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"POLARON EFFECTS ON Si(111)2x1 SURFACE STATES"

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CONTENTS

I. INTRODUCTION

The quantitative experimental detection of surface state energies on clean semiconductor surfaces has become possible in the last decade mostly by means of photo-emission(1) and also optical(2) and energy loss(3) techniques.

At present, these experimental results are being compared with very elaborate self-consistent one-electron calculations(4), also in order to learn about the surface geometry, which is generally unknown. The implication is that effects not contained in one-electron calculations, notably many-body effects and electron-phonon coupling, can be disregarded which is not always obvious. While some works have been directed to investigating many-body effects(5) and lattice relaxation effects(6), there seems to be no discussion available of polaron effects on surface states.

This is a preliminary report of a first attempt to study some effects produced by coupling of the surface state electrons(and holes) to the vibrating surface lattice. For specificity, and also because of its high current interest, we have chosen the clean Si(111)2x1 surface as our working example. Since at least two widely discussed models--the buckling model and the chain model--are available for this surface, we have decided to consider both of them. This was done also in the hope that our predicted behavior could be sufficiently different for the two cases so as to allow some conclusions to be drawn from a comparison of these predictions with existing or with future experiments.

This paper is then organized as follows.

We first construct the model Hamiltonian suitable for our purpose and fix the parameters used. This is done in sec.2.1 for the buckling model,and in sec.3.1 for the chain model. In sec.2.2 and 3.2 ,we calculate for the two model respectively the energy shift and the lattice deformation that occurs when one extra electron--or one hole--is injected in a surface state,otherwise at equilibrium. This is what we shall call a surface state polaron.

Since our main interest will be in optical absorption,we next want to consider the electron-hole pair creation at a semiconductor surface. We do this by neglecting at first the lattice coupling,in sec.2.3 and 3.3 respectively. The lattice relaxation that occurs when such an optically excited electron-hole pair is present is then calculated in sec.2.4 and 3.4. In these sections one also extracts the overall Huang-Rhys factor S(7),which characterizes the strength of the exciton-lattice coupling. We calculate in sec.2.5 and 3.5 the predicted temperature dependence of optical absorption between surface states ,for the two models. Finally,critical comparison with existing evidence and future developments is given in conclusion in sec. 4.

2. BUCKLING MODEL

2.1 The Model and The Parameters

The buckling model of Si(111)2x1 reconstructed surface was proposed by Haneman(8). It consists of alternating rows of raised and lowered atoms, as indicated in Fig.2.1.

