

# Analysis of Colour Centres in 2D Ionic Crystals by use of Green's Functions

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## Introduction

In this project I attempted to calculate bound state energies for colour centres found in typical ionic crystals. A Colour centre occurs when a negative ion is removed from an ionic crystal. Charge neutrality is normally conserved in through 2 processes. Either the addition of a negative ion interstitially in the lattice (Frenkel defect) or, through removal of a positive ion (Schottky defect). A third process however, can occur. In the vicinity of the defect there is a build up of positive charge as the hole is surrounded by positive ions. It is possible for an electron to become bound to this area of positive charge in much the same way as an electron is bound to a nucleus. These are called F-centres and they can then have their own energy states which occur inside the band gap. These new electronic states can allow adsorption and emission of light at visible wavelengths and thus can add colour to normally colourless transparent crystals.<sup>[1]</sup>

## 1.0 Electronic Structure of ionic crystals

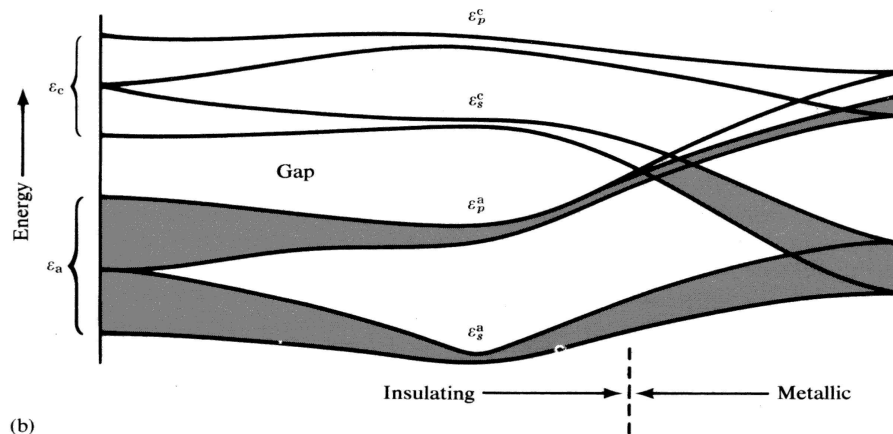


Figure 1-1: Transition of Band Structure from a covalently bound semi conductor on the left through an ionically bound insulator in the center to a mono-atomic metal on the right.<sup>[2]</sup>

If we consider a crystal of atoms of differing types then we get a typical band structure. As the atoms in the crystal become more and more dissimilar the electron involved in bonding the two atoms together will be more and more attracted to the atom with a higher electronegativity. As the bond becomes increasingly polar the band gap widens and the band widths become narrower as the two atoms interact less with each other. As you reach a state of maximum polarity in the crystal the electron can be considered bound to one of the atoms, leaving the other atoms outer shell vacant, producing a lattice of positively and negatively charged ions.<sup>[2]</sup>

## 1.1 Tight Binding Calculation of NaCl structured ionic crystals.

The elements from opposite ends of the periodic table tend to form ionic crystals. I will limit my discussion to the Alkali Halides which tend to have a NaCl crystal structure. This method should also be valid for the II-VI oxides such as MgO as well.

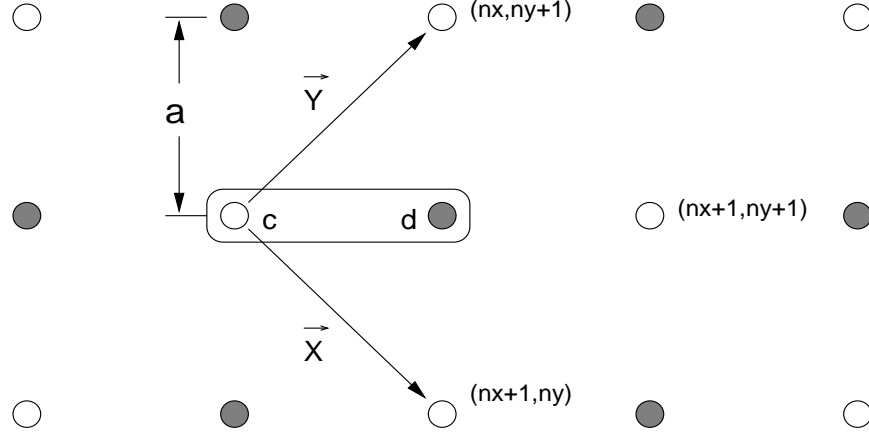


Figure 1-2: NaCl structured lattice with positive ion sites c and negative ion sites d.

