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The Kronig-Penney Model

Inspired by the work of Felix Bloch, Ralph Kronig and William Penney came up with a simple way to model a crystal lattice. Born June 24, 1909 William Penney studied at the Imperial College of Science and completed his post-doctoral research at London University.[1] Subsequently during WWII, he studied explosions and shockwaves, and eventually began working on the Manhattan Project using his previous research to estimate the atomics bomb's power. He continued research into a British hydrogen bomb and his work with these types of weapons became the primary focus of most of the later part of his life, and some believe tainted his legacy, he died March 3rd, 1991. On the other hand, Ralph Kronig was born March 10th, 1904 and received his PhD in 1925 from Columbia University, and before even graduating he had proposed the idea of spin which was shut down by other scientists, including Pauli who would later publish about it.[2] He then moved to Europe for his studies where he eventually became a full professor at Delft University of Technology. Over his career he was friends with many other prominent physicists. He stayed in academia, where he studied x-ray spectroscopy, until his eventual retirement. A prolific number of papers where published that invoked his theories and he died November 16th, 1995.

Kronig and Penney's work was encouraged by previous studies into periodic potentials and they hoped that they could come up with a model more similar to actual physical systems that gave quantitative results. They begin their model assuming a finite width and height of the potential giving them the Schrödinger's equation of $\frac{d^2\psi}{dx^2} + \kappa^2[W - V(x)]\psi = 0$ with $\kappa^2 = \frac{8\pi^2 m}{h^2}$.[3] With a finite width they use continuity at boundaries of the wave function and its derivative, along with

the Bloch condition to come up with: $\frac{\gamma^2-\beta^2}{2\beta\gamma}\sinh(\gamma b)\sin(\beta a)+\cosh(\beta a)\cos(Ba)=\cos(\alpha(a+b))$, where $\gamma=\kappa\sqrt{V_0-W}$ and $\alpha=\frac{2\pi k}{L}$ $\beta=\kappa\sqrt{W}$, which by applying the width of the potential, b, goes to 0 they get the familiar equation $\frac{Psin(\beta a)}{\beta a}+\cos(\beta a)=\cos(\alpha a)$, where $\lim_{\substack{b\to 0\\ \gamma\to\infty}}\frac{\gamma^2 ab}{2}=P$. To solve this, they plot each side of the equation and seeing where they overlap, noting that there are disallowed regions. They note that as P goes to infinity this becomes the case of a free electron, while as P increases it has discrete energy values as the electrons become bound. They similarly use the boundary conditions and normalization to find the constants of the wave function and they find that as the distance between the potentials increases the energy values get closer together. Using the wavefunction they are able to calculate the average momentum, and thus how current behaves in this solid due to any stationary state.

They reach a motivation for their theory by examining how an electron entering the crystal would react. In doing so they are able to calculate a coefficient of reflection dependent on velocity and the spacing of a crystal and find that as velocity increases that reflections only can occur when the lattice spacing is very close to the de Broglie wavelength or an integer multiple of such (Fig 1). They do however acknowledge that its is difficult to quantitatively compare this to experimental results as their model is one dimensional, the periodic behavior of potentials in metals isn't fully analogous to what it is in real life and it does not include the scattering of electrons off of each other, general features such limit of the reflection maxima, and its decrease as velocity increases can be seen in research done by Rupp. However, much of Rupp's work was discredited in 1935, it is unclear how legitimate those results are.

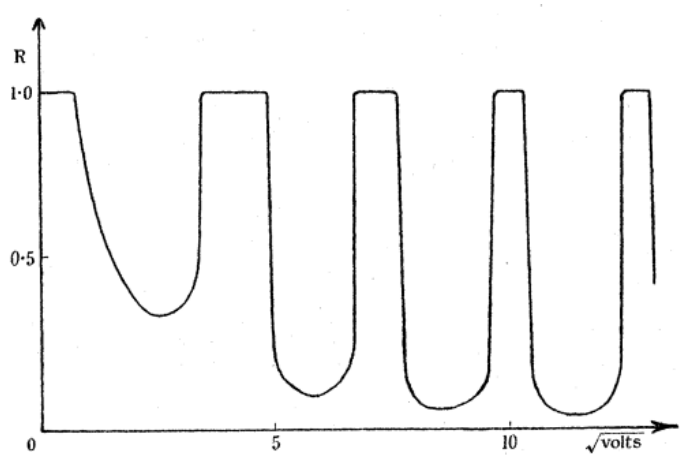

Figure 1: Velocity vs Reflection Coefficient for Kronig-Penney Model [3]

They then postdict something that appears in Rupp's experiments where "new radiations appear in the soft X-ray spectrum of the substance bombarded at about the same velocity at which the reflection coefficient has a maximum" which they explain from their look at the average momentum finding that as it increases to a disallowed regime it enters a new set of energy values. They also note that an electron can transition to other stationary states when radiation is absorbed.