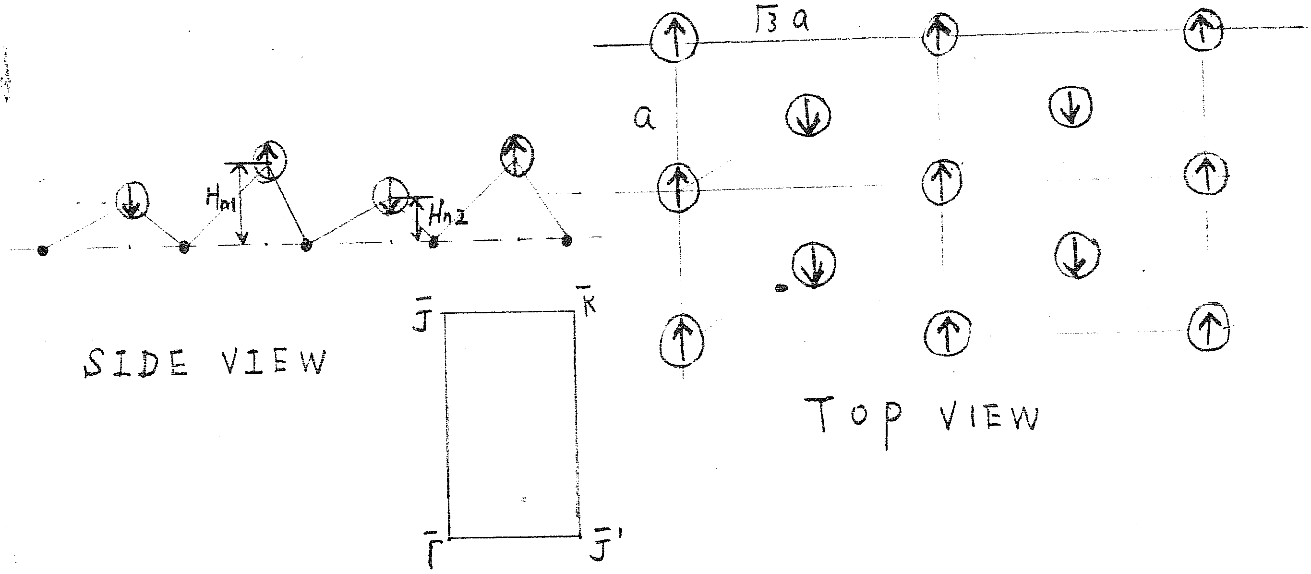


Fig.2.1. Surface geometry of Si(111)2x1 buckling model: Alternate rows of surface atoms(circles) are displaced in and out as shown schematically by arrows. also shown is the surface Brillouin zone.

Each surface unit cells, labeled by n, consists of one buckled up atom, labeled by n,1, and one buckled down atom, labeled by n,2. The dangling bond(DB) atomic orbital on each atoms, denoted by $|n,i\rangle$, is a combination of S orbital $|s,i\rangle$ and Pz orbital $|Pz,i\rangle$ of the same atom with coefficients which depend on the perpendicular distance $H_{n,i}$ of that atom. $H_{n,i}$ is measured from the subsurface layer, as also shown in Fig.2.1.

As shown in Appendix A,

$$|n,i\rangle=\sqrt{6}\,\frac{H_{n,i}}{a}\,|S,i\rangle+\sqrt{1-6\left(\frac{H_{n,i}}{a}\right)^2}\,|P_z,i\rangle \qquad (2.1)$$

and its atomic orbital energy

$$\mathcal{E}(H_{n,i}) = 6\left(\frac{H_{n,i}}{a}\right)^2 E_s + \left[1-6\left(\frac{H_{n,i}}{a}\right)^2\right] E_p$$

$$= E_p - \frac{C}{2}\left(\frac{H_{n,i}}{a}\right)^2 \qquad (2.2)$$

where a is the surface lattice constant,a=3.85A for Si(111)2x1 surface,and E_p,E_s are the s and p atomic orbital energies,respectively. We take Clementi and Roetti's atomic data(9)of Si, which is cited in Table I,for $E_p-E_s \cong 6$ ev. While

$$C = 12(E_p - E_s) = 72 \text{ eV}$$

A lot of elaborate work has been done on this buckling model(4). All of them found out a large charge transfer the amount of which depends somewhat on the degree of reconstruction. For simplicity,we assume a fixed charge transfer occured only from the "down" atoms to the "up" atoms,keeping the top surface layer neutral on average.

```
SILICON     K(2)L(8)3S(2)3P(2), 3P
T.E.=-0.28808996D+03   P.E.=-0.57617682D+03   K.E.= 0.28808648D+03   V/T.=-0.20000122D+01

      S             1S          2S          3S            P             2P          3P
BASIS/ORB E     -68.59169   -5.94851    -0.49232    BASIS/ORB E     -4.00137    -0.26975
1S  13.57450    -0.99720     0.30060     0.07615    2P  4.97254      0.98739     0.22674
2S   4.51000    -0.00990    -1.04174    -0.29222    3P  1.42841      0.06255-   -1.01165
3S   1.63429     0.00166     0.00055     1.03878
```

Table 1. Atomic data of Si cited from (9).

Assuming a neglegible overlap between DB orbitals,we may construct the filled DB band(hereafter referred to as "valence band")Wannier state located at unit cell n as

$$|n^{(v)}\rangle = \alpha_1|n,1\rangle + \alpha_2|n,2\rangle \qquad (2.3)$$

and the corresponding empty DB band(hereafter referred to as "conduction band") Wannier state,being orthogonal to $|n^{(v)}\rangle$,as

$$|n^{(c)}\rangle = -\alpha_2 |n,1\rangle + \alpha_1 |n,2\rangle \qquad (2.4)$$

with $\alpha_1^2 + \alpha_2^2 = 1$.

