \frac{2m(V_0-E)}{\hbar^2} = \frac{2mV_0}{\hbar^2}(1-\varepsilon) \tag{20}$$

where $\varepsilon = E/V_0$. Therefore

$$\frac{\beta^2-\alpha^2}{2\alpha\beta} = \frac{1-2\varepsilon}{2\varepsilon^{1/2}(1-\varepsilon)^{1/2}} \tag{21}$$

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Furthermore,

$$\beta b = \frac{b}{a}\left(\frac{2mV_0}{\hbar^2}\right)^{1/2} a\varepsilon^{1/2} = rA(1-\varepsilon)^{1/2} \tag{22}$$

and

$$\alpha a = \left(\frac{2mV_0}{\hbar^2}\right)^{1/2} a\varepsilon^{1/2} = A\varepsilon^{1/2} \tag{23}$$

where $r = b/a$ and $A = (2mV_0/\hbar^2)^{1/2}a$ are parameters whose values are fixed by the potential. Using Equations 21 through 23, Equation 18 becomes

$$\begin{aligned}\frac{(1-2\varepsilon)}{2\varepsilon^{1/2}(1-\varepsilon)^{1/2}}&\sinh[rA(1-\varepsilon)^{1/2}]\sin(A\varepsilon^{1/2}) + \\ &\cosh[rA(1-\varepsilon)^{1/2}]\cos(A\varepsilon^{1/2}) = \cos[ka(1+r)] \quad \varepsilon < 1\end{aligned} \tag{24}$$

Equation 24 is valid for the case in which $\varepsilon < 1$. For the case in which $\varepsilon > 1$, we replace the factor $(1-\varepsilon)^{1/2}$ by $i(\varepsilon-1)^{1/2}$ and use the identities $\sinh iz = i\sin z$ and $\cosh iz = \cos z$ for $\varepsilon > 1$. For $\varepsilon > 1$, Equation 18 becomes

$$\begin{aligned}\frac{(1-2\varepsilon)}{2\varepsilon^{1/2}(\varepsilon-1)^{1/2}}&\sin[rA(\varepsilon-1)^{1/2}]\sin(A\varepsilon^{1/2}) + \\ &\cos[rA(\varepsilon-1)^{1/2}]\cos(A\varepsilon^{1/2}) = \cos[ka(1+r)] \quad \varepsilon > 1\end{aligned} \tag{25}$$

At the point $\varepsilon = 1$ both Equations 24 and 25 give

$$\cos A - \frac{rA}{2}\sin A = \cos[ka(1+r)] \qquad \varepsilon = 1 \tag{26}$$

For notational convenience, we shall write Equations 24 through 26 collectively as

$$F(\varepsilon) = \cos[ka(1+r)] \tag{27}$$

where $F(\varepsilon)$ is given by the left-hand sides of Equations 24 for $\varepsilon < 1$ and by the left-hand side of Equation 25 for $\varepsilon > 1$. Equation 27 gives ε as a function of ka for all values of ε for fixed values of r and A, or, in other words, it gives $\varepsilon(ka)$, at least in principle, for a fixed potential. Although it is not possible to solve Equation 27 analytically, it can

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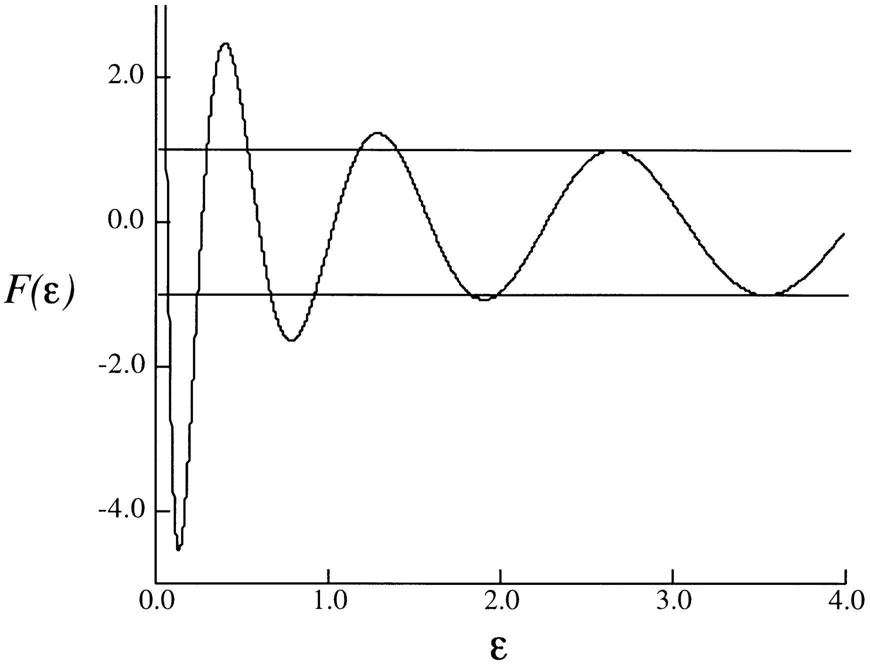

FIGURE 2. A PLOT OF $F(\varepsilon)$, THE LEFT-HAND SIDE OF EQUATION 27, AGAINST ε. THE ONLY ALLOWED VALUES OF ε ARE THOSE FOR WHICH $F(\varepsilon)$ LIES BETWEEN $+1$ AND -1.

be easily solved graphically. The function $F(\varepsilon)$, which is just a function of ε for a fixed potential, is plotted against ε in Figure 2 for $A = 10$ and $rA = 2$.