I will treat the lattice as a square lattice with a basis of 2. The Positive ion will be the c site located at  $(0,0)$  and the negative ion will be the d site located at  $(\frac{1}{2}, \frac{1}{2})$ . The lattice vectors are shown in Figure 1-2 and have a length of  $\sqrt{2}a$ . The vectors  $\vec{R}_c$  and  $\vec{R}_d$  point to lattice sites c and d respectively. They are represented by

$$\begin{aligned}\vec{R}_c &= \sqrt{2}a(n_x \hat{x} + n_y \hat{y}) \\ \vec{R}_d &= \vec{R}_c + \frac{a}{\sqrt{2}}(\hat{x} + \hat{y})\end{aligned}\quad (1.1)$$

where  $n_x$  and  $n_y$  are integers corresponding to lattice points in the crystal. Let the crystal have  $N^2$  lattice points with  $N$  points along each side. We can define a reciprocal lattice vector.

$$\vec{k} = k_x \hat{x} + k_y \hat{y} \quad -\pi/\sqrt{2}a \leq (k_x, k_y) \leq \pi/\sqrt{2}a \quad (1.2)$$

The first Brillouin zone will be square. By applying Born-von Karman boundary conditions to our  $N \times N$  lattice  $k_x$  and  $k_y$  become quantised to the following values.

$$k_x = \frac{\pi}{\sqrt{2}a} \frac{l_x}{N}, \quad k_y = \frac{\pi}{\sqrt{2}a} \frac{l_y}{N} \quad l_x, l_y \rightarrow -N \dots 0 \dots N \quad (1.3)$$

The strongly localized electrons in the system make the tight bonding model an ideal candidate to describe the system. Ionization of the crystal is caused by the d atom having a much lower on site energy than the c atom so we will define the d on site energy to be 0 and the c on site energy to be  $E_0$ . If we confine hopping terms to nearest neighbours then hopping occurs between the c and d sites only. We can now apply the low energy approximation from class, and ignore all states except those close to the Fermi energy.<sup>[3]</sup> Hopping will then only occur between the c atoms  $s^1$  shell and the d atoms  $p^5$  shell. Through symmetry we expect an electron to hop between

the s shell and only one of the 3 p shells as the other two are orthogonal and will give 0 matrix elements.<sup>[2]</sup> As hopping in x and y directions should be of the same magnitude we can treat the hopping as occurring between 2 s orbitals. Additionally we can ignore spin in this problem as our Hamiltonian does not contain any operators which act on spin. We can now write the Hubbard Hamiltonian as

$$H_0 = \sum_{n_x n_y} E_0 c^\dagger(\vec{R}) c(\vec{R}) - t \sum_{n_x n_y} \sum_{\delta} (c^\dagger(\vec{R} + \delta) d(\vec{R}) + d^\dagger(\vec{R} + \delta) c(\vec{R})) \quad (1.4)$$

$\delta$  represents the 4 nearest neighbours atoms at  $(n_x, n_y)$ ,  $(n_x + 1, n_y)$ ,  $(n_x, n_y + 1)$  and  $(n_x + 1, n_y + 1)$ . We can Fourier transform the creation and destruction operators as follows.

$$\begin{aligned} c^\dagger(\vec{R}) &= \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i\vec{k} \cdot \vec{R}_c} c_k^\dagger & c(\vec{R}) &= \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{R}_c} c_k \\ d^\dagger(\vec{R}) &= \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i\vec{k} \cdot (\vec{R}_c + \frac{a}{\sqrt{2}}(\hat{x} + \hat{y}))} d_k^\dagger & d(\vec{R}) &= \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{i\vec{k} \cdot (\vec{R}_c + \frac{a}{\sqrt{2}}(\hat{x} + \hat{y}))} d_k \end{aligned} \quad (1.5)$$

which gives us our Hamiltonian in k-space.

$$H_0 = \sum_{k_x k_y} E_0 c_k^\dagger c_k - t \sum_{k_x k_y} \sum_{\delta} e^{-i\vec{k} \cdot (\delta + \frac{a}{\sqrt{2}}(\hat{x} + \hat{y}))} (c_k^\dagger d_k + d_k^\dagger c_k) \quad (1.6)$$