The coefficients, α_1 and α_2, describe the amount of charge transfer, and in our present work they are taken to be $\alpha_1^2 = 0.85$ $\alpha_2^2 = 0.15$. It is in general agreement with the works by Pandey (4) and Casula and Selloni (6).

The model Hamiltonian of the surface states is then assumed as follows:

$$H = \sum_n \left[|n^{(v)}\rangle E_n^{(v)} \langle n^{(v)}| + |n^{(c)}\rangle E_n^{(c)} \langle n^{(c)}| \right] + \sum_{\substack{n \\ m:\text{ the n. n. of nth cell}}} t^{(v)}_{(m-n)} |m^{(v)}\rangle\langle n^{(v)}| + \sum_{\substack{n \\ m:\text{ the n. n. of nth cell}}} t^{(c)}_{(m-n)} |m^{(c)}\rangle\langle n^{(c)}| \qquad (2.5)$$

where

$$E_n^{(v)} = \alpha_1^2 \, \varepsilon(H_{n,1}) + \alpha_2^2 \, \varepsilon(H_{n,2}) = E_p - \frac{c}{2}\left[\alpha_1^2 \left(\frac{H_{n,1}}{a}\right)^2 + \alpha_2^2 \left(\frac{H_{n,2}}{a}\right)^2\right] \qquad (2.6)$$

$$E_n^{(c)} = \alpha_2^2 \, \varepsilon(H_{n,1}) + \alpha_1^2 \, \varepsilon(H_{n,2}) = E_p - \frac{c}{2}\left[\alpha_2^2 \left(\frac{H_{n,1}}{a}\right)^2 + \alpha_1^2 \left(\frac{H_{n,2}}{a}\right)^2\right] \qquad (2.7)$$

$t^{(v)}_{(m-n)}$ ($t^{(c)}_{(m-n)}$) is the hopping integral between valence(conduction) band Wannier states. We take into account only the nearest neighbor hopping integral. To reproduce the general feature of the elaborate calculations by Pandey and by Del Sole and Chadi (4), the hopping integral in $\bar{\Gamma}\bar{J}$ direction is taken as

$$t_y^{(v)} = t_y^{(c)} = 0.05\,\mathrm{eV}$$

and that in $\bar{\Gamma}\bar{J}'$ direction as

$$t_x^{(v)} = t_x^{(c)} = -0.04\,\mathrm{eV}$$

In principle, all the hopping integrals depend on $H_{n,i}$, mainly via the atomic orbitals $|n,i\rangle$. For our purpose, however, the primary properties of t's is their order of magnitude relative to other energies. Hence, for simplicity, their $H_{n,i}$ dependence will be neglected. We also neglect the intra-atomic interaction and the Madelung energy.

The energy of the valence band Bloch state with wave vector $\vec{k}$, $\psi_{\vec{k}}^{(v)}=\frac{1}{\sqrt{N}}\sum_n e^{i\vec{k}\cdot\vec{R}_n}|n^{(v)}\rangle$ is then given by

$$E^{v}(\vec{k})=\langle\psi_{\vec{k}}^{(v)}|H|\psi_{\vec{k}}^{(v)}\rangle=\frac{1}{N}\sum_n E_n^{(v)}+t_x^{(v)}\cdot 2\cos(\sqrt{3}k_x\cdot a)+t_y^{(v)}\cdot 2\cos(k_y\cdot a)$$

$$=E_n^{(v)}-0.08\cos(\sqrt{3}k_x\cdot a)+0.10\cos(k_y\cdot a) \qquad (2.8)$$

While that of conduction band Bloch state, $\psi_{\vec{k}}^{(c)}=\frac{1}{\sqrt{N}}\sum_n e^{i\vec{k}\cdot\vec{R}_n}|n^{(c)}\rangle$, by

$$E^{(c)}(\vec{k})=\langle\psi_{\vec{k}}^{(c)}|H|\psi_{\vec{k}}^{(c)}\rangle=\frac{1}{N}\sum_n E_n^{(c)}+t_x^{(c)}\cdot 2\cos(\sqrt{3}k_x\cdot a)+t_y^{(c)}\cdot 2\cos(k_y\cdot a)$$

$$=E_n^{(c)}+0.08\cdot\cos(\sqrt{3}k_x\cdot a)+0.10\cos(k_y\cdot a) \qquad (2.9)$$

In the following, the values of E_n^v and E_n^c are determined as follows.