While the Kronig-Penney model is easy to understand it lack certain details that would allow it to be more directly comparable to experimental results. Its assumptions do not take into account other electrons nor how different structures of the lattice might affect the behavior of electrons.

William Shockley continues this investigation into 1D periodic lattices in "On the Surface States Associated with a Periodic Potential" where he brings up the problem with using infinite crystals just to simplify the wave function, the edge effects in real systems.[4] Following up on the research of Tamm, he examines a finite 1D lattice and examines how surface states come into being. One result to note is that now that the crystals are finite it has a defined center, the wave function can be either symmetric or anti symmetric depending on edge behavior. By requiring

periodicity he finds that $\tan(\frac{ka}{2})^2 = -(\frac{g'}{g})/(\frac{u'}{u})$ where the function in each cell is expanded into a symmetric and anti-symmetric function where g and u, and g' and u' represent the value of those functions at the edge of the cell and their derivatives respectively. Energy bands can only occur when only one of $(\frac{u'}{u})$ and $(\frac{g'}{g})$ are negative as they result on the left side of the equation must be positive. (Fig 2) Then using a similar potential and applying perturbation theory to the previous calculation he finds 2 states with energies above the boundary curves as in the previous case, which he labels as surface states, these surface states are noted to diverge from their energy bands after the crossing of the boundary curves.

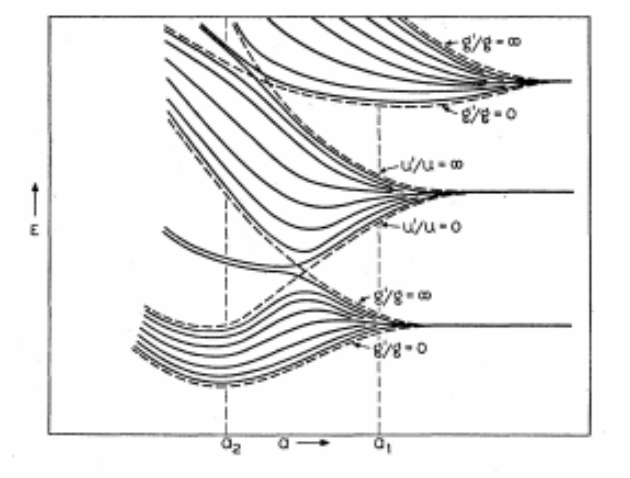

Figure 2: The energy spectrum of the periodic array of 8 atoms. Two state can be seen to split off. [4]

He explains that if the bands are full then after crossing the boundary curve there is now one too few states for the electrons and they are pushed into a surface state. Seeing as there are now *N-1* states by looking in three dimensions this gives a result of $3N^2$ electrons pushed out and $6N^2$ states so it is expected that this "surface band" will be half filled. As such he predicts that this surface band would be conducting though he also notes that while it should work in diamond it does not, possibly due to additionally adsorbed atoms donating electrons to the surface band and

that these surface state should be present in numerous metals and needs to be taken into account when looking at the charge distribution of metals, this description of surface states became known as Shockley states.

The Kronig-Penney model was especially interesting to people studying x-ray scattering. George H Vineyard uses a method for calculating x-ray scattering which he compares to the Kronig-Penney Model. Rather than the Born approximation which uses a plane wave, he uses the distorted wave approximation which involves simpler scatterer distribution where a field is then calculated based on how a plane wave interacts with it and is calculated exactly, this is the distorted wave which is then used with the real scatterer to get a more accurate representation than the Born approximation.[5] This can then be done to higher orders. He begins by assuming a varying permittivity which has a can be broken into both small- and large-scale variations, solving for how a wave scatters on the large-scale variation first, then then using that resulting wave to scatter on the small-scale variation. Using Maxwell's equations and Snell's law the different components of the incident wave vector. He then calculates the different components of *E',* the wave interacting with the large-scale variation of the permittivity, and uses this as a distorted wave to interact with the small-scale variation of the permittivity. He finds that the scattering intensity peaks when the different components of the wave vector line up with reciprocal lattice points.

In the appendix he performs these calculations again using a permittivity based on the Kronig-Penney model of a layered lattice $\epsilon(\vec{r}) = 1 - \frac{r_e \lambda^2 M f_0}{\pi} \sum_{n=0}^{\infty} \delta_D(z - nd)$ where M is the number of atoms per unit area, f_0 is the electrons per atom, d is the spacing between planes, λ is the wavelength of light on the samples and r_e is the classical electron radius. He finds that there is a simple harmonic wave between each lattice point and finds the field of the wave to agree with the field of the homogenous slab calculated with the distorted wave.