Now the sum over  $\delta$  is an important quantity as it appears later in our calculations as well. With a little bit of algebra and some trig identities we can get the following relation.

$$\begin{aligned} \sum_{\delta} e^{-i\vec{k} \cdot (\delta + \frac{a}{\sqrt{2}}(\hat{x} + \hat{y}))} &= 2 \cos\left(\frac{a}{\sqrt{2}}(k_x + k_y)\right) + 2 \cos\left(\frac{a}{\sqrt{2}}(k_x - k_y)\right) \\ &= 4 \cos\left(\frac{a}{\sqrt{2}}k_x\right) \cos\left(\frac{a}{\sqrt{2}}k_y\right) \end{aligned} \quad (1.7)$$

When we put  $H_0$  into the time dependant Schroedinger's equation we get the following coupled equations to solve for

$$E \begin{pmatrix} c \\ d \end{pmatrix} = \begin{pmatrix} E_0 & -4t \cos\left(\frac{a}{\sqrt{2}}k_x\right) \cos\left(\frac{a}{\sqrt{2}}k_y\right) \\ -4t \cos\left(\frac{a}{\sqrt{2}}k_x\right) \cos\left(\frac{a}{\sqrt{2}}k_y\right) & 0 \end{pmatrix} \begin{pmatrix} c \\ d \end{pmatrix} \quad (1.8)$$

Diagonalizing this matrix gives us the energies of our lattice.

$$E_k = \frac{1}{2} \left( E_0 \pm \sqrt{E_0^2 + 64t^2 \cos^2\left(\frac{a}{\sqrt{2}}k_x\right) \cos^2\left(\frac{a}{\sqrt{2}}k_y\right)} \right) \quad (1.9)$$

We clearly see two bands appearing. This splitting is due to the difference between the two atoms in the basis of the lattice. When the off diagonal elements of a matrix like the one in eq 1.8 are much smaller in magnitude than the difference between the diagonal elements we can treat this problem in perturbation theory, as discussed in chap 1 of Harrison.<sup>[2]</sup> Essentially we expand the square root in terms of  $t/E_0$  and keep only the first two terms in the expansion. The result is a much nicer equation for the energy of the conduction and valence bands.

$$\begin{aligned} E_k^c &= E_0 + E_0 \varepsilon_k^2 \\ E_k^v &= -E_0 \varepsilon_k^2 \end{aligned} \quad \varepsilon_k = 4 \frac{t}{E_0} \cos\left(\frac{a}{\sqrt{2}} k_x\right) \cos\left(\frac{a}{\sqrt{2}} k_y\right) \quad (1.10)$$

this gives us a band gap of  $E_0$  and a band width for the conduction and valence bands of  $16t^2/E_0$ . Generally the conduction band is around 1/10 the width of the band gap so our expansion in  $\varepsilon_k$  is a good approximation.<sup>[4]</sup>

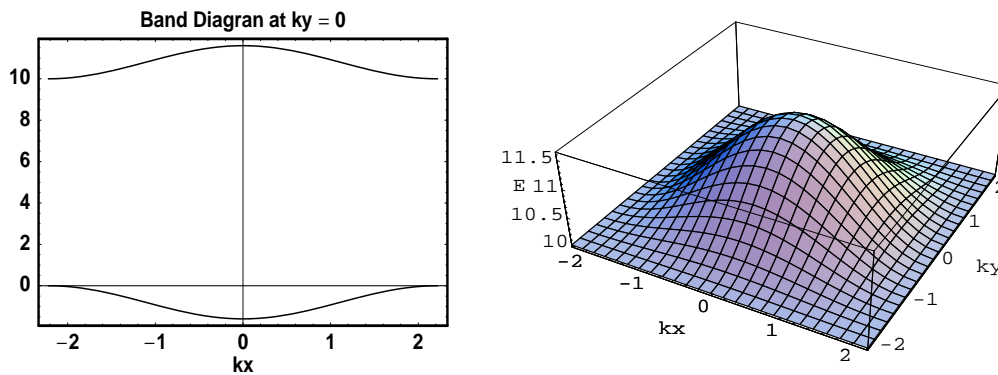


Figure 1-3 right: band structure of 2D NaCl crystal for 1:10 band width:band gap ratio  
left: 3D representation of the conduction band for the same crystal