At the ground state, within Born-Oppenheimer' adiabatic approximation, the adiabatic energy of the system which consists of 2N valence electrons and 2N surface atoms(N being the number of unit cells) can be expressed as

$$\mathcal{E}_{2N}^{adia}=\sum_n\sum_{i=1}^{2}\frac{\gamma}{2}(H_{n,i}-H_0)^2+2\cdot\sum_{\vec{k}}E^{(v)}(\vec{k})$$

$$=\frac{\gamma}{2}\sum_{n=1}^{N}\sum_{i=1}^{2}h_{n,i}^2+2\sum_n E_n^{(v)} \qquad (2.10)$$

Where the factor of 2 takes care of the spin; $h_{n,i}=H_{n,i}-H_0$ is the displacement of the (n,i)atom from H_0 which is to be determined below; γ is the force constant of the top surface atom along the direction perpendicular to the surface, which represents the interactions of the back-bonds and the bulk on the top surface atoms.

By eq.(2.6),eq.(2.10) can be expressed as

$$\mathcal{E}_{2N}^{adia}=\sum_{n,i}\frac{\gamma-2C\alpha_i^2/a^2}{2}h_{n,i}^2+2\cdot\sum_n\Big[E_p-\frac{C}{2}\frac{\alpha_1^2}{a^2}(H_0^2+2H_0h_{n,1})-\\ -\frac{C}{2}\frac{\alpha_2^2}{a^2}(H_0^2+2H_0h_{n,2})\Big] \qquad (2,11)$$

If we consider each surface atoms as an oscillator and put the factor in front of $h_{n,i}^2$ in the above eq. as

$$\frac{\gamma-2C\alpha_i^2/a^2}{2}=\frac{1}{2}M\omega_0^2$$

where M is the atom mass, $\hbar\omega_0$ should then be about the surface phonon energy which is experimentally measured as around 0.055 ev(10), $\hbar\omega_0$=0.055 ev.

To determine γ,we take $\alpha_1^2=\alpha_2^2$=0.5(corresponding to the ideal non-reconstructed surface),then

$$\gamma a^2=Ma^2\omega_0^2+C=370\,eV \qquad (2.12)$$

Remember a=3.85A.

At equilibrium,

$$\frac{\partial\mathcal{E}_{2N}^{adia}}{\partial H_{n,i}}=0=\gamma h_{n,i}+2\frac{\partial E_n^{(v)}}{\partial H_{n,i}} \qquad (2.13)$$

From (2.6) and (2.13),we get

$$h_{n,i}=\frac{2C\alpha_i^2}{\gamma a^2}(H_0+h_{n,i})=\frac{2C\alpha_i^2H_0}{\gamma a^2-2C\alpha_i^2} \qquad (2.14)$$

We determine H_0 by considering the un-reconstructed ideal surface. In which case,$\alpha_1^2=\alpha_2^2$=0.5 and $H^o_{n,1}=H^o_{n,2}=H_0+h^o_{n,1}=H_0+h^o_{n,2}=$ 0.79A. Putting in eq.(2.14),we get

$$H_0=0.64A$$

H_0 would be the position of surface atoms if no electron were present in the DB state.

The equilibrium positions of the buckled surface atoms,using eq.(2.14),are then

$$h_{n,1}=0.32A \quad , \quad H_{n,1}=H_0+h_{n,1}=0.96A$$

$$h_{n,2}=0.04A \quad , \quad H_{n,2}=H_0+h_{n,2}=0.68A$$

Finally, the valence and conduction band Wannier state energies, E_n^V and E_n^C, using eqs.(2.6) and (2.7), are determined as

$$E_n^{(V)} = E_P - 2.07\,\mathrm{eV} \qquad (2.15)$$

$$E_n^{(C)} = E_P - 1.29\,\mathrm{eV} \qquad (2.16)$$

The surface state energy band structure obtained is shown in Fig.2.2.