While this paper generally took a larger scale approach to the problem of x-ray scattering, he still used the Kronig-Penney model to check his work on the small-scale interactions, showing that the 1D potential being use for modelling stratified lattices stacked on top of each other. The simplicity of the Kronig-Penney model illustrates its usefulness here. It is worth noting that this is still a very idealized case and is only checked on a homogenous crystal, but as a sanity check between the two methods it gives an appreciative result.

The Kronig-Penney model is useful for this kind of simplicity, but it is difficult to take into many variations. L. R. Ram-Mohan, K. H. Yoo, and R. L. Aggarwal set out to develop a method an extended transfer-matrix in order to calculate wave functions and energy spectra for more arbitrary lattices. By expanding their wave functions into a slowly varying envelope function around a faster oscillating term and having their Hamiltonian included potential from the conduction-band and valence-band they get a series of differential equations.[6] The solution to which allows for the construction of a 16x16 transfer matrix $\mathcal{T}(z)$ from as $\Phi(z) = \mathcal{T}(z)\Phi(0)$ where $\Phi(z)$ is the system of 16 first order differential equations from their Hamiltonian. By diagonalizing the total transfer matrix, a wavefunction can be obtained. Their model produces the band structure of GaAs/GaAlAs superlattice which is relatively similar to those calculated by Guido Altarelli, with a few differences, such as valence bands having higher dispersion, band-edge energies differing, and the light hole band having a maximum at a different location in k space. They notice a large change in the valence bands due to the use of a spherical approximation that does not take into account the warping of the valence bands of the bulk material, noting that these values are sensitive to the small changes this includes. The spherical approximation changes some constants which the valence bands depend on, one of which occurs from a Kronig-Penney arrangement and is inversely dependent on the changed constants.

They then leverage their methodology to look at the effects of magnetic fields on these calculations. Using a standard practice, they rewrite this magnetic field Hamiltonian in terms of creation and annihilation operators and apply their transfer matrix method to calculate the Landau levels dependence on the magnetic field. They follow this by comparing their calculations to the tight binding model of a different super lattice which line up well with calculations done by others. The method they use extends the of the one band transfer matrix to solve Kronig-Penney model into a larger structure, maintaining its conceptual simplicity while also being able intake applied magnetic fields and strain.

In general, the Kronig-Penney model is used for comparison to newer methods, one such method used by A Tanimu and E A Muljarov is the resonant-state expansion, a type of perturbation theory developed for electrodynamics, they applied to a one-dimensional quantum system. They use resonant states, which have a complex frequency and can be used to replace a continuum, of the unperturbed Hamiltonian as their basis to construct perturbed resonant states.[7] They use Dirac δ to model the potential and they use the resonant states as their unperturbed basis. $V(x) = -\gamma\delta(x-a) - \gamma\delta(x+a)$, where γ is the strength of the potential and a is half the distance between them, and thus have three different regimes and give the secular equation $1 + \frac{2ik_n}{\gamma} = \mp e^{2ik_n a}$. The perturbation is $\Delta V(x) = -\beta\delta(x-b)$ where $|b| < a$. They find an analytic solution to both the double and triple well potentials and numerically solve for RSs. They find that the symmetric triple well system it is similar to a double-well system with small oscillations around it, but that the asymmetric triple-well is fairly different showing a larger oscillation in the wavefunction.

They then calculate the elements of the perturbation matrix and find that if the unperturbed and perturbed potentials are symmetric, the resonant state wavefunction are the in each are either even or odd. Thus, the perturbation does not mix any of the resonant states of different parity.