Now we substitute our values for the energy bands back into equation (1.8) and solve for the eigenfunctions of the system

$$\begin{aligned} k^+ &= \frac{1}{A} (c_k - \varepsilon_k d_k) \\ k^- &= \frac{1}{A} (\varepsilon_k c_k + d_k) \end{aligned} \quad A = \sqrt{1 + \varepsilon^2} \quad (1.11)$$

We can see from these eigenstates that as  $\varepsilon_k$  is small the electron is mostly centred on the c site when in the conduction band and on the d site when in the valence band. The Fermi energy exists in the band gap so the valence band is full and the conduction band empty thus all the electrons are on the d sites as expected in an ionic crystal.

## 1.2 Greens Functions of Ho

The first step in determining colour center bound states is to calculate the green's function of the unperturbed system then we can use these functions to determine the green's function of the true Hamiltonian with the F-centre defect added.

The greens function as we have seen in class is a very useful quality as it's poles correspond to the eigenenergys of and it's residue corresponds to eigenstates of the system. The greens function, for our unperturbed Hamiltonian  $H_0$ , for a particle initially at site  $\mathbf{n}$  travelling to site  $\mathbf{m}$  is

$$G_{\gamma\nu}^o(\vec{n}, \vec{m}) = \langle \vec{n}_\gamma | G(E_k) | \vec{m}_\nu \rangle = \sum_{\vec{k}} \left( \frac{\langle \vec{n}_\gamma | \vec{k}^+ \rangle \langle \vec{k}^+ | \vec{m}_\nu \rangle}{E - E_{\vec{k}}^c + i\eta} + \frac{\langle \vec{n}_\gamma | \vec{k}^- \rangle \langle \vec{k}^- | \vec{m}_\nu \rangle}{E - E_{\vec{k}}^v + i\eta} \right) \quad (1.12)$$

where  $\mathbf{n}$  and  $\mathbf{m}$  are lattice vectors as described by equation 1.1 and  $\vec{k}^+$  and  $\vec{k}^-$  are the eigenstates described in equation 1.11. The  $\gamma$   $\nu$  indices are to differentiate between the c and d sites in the basis. It will be useful for later derivations to have these greens functions written in full. Excluding the summation there are 8 terms on the RHS of this equation for the 4 different combinations of c and d sites in the valance and conduction bands. There are 4 possible greens functions depending on which atoms  $\mathbf{n}$  and  $\mathbf{m}$  point to. If we Fourier transform the vectors to reciprocal space we see that only 2 terms give non 0 results for any choice of c and d. The 4 possible greens functions are given below in full.

$$\begin{aligned} G_{cc}^o(\vec{n}, \vec{m}) &= \sum_{\vec{k}} \frac{1}{N^2 A^2} e^{-i\vec{k}(\vec{n}-\vec{m})} \left( \frac{1}{E - E_{\vec{k}}^c} + \frac{\epsilon_k^2}{E - E_{\vec{k}}^v} \right) \\ G_{dd}^o(\vec{n}, \vec{m}) &= \sum_{\vec{k}} \frac{1}{N^2 A^2} e^{-i\vec{k}(\vec{n}-\vec{m})} \left( \frac{\epsilon_k^2}{E - E_{\vec{k}}^c} + \frac{1}{E - E_{\vec{k}}^v} \right) \\ G_{cd}^o(\vec{n}, \vec{m}) &= \sum_{\vec{k}} \frac{\epsilon_k}{N^2 A^2} e^{-i\vec{k}(\vec{n} + \frac{a}{\sqrt{2}}(\hat{x} + \hat{y}) - \vec{m})} \left( \frac{-1}{E - E_{\vec{k}}^c} + \frac{1}{E - E_{\vec{k}}^v} \right) \\ G_{dc}^o(\vec{n}, \vec{m}) &= \sum_{\vec{k}} \frac{\epsilon_k}{N^2 A^2} e^{-i\vec{k}(\vec{n} - \vec{m} - \frac{a}{\sqrt{2}}(\hat{x} + \hat{y}))} \left( \frac{-1}{E - E_{\vec{k}}^c} + \frac{1}{E - E_{\vec{k}}^v} \right) \end{aligned} \quad (1.13)$$

The greens functions are real when E is in the band gap. This is expected as there are no bound states in the band gap. This also means the  $i\eta$  term is unnecessary as it was only added to help integration around possible poles. I shall discuss methods of calculating these functions later.