2.2 Electron Polaron and Hole Polaron

2.2.1 General outline

When one electron is added to the surface, the system is then composed of 2N surface atoms and (2N+1)electrons with full valence band and one electron in the conduction band. The electron in the conduction band is subjected to competition of two opposing tendencies :one to delocalization and the other to localization. The former is characterized by B, the maximum energy released when the electron perfectly localized on one cell is allowed to extend throughout the surface;In our case, B is just the energy difference between the conduction band Wannier state energy E_n^C and the energy of the bottom of the conduction band. The later--the localizing interaction--is characterized by the relaxation energy E_R of the deformed system due to the localized electron.

In the absence of transfer, the electron would be localized on one single cell and the system would be stabilized by energy E_R as the lattice is distorted to new equilibrium positions, as shown schematically in Fig.2.3a. In the presence of transfer and the absence of lattice distortion, the electron would move freely throughout the lattice with band energy $E^C(k)$ as

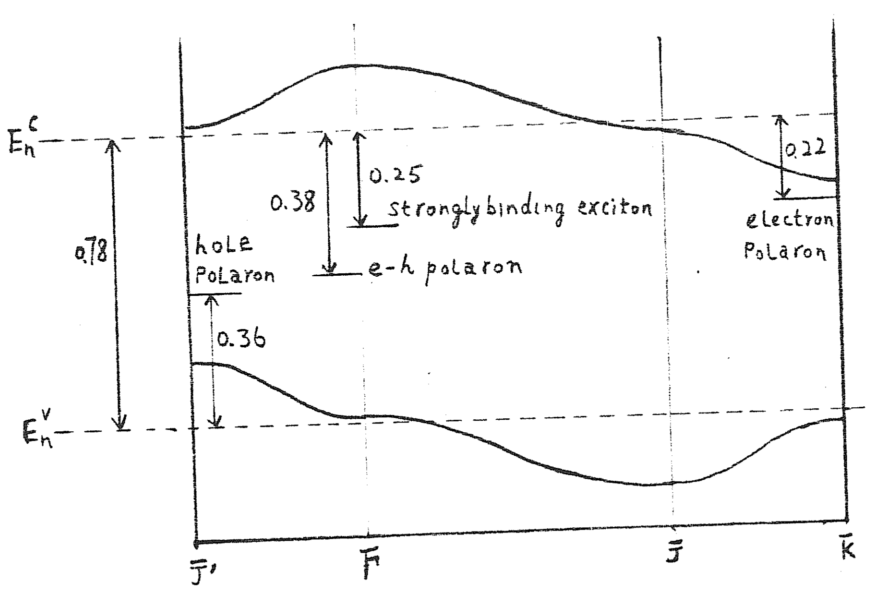


Fig.2.2 Simplified surface state energy of the buckling model calculated by our parameter. The energy levels of "valence band" and "conduction band" Wannier state, E_n^v and E_n^c, of electron-, hole-, e-h pair-polaron and of exciton are also shown.

Fig.2.3 Schematic diagram showing the competition between localization and delocalization of an electron in deformable lattice.

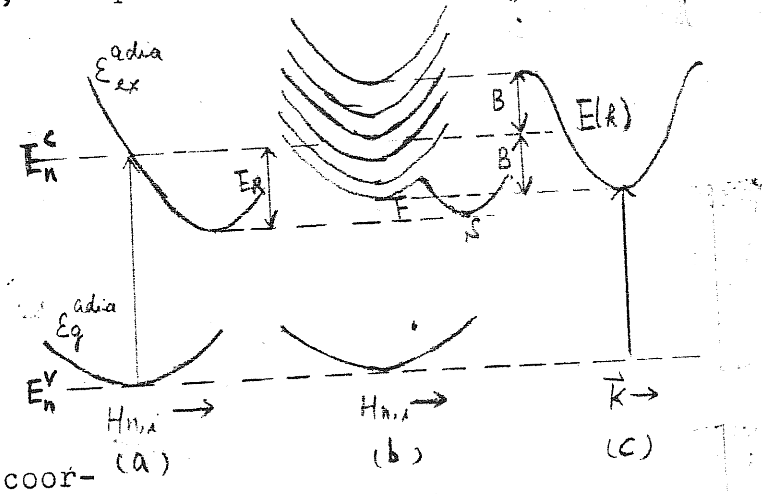
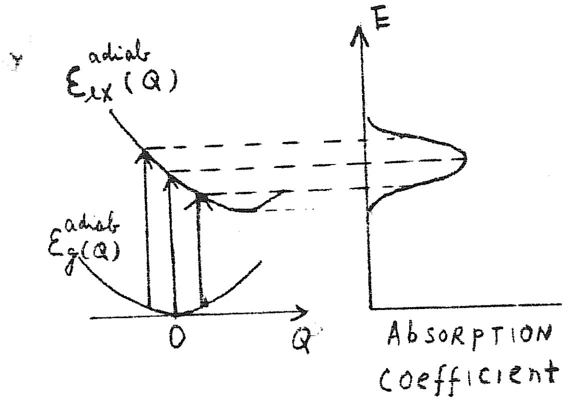