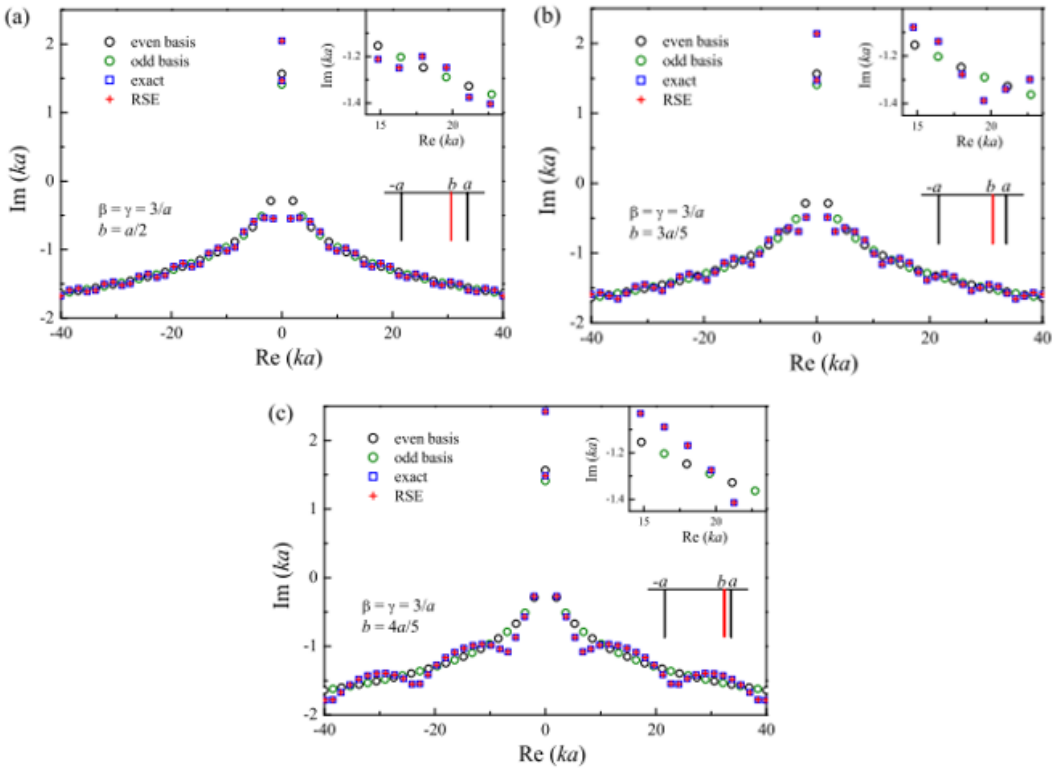

FIG. 3. As Fig. 2(a), but for $b = a/2$ (a), $b = 3a/5$ (b), and $b = 4a/5$ (c).

Figure 3: Wave numbers of Resonant States, note the quasi-periodicity [5]

Additionally, if the perturbation is in at $b=0$ then the odd states are not perturbed at all, and this is seen in the exact solution. By comparing their resonant state expansion to the exact solution, they find that it matches up very well. Following this they apply their method to a finite periodic lattice. They claim the advantage their method has is that when using resonant states in a certain spectral range they have access to all observables without needing to completely redo the calculation for a different energy. Their potential is N evenly spaced delta functions of strength γ and a perturbation $\Delta V_{nm} = -\gamma \sum_{k=2}^{N-1} \delta(x - b_k)$ where $b_k = -a + d(k-1)$. As they increase N the numerical

complexity remains the same as long as the integral strength of the perturbation does not, if it does it requires an increase in the basis size *M*. As N increases the number of states in the periodic deviation from the unperturbed states increases as well (Fig 3). As N goes to infinity this becomes the Kronig-Penney model. They compare the Kronig Penney model to their model at N=20 and realize that the periodic groups of resonant states they saw earlier form the allowed energy bands. As they increase γ they see that and find that the separation between the periodic dependence is strongly dependent on it. This matches up the Kronig-Penney model results.

Generally, they seek validation for this method of solving 1D quantum systems, so they compare it to either an analytical solution that can be calculated or other models, but do not apply it to a novel system. It does replicate those other methods and models well but does not predict any new behavior. The most notable thing they discover is that the periodic groups of resonant state become the band structure as the number of wells increases, showing how a certain size of crystal is necessary for band structure, but again this is only explaining a phenomenon that also appeared in the analytic solution that already existed for these potentials. And still this is an explanation for behavior that is seen in a theoretical system, not actually looking at experimental results.

In general, while some earlier work may have been based directly on the Kronig-Penney model many subsequent researchers used the model as a comparison to their own. Due to its analytic solution they can apply their method to solve the Kronig-Penny potential, or a similar high N system and see if the solutions are at least qualitatively similar to validate their model. While the Kronig-Penney, is very simple it was useful for showing that the electron in the potential have similar characteristics to free and bound electrons. For the most part it is most useful as a toy model to check the validity of other models or methods of solving for the energies of a potential structure.

[1] https://en.wikipedia.org/wiki/William_Penney,_Baron_Penney

[2] https://en.wikipedia.org/wiki/Ralph_Kronig

[3] R. de L. Kronig, W. G. Penney, *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **130**, 814 (1931).

[4] W. Shockley, *Physical Review* **56**, 317(1939).

[5] G. H. Vineyard, *Physical Review B* **26**, 8 (1982).

[6] L. R. Ram-Mohan, K. H. Yoo, and R. L. Aggarwal, *Physical Review B* **38**, 6151 (1988).

[7] A. Tanimu and E. A. Muljarov, *Phys. Rev. A* **98**, 022127 (2018).