## 1.4 Greens Function of a Colour Centre

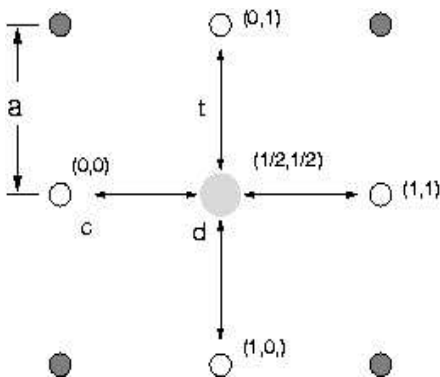


Figure 1-4: Nearest neighbours hopping for colour centre.

To calculate the bound state energies of our colour centres we need a Hamiltonian for our system. As was done in the notes we will take our Hamiltonian to be the Hamiltonians for a perfect crystal and remove the hopping and on site energy terms for one of the d site atoms shown in figure 1.4. We will call this site (0,0) and our Hamiltonian will be.

$$H = H_0 + V = H_0 + t \sum_{\delta} (d^\dagger(0)c(\vec{\delta}) + c^\dagger(\vec{\delta})d(0)) \quad (1.14)$$

When we have a Hamiltonian of this type we can use Dyson's equation to determine the full Green's function of our system in terms of the greens functions of the unperturbed system. This was done for a 1D mono-atomic chain in our notes<sup>[3]</sup> Dyson's equation for H is.

$$G_{y,v}(\vec{n}, \vec{m}) = G_{y,v}^o(\vec{n}, \vec{m}) + \sum_{x_1, x_2} G_{y,\lambda_1}^o(\vec{n}, \vec{x}_1) \langle \vec{x}_1 \lambda_1 | V | \vec{x}_2 \lambda_2 \rangle G_{\lambda_2, v}(\vec{x}_2, \vec{m}) \quad (1.15)$$

The two different atoms in our basis again give us 4 possible Green's functions. To make matters worse Dyson's equation is self consistent so at first glance you may suspect that all 4 Greens function solutions are coupled together. In fact the greens functions are coupled in pairs so we only need 2 of the 4 functions to calculate our bound states. Consider the Green's function acting on two c sites.

$$G_{cc}(\vec{n}, \vec{m}) = G_{cc}^o(\vec{n}, \vec{m}) + t G_{cd}^o(\vec{n}, 0) \sum_{\delta} G_{cc}(\vec{\delta}, \vec{m}) + t \sum_{\delta} G_{cc}^o(\vec{n}, \vec{\delta}) G_{dc}(0, \vec{m}) \quad (1.16)$$

We see that  $G_{cc}(\mathbf{n}, \mathbf{m}; E)$  only depends on  $G_{dc}(0, \mathbf{m}; E)$  and itself. Also, it only depends on it self when  $\mathbf{n}$  points to a nearest neighbour atom. Let's rewrite 1.16 substituting  $\mathbf{n}$  for nearest neighbours atoms  $\boldsymbol{\eta}$  and summing over all nearest neighbours.

$$\sum_{\eta} G_{cc}(\vec{\eta}, \vec{m}) = \sum_{\eta} G_{cc}^o(\vec{\eta}, \vec{m}) + t \sum_{\eta} G_{cd}^o(\vec{\eta}, 0) \sum_{\delta} G_{cc}(\vec{\delta}, \vec{m}) + t \sum_{\eta} \sum_{\delta} G_{cc}^o(\vec{\eta}, \vec{\delta}) G_{dc}(0, \vec{m}) \quad (1.17)$$

Now we can remove the  $G_{cc}$  term from the RHS of the equation and rewrite the equation as

$$\sum_{\eta} G_{cc}(\vec{\eta}, \vec{m}) = \frac{\sum_{\eta} G_{cc}^o(\vec{\eta}, \vec{m}) + t \sum_{\eta} \sum_{\delta} G_{cc}^o(\vec{\eta}, \vec{\delta}) G_{dc}(0, \vec{m})}{1 - t \sum_{\eta} G_{cd}^o(\vec{\eta}, 0)} \quad (1.18)$$