The value of $\cos[ka(1 + r)]$, the right-hand side of Equation 27, must lie between $+1$ and -1; consequently, the only allowed values of ε are those for which $F(\varepsilon)$, the left-hand side of Equation 27 lies between $+1$ and -1. The two horizontal lines in Figure 2 represent the two extreme values of $\cos[ka(1 + r)]$. The only allowed values of ε are those for which $F(\varepsilon)$ lies between the two horizontal lines. These values are given in Table 1.

As either Figure 2 or Table 1 indicates, the allowed values of ε fall into continuous regions separated by gaps. This distribution of allowed energies illustrates the band structure of crystalline solids. A solid will act as a conductor, an insulator, or a semiconductor, depending upon the electronic population of the bands and their separations.

It is customary to present the results in Table 1 as a plot of ε against the wave vector k, as shown in Figure 3.

To see how this plot is obtained, let's invert Equation 27 and write $k \propto \cos^{-1} F(\varepsilon)$.

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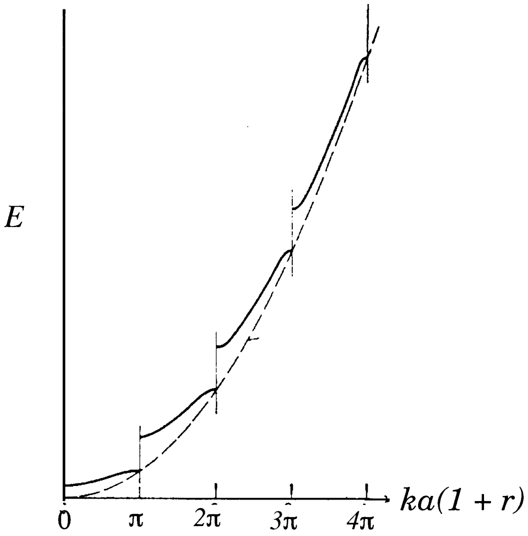

FIGURE 3. A PLOT OF ENERGY ε AGAINST WAVE NUMBER K SHOWING THE BAND GAPS THAT APPEAR WHEN $KA(1+R) = N\pi$. THE DASHED LINE IS THE PARABOLIC RESULT FOR FREE ELECTRONS.

According to Figure 2 and Table 1, for values of ε from 0 to 0.0616, $F(\varepsilon)$ is greater than one and so there is no real value of k (or really $ka(1+r)$) that satisfies Equation 27. At $\varepsilon = 0.0616$, $k = 0$. As ε varies from 0.0616 to 0.0744, $\cos[ka(1+r)]$ varies from $+1$ to -1, and so $ka(1+r) = p$. As ε varies from 0.0744 to 0.2425, there is no real

TABLE 1. The allowed values of $\varepsilon = E/V_0$ for the potential shown in Figure 1 with $r = b/a = 0.20$ and $A = (2mV_0)^{1/2}/\hbar = 10$.

band	range of ε
1	0.0616–0.0744
2	0.2425–0.2965
3	0.5325–0.6652
4	0.9192–1.1776
5	1.3980–1.8305
6	1.9791–2.6190
7	2.6850–

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value of k that satisfies Equation 27. At $\varepsilon = 0.2425$, $ka(1+r)$ once again equals π. At $\varepsilon = 0.2965$, $ka(1+r)$ now equals 2π, and another band gap appears in Figure 3. Continuing this argument, we get the series of discontinuities in the plot of ε against k (or really $ka(1+r)$) as shown in Figure 3.

It is instructive to compare the result shown in Figure 3 with that of a free electron. We can obtain this result by letting $V_0 = 0$ in Equation 18. In that case, $\beta = i\alpha$ and so $(\beta^2 - \alpha^2)/2\alpha\beta = i$. Using the fact that $\sinh i\alpha b = i \sin \alpha b$ and that $\cosh i\alpha b = \cos \alpha b$, Equation 18 becomes

$$-\sin \alpha b \sin \alpha a + \cos \alpha b \cos \alpha a = \cos \alpha(a+b) = \cos k(a+b) \tag{28}$$

or that $\alpha = k$. Therefore, from Equation 4 we find that

$$E = \frac{\hbar^2 k^2}{2m} \tag{29}$$

for a free particle. Equation 29 is shown as the parabola in Figure 3.

The other extreme limit is to let V_0 be large, in which case we should obtain the energies of a particle in a box. If V_0 is large, then ε is small, so that the factor multiplying the first term in Equation 24 becomes $1/2\varepsilon^{1/2}$, which is a large quantity. Therefore, the first term in Equation 24 dominates the second term and we have

$$\frac{e^{rA}}{4\varepsilon^{1/2}} \sin A\varepsilon^{1/2} = \cos[ka(1+r)] \tag{30}$$

The factor in front of $\sin A\varepsilon^{1/2}$ approaches infinity for large values of V_0 and so $\sin A\varepsilon^{1/2}$ must approach zero in order that the value of left-hand side of Equation 30 lie between $+1$ and -1. In the limit, then, $\sin A\varepsilon^{1/2}$, and so $A\varepsilon^{1/2} = \pm n\pi$, or, using the definition of A,

$$E = \frac{n^2 h^2}{8ma^2} \tag{31}$$

which represent the allowed energies of a particle in a box.

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Appendix

The recipe for reducing Equation 17 to Equation 18 is as follows [5]: (1) First multiply row 3 of Equation 17 by ik and add the result to row 4. (2) Multiply rows 3 and 4 of the result of step (1) by e^{-ikb} and note that $c = a + b$. (3) Now add column 1 to column 2 and column 3 to column 4. (4) Subtract 1/2 of column 2 from column 1 and 1/2 of column 4 from column 3. (5) Expand the resulting determinant about row 4 and finally get Equation 18.

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