Fig.2.4 The configuration-coordinate model with interaction mode, the Franck-Condon principle, and the absorption line shape.



shown in Fig.2.3c. Referred to the perfectly-localized state with energy E_n^c, the electron would be stabilized with energy B at the conduction band bottom.

A very rough conclusion from the above argument is that the electron will be localized by inducing lattice distortion around itself or will be delocalized in perfect lattice according to $E_R \gtrless B$, as shown schematically in Fig.2.3b where two extreme types of relaxed states are denoted by S(Self-trapped state) and F(Free state).

2.2.2 Electron Polaron

If the surface lattice is frozen at ground state equilibrium configuration, $H_{n,1}=0.96A$ and $H_{n,2}=0.68A$, and if the injected electron spreads throughout the whole surface lattice, this electron will then be stabilized at the conduction band bottom, which is at K point in our model, with energy lowered by 0.18 ev referred to E_n^c,

$$E^{(c)}(\bar{K}) = E_n^{(c)} - 0.18\,eV \qquad (2.17)$$

as can be seen from Fig.2.2.

On the other hand, if the excess electron is perfectly localized at one particular cell, say cell 0, the adiabatic energy of the system which now consists of (2N+1) electrons and 2N atoms, before lattice relaxes further, is

$$\mathcal{E}_{2N+1}^{unrel} = \frac{\gamma}{2}\sum_{n,i}(H_{n,i}-H_0)^2 + 2\cdot\sum_{n} E_n^{(v)}(h_{n,i}) + E_0^{(c)}(h_{o,i}) \qquad (2.18)$$

where $E_n^v(h_{n,i})$ and $E_o^c(h_{o,i})$ are given by eqs.(2.15) and (2.16).

After the surface lattice relaxes, the surface atoms take new equilibrium positions, denoted by $H_{n,i}^e$ (or $h_{n,i}^e$), which is determined by $\frac{\partial \mathcal{E}_{2N+1}^{adia}}{\partial H_{n,i}}=0$. For the 0-th cell, in which the injected electron is located, this condition gives

$$\gamma h_{o,i}^{(e)} + 2\frac{\partial E_o^{(v)}}{\partial h_{o,i}^{(e)}} + \frac{\partial E_o^{(c)}}{\partial h_{o,i}^{(e)}} = 0$$

or

$$h_{o,1}^{(e)} = \frac{c(2\alpha_1^2+\alpha_2^2)H_o}{\gamma a^2 - c(2\alpha_1^2+\alpha_2^2)} = 0.36\,A$$

$$h_{o,2}^{(e)} = \frac{c(2\alpha_2^2+\alpha_1^2)H_o}{\gamma a^2 - c(2\alpha_2^2+\alpha_1^2)} = 0.185\,\dot{A}$$

For the other cells, $h_{n,i}^{e}$ remain unchanged and equal $h_{n,i}$.