We still require  $G_{dc}(0, \mathbf{m}; E)$ . Using equation 1.15 and solving for  $G_{dc}(0, \mathbf{m}; E)$  we get the following equation.

$$G_{dc}(0, \vec{m}) = \frac{G_{dc}^o(0, \vec{m}) + t G_{dd}^o(0, 0) \sum_{\delta} G_{cc}(\vec{\delta}, \vec{m})}{1 - t \sum_{\delta} G_{cc}^o(0, \vec{\delta})} \quad (1.19)$$

Equations 1.18 and 1.19 form a pair of coupled equations

$$\begin{aligned} \left[1-t \sum_{\eta} G_{cd}^o(\vec{\eta}, 0)\right] \sum_{\eta} G_{cc}(\vec{\eta}, \vec{m}) - \left[t \sum_{\eta\delta} G_{cc}^o(\vec{\eta}, \vec{\delta})\right] G_{dc}(0, \vec{m}) &= \sum_{\eta} G_{cc}^o(\vec{\eta}, \vec{m}) \\ \left[-t G_{dd}^o(0,0)\right] \sum_{\eta} G_{cc}(\vec{\eta}, \vec{m}) + \left[1-t \sum_{\delta} G_{dc}^o(0, \vec{\delta})\right] G_{dc}(0, \vec{m}) &= G_{dc}^o(0, \vec{m}) \end{aligned}$$

Our unperturbed green's functions, 1.13, are real inside the band gap therefor the RHS of these coupled equations are real and finite. We need to find the poles in  $G_{cc}(\mathbf{\eta}, \mathbf{m}; E)$  and  $G_{dc}(\mathbf{0}, \mathbf{m}; E)$ . What we see is that if the determinant of these coupled equations goes to 0 then the Green's functions 1.18 and 1.19 will have to go towards infinity to keep the RHS of the equation finite. Our bound state energies can then be found by solving the following equation

$$F(E) - H(E) = 0 \quad (1.20)$$

$$\left[1-t \sum_{\delta} G_{cd}^o(\vec{\delta}, 0)\right] \left[1-t \sum_{\delta} G_{dc}^o(0, \vec{\delta})\right] - t^2 G_{dd}^o(0,0) \left[\sum_{\eta\delta} G_{cc}^o(\vec{\eta}, \vec{\delta})\right] = 0$$

## 1.5 Bound State Energy Calculation for Colour Centre

The unperturbed Green's function 1.12 is solvable for a mono atomic crystal using Elliptic integrals.<sup>[5]</sup> However the added complication of 2 bands and more complicated eigenfunctions in the diatomic case makes this type of solution intractable. Equation 1.20 is not a trivial either. the  $H(E)$  function alone has 16 terms in it. In the end I had to resort to a numerical solution for this problem.

Looking at the terms for  $G_{cd}(\mathbf{\delta}, \mathbf{0}; E)$  and  $G_{dc}(\mathbf{0}, \mathbf{\delta}; E)$  in equation 1.13 we see that the only difference between them is the sign of the exponential. If you sum over all nearest neighbours for the positive exponential, the result from equation 1.7 still holds. Both these terms are identical and  $F(E)$  reduces to.

$$F(E) = \left(1 - 4t \sum_k \frac{\epsilon_k}{N^2 A^2} \cos^2\left(\frac{a}{\sqrt{2}} k_x\right) \cos^2\left(\frac{a}{\sqrt{2}} k_y\right) \left(\frac{-1}{E - E_k^c} + \frac{1}{E - E_k^v}\right)\right)^2 \quad (1.21)$$

We expect that the effects of the colour centre will be fairly localised in the lattice so  $F(E)$  may converge over a finite number of lattice points. The number of points necessary in our summation was initially estimated by summing over a greater and greater number of lattice points and observing the change in the function each time. After  $N = 6$  (36 atoms) there was no noticeable change in the function and our calculated binding energies changed by less than 1%.