The minimum of adiabatic energy in the relaxed configuration is

$$\mathcal{E}_{2N+1}^{relax} = \frac{\gamma}{2}\sum_{n,i} h_{n,i}^{(e)2} + 2\cdot\sum_{n} E_n^{(v)}(h_{n,i}^{(e)}) + E_o^{(c)}(h_{o,i}^{(e)})$$

with

$$E_o^{(c)}(h_{o,i}^{(e)}) = E_p - \frac{c}{2}\left[\alpha_2^2\frac{(H_o+h_{o,1}^{(e)})^2}{a^2} + \alpha_1^2\frac{(H_o+h_{o,2}^{(e)})^2}{a^2}\right]$$

$$= E_p - 1.77\,eV \qquad (2.20)$$

$$E_o^{(v)}(h_{o,i}^{(e)}) = E_p - \frac{c}{2}\left[\alpha_1^2\frac{(H_o+h_{o,1}^{(e)})^2}{a^2} + \alpha_2^2\frac{(H_o+h_{o,2}^{(e)})^2}{a^2}\right]$$

$$= E_p - 2.31\,eV \qquad (2.19)$$

The lattice relaxation energy $E_R^{(e)}$ is then

$$E_R^{(e)} = \mathcal{E}_{2N+1}^{unrel} - \mathcal{E}_{2N+1}^{rel}$$

$$= \frac{\gamma}{2}\left[(h_{o,1}^2 - h_{o,1}^{(e)2}) + (h_{o,2}^2 - h_{o,2}^{(e)2})\right] + 2\cdot\left[E_o^{(v)}(h_{o,i}) - E_o^{(v)}(h_{o,i}^{(e)})\right] + E_o^{(c)}(h_{o,i}) - E_o^{(c)}(h_{o,i}^{(e)})$$

$$= 0.22\,eV$$

$E_R^{(e)}$ is larger than the energy 0.18 ev gained if the electron was allowed to spread throughout the frozen lattice. Thus the electron will prefer to be localized at some cell.

By including transfer as well as lattice distortion, the localized electron will tend to spread out. In Appendix B, assuming rigid valence band electron distribution, we solve this problem by the perturbation method up to second order. It turns out that the probability amplitude of finding the electron in the neighboring cell's Wannier state is

$$a_n = \frac{t_{on}}{E^{(c)}(h_{o,i}) - E^{(c)}(h_{o,i}^{(e)})} = \frac{t_{on}}{E_b^{POLARON}}$$

Where $E^c(h_{o,i})$ and $E^c(h_{o,i}^{e})$ are the conduction band Wannier state energy before and after lattice relaxation, respectively, and are given in eqs.(2.16) and (2.20). $E^c(h_{o,i})-E^c(h^e_{o,i})=E_b^{polaron}$ may be called the electron-polaron binding energy. In our case, $a_n=0.05/0.48=0.10$, which means only 1% electron spreads into each neighboring cells. It is therefore a good approximation to consider the electron being perfectly self-trapped and forms a small polaron. Its energy level is also indicated in Fig.2.2.

If the actual position of the (n,i)th atom is represented by $Q_{n,i}$ while $h_{n,i}$ denote the equilibrium position of that atom in the ground electronic state, the adiabatic potential energy can then be expressed as

$$\begin{aligned}\mathcal{E}_{2N}^{adia} &= \frac{1}{2}\sum_{n,i}\frac{\gamma a^2-C\cdot 2\alpha_i^2}{a^2}(Q_{n,i}-h_{n,i})^2+\mathcal{E}_0 \\ &= \frac{1}{2}\sum_{n,i}\gamma_i^{(g)}(Q_{n,i}-h_{n,i})^2+\mathcal{E}_0 \qquad (2.22)\end{aligned}$$

where

$$\begin{aligned}\gamma_1^{(g)}a^2 &= \gamma a^2-2c\alpha_1^2 = 247.6\,eV \\ \gamma_2^{(g)}a^2 &= \gamma a^2-2c\alpha_2^2 = 348.4\,eV\end{aligned} \qquad (2.23)$$

the corresponding phonon energies are

$$\begin{aligned}\hbar\omega_1^{(g)} &= \hbar\sqrt{\gamma_1^{(g)}/M} = 0.050\,eV \\ \hbar\omega_2^{(g)} &= \hbar\sqrt{\gamma_2^{(g)}/M} = 0.059\,eV\end{aligned} \qquad (2.24)$$

The electron-phonon wave function of the ground electronic state at T=0° K is given by

$$\Phi_g = \prod_{n,i}\chi_0^{(g)}(Q_{n,i}-h_{n,i})\,|0\rangle \qquad (2.25)$$

where

$$\chi_0^{(g)}(Q_{n,i}-h_{n,i}) = \left(\frac{M\omega_i^{(g)}}{\pi\hbar}\right)^{1/4} e^{-\frac{M\omega_i^{(g)}}{2\hbar}(Q_{n,i}-h_{n,i})^2} \qquad (2.26)$$

is the ground state wave function of the oscillator. $|0\rangle$ denotes the electronic ground state.