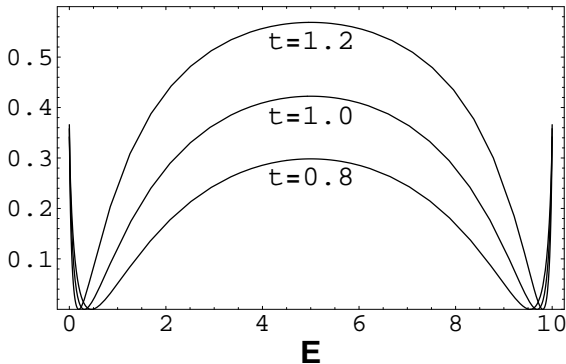


Figure 1-5 : Form of function  $F(E)$  for different values of  $t$  ( $E_0 = 10$ )

We see from figure 1-5 that increasing  $t$ , increases the value of the function in the centre and shifts the minimum values in the function outwards towards the band gap. This function is not asymptotic, it has a finite value of around 0.35 at the band gap for  $t = 1$

and does not seem to change significantly for different values of  $t$ . Altering the value of  $E_0$  while keeping the ratio of  $t/E_0$  constant only scales the function so it remains finite in the band gap.

Function  $H(E)$  describes hopping of electrons amongst the 4 nearest neighbour atoms around the colour centre. The exponential in the  $G_{cc}(\delta, \mathbf{\eta}; E)$  term just gives a cosine as the rest of the greens function is even so we can drop the sin term dew to symmetry. When we do the double summation we get 16 cosine functions however only 4 of them are unique so the summation just becomes.

$$\sum_{\delta \eta} e^{-i\vec{k} \cdot (\vec{\eta} - \vec{\delta})} = 4(1 + \cos(\sqrt{2} a k_x) + \cos(\sqrt{2} a k_y) + \cos(\sqrt{2} a k_x + \sqrt{2} a k_y)) \quad (1.22)$$

the  $H(E)$  function then becomes

$$H(E) = t^2 \left[ \sum_k \frac{1}{N^2 A^2} \left( \frac{\epsilon_k^2}{E - E_k^c} + \frac{1}{E - E_k^v} \right) \right] \left[ \sum_k \sum_{\delta \eta} e^{-i\vec{k} \cdot (\vec{\eta} - \vec{\delta})} \frac{1}{N^2 A^2} \left( \frac{1}{E - E_k^c} + \frac{\epsilon_k^2}{E - E_k^v} \right) \right] \quad (1.23)$$

$\epsilon_k$  is very small so when  $E$  is in the band gap the left hand sum will be generally positive and the right hand sum will be negative. This suggests no solution to 1.20. However, we have seen in function  $F(E)$  that as  $\epsilon_k$  and  $E - E_k$  both go to 0 near the band edge the function converges to a finite number. If this number is positive we can have bound state if it is negative we will not.

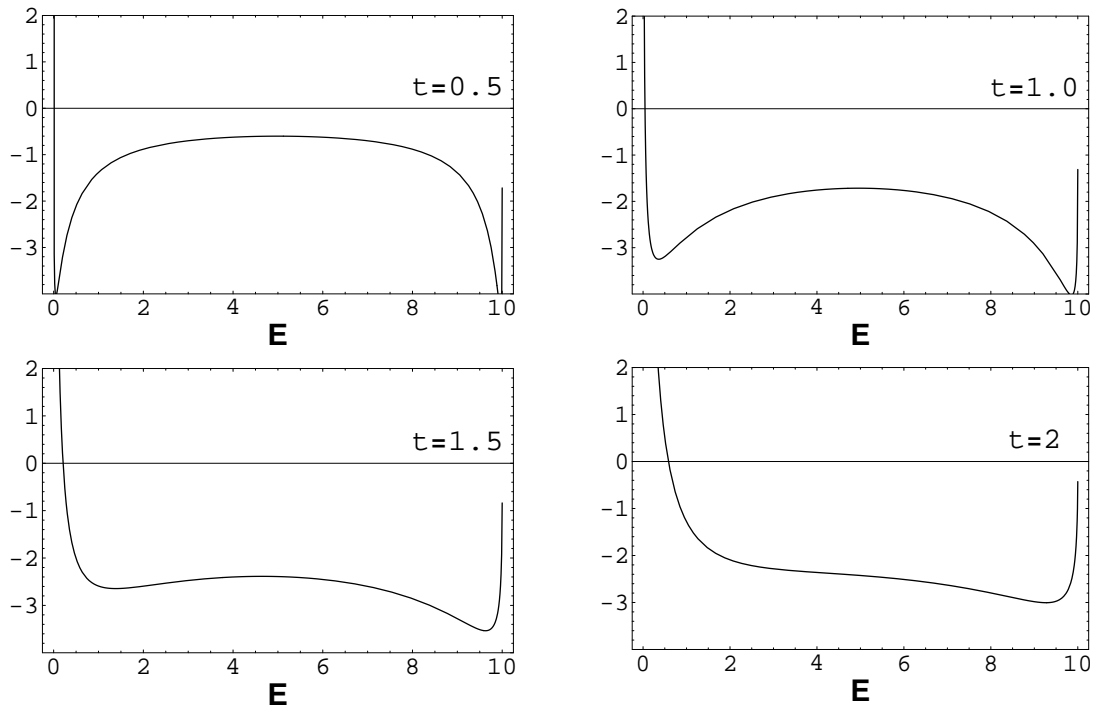


Figure 1-6: Function  $H(E)$  for different values of  $t$  ( $E_0 = 10$  eV)



We see from the diagrams that changing  $t$  in  $H(E)$  can alter its shape much more dramatically than seen in  $F(E)$ . If we change  $E_0$  but keep  $t/E_0$  constant then the only effect is a scaling of the  $y$  axis so that the function still fits within the band gap. This function also required a lot more terms to converge. A  $N = 16, 256$  atom, lattice was required to give negligible change in the function and less than a 1% change in our calculated binding energies.

The tail of the  $H(E)$  function seems to converge to a finite negative number at the edge of the conduction band so no bound state close to the conduction band will be found. The tail close to the valance band however seems to grow asymptotically large as we approach the band edge. This implies that since  $F(E)$  is finite at the band edge we will always have a bound state as the two functions will cross at some value of  $E$ . We see as the coupling between nearest neighbours gets larger the tail moves farther to the left indicating a larger binding energy. We can solve for the point when  $F(E) = H(E)$  numerically to determine the energy of the bound state.

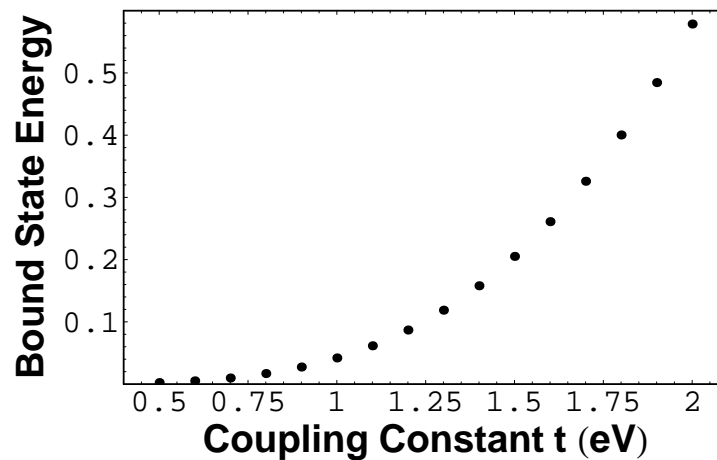


Figure 1-7 : Bound State Energies for various coupling constants  $t$  and constant band gap  $E_0 = 10$  eV

For a 10 eV band gap and a coupling term  $t = 1$  we calculate there to be a bound state at 0.042 eV. Even when  $t=0.5$  we still get a bound state although it is at 0.0024 eV. This is around 27 Kelvin so we expect it to be thermally populated. The binding energy seems to increase exponentially with respect to the coupling constant. Care must be taken to extrapolate much beyond  $t=2$  as our approximations based on the small value of  $t/E_0$ . Knowing now that we need to solve for the bound states numerically it would be possible to go back through and calculate equations 1.13 without any approximations. We could then solve for our bound states exactly. The exact numbers would be different but the general trend would be similar and with strong enough coupling our bound state could act on photons in the visible spectrum.

One question remaining unanswered, is whether the new bound state above or below the Fermi energy. We know there should be  $2N^2$  states in the valance band as each site contributes two states. Near the band gap  $\epsilon_k$  is at its largest. Our eigenfunctions tell us that the states in the valance band come mostly from the  $d$  sites but partially from the  $c$  sites as well. By removing a  $d$  site do we lose a state in the valance band or not? The answer to this question will tell us whether the new bound state we calculated is populated in the ground state and thus whether we can have transitions to it at low energies. In order to conserve the charge neutrality of the crystal it should be populated but we made a lot of assumptions so our model may not reflect this. Density of state calculations are required to determine this.

## References

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