The adiabatic potential energy in the presence of an excess electron self-trapped in the (k)th cell are

$$\mathcal{E}_{2N+1}^{adia} = \frac{1}{2}\sum_{n(\neq k)}\sum_i\gamma_i^{(g)}(Q_{n,i}-h_{n,i})^2+\frac{1}{2}\sum_i\gamma_i^{(e)}(Q_{k,i}-h_{k,i}^{(e)})^2+\mathcal{E}_0+E_n^{(c)}(h_{n,i})-E_R^{(e)} \qquad (2.27)$$

Where $E_R^{(e)}$, given in eq.(2.21), is the relaxation energy. E_n^c is the ground state conduction band Wannier state energy, givenin eq. (2.16), while

$$\gamma_1^{(e)} a^2 = \gamma a^2 - C(2\alpha_1^2 + \alpha_2^2) = 236.8\,\mathrm{eV}$$
$$\gamma_2^{(e)} a^2 = \gamma a^2 - C(2\alpha_2^2 + \alpha_1^2) = 287.2\,\mathrm{eV} \qquad (2.28)$$

The corresponding phonon energies are

$$\hbar\omega_1^{(e)} = 0.049\,\mathrm{eV}$$
$$\hbar\omega_2^{(e)} = 0.054\,\mathrm{eV} \qquad (2.29)$$

The corresponding electron-phonon wave function is

$$\Phi^{(e)}(k) = \prod_{i=1}^{2} \chi_0^{(e)}(Q_{k,i} - h_{k,i}^{(e)}) \prod_{\substack{n(\neq k)\\ i}} \chi_0^{(g)}(Q_{n,i} - h_{n,i}) \, |k^{(c)}\rangle \, |0\rangle \quad (2.30)$$

Where $\chi_0^{(e)}(Q_{k,i} - h_{k,i}^{(e)}) = \left(\frac{M\omega_i^{(e)}}{\pi\hbar}\right)^{1/4} \exp\left[-\frac{M\omega_i^{(e)}}{2\hbar}(Q_{k,i} - h_{k,i}^{(e)})^2\right]$ (2.31)

The local distortion $(h_{k,i}^{e} - h_{k,i})$ has the effect of reducing the hopping integral between $\Phi^e(k)$ and $\Phi^e(k')$ by a factor of

$$\prod_{i=1}^{2} \int \chi_0^{(e)}(Q_{k,i} - h_{k,i}^{(e)}) \cdot \chi_0^{(g)}(Q_{k,i} - h_{k,i}) dQ_{k,i} \prod_{i=1}^{2} \int \chi_0^{(g)}(Q_{k',i} - h_{k',i}) \chi_0^{(e)}(Q_{k',i} - h_{k',i}^{(e)}) dQ_{k',i}$$
$$= \prod_{i=1}^{2} \frac{2 \cdot (\omega_i^{(g)} \omega_i^{(e)})^{1/2}}{(\omega_i^{(g)} + \omega_i^{(e)})} \exp\left[-\frac{M\omega_i^{(g)}\omega_i^{(e)}}{\hbar(\omega_i^{(g)} + \omega_i^{(e)})} (h_{k,i} - h_{k,i}^{(e)})^2\right] = 0.999\,e^{-4.25}$$
$$= 0.014 \qquad (2.32)$$

Correspondingly, the effective mass of the phonon-dressed electron--electron-polaron--increases by about 2 orders of magnitude which is practically immobile and the band picture breaks down.

In the case of $\gamma_i^{(g)} = \gamma_i^{(e)}$, the factor in the exponent in the above equation is just the T=0 Huang-Rhys factor(7) S which characterizes the strength of the electron-phonon coupling. Therefore $S^e = 4.25$ also means that the electron-phonon coupling is quite strong in the buckling model.

2.2.3 Hole-Polaron

If the hole is allowed to spread throughout the whole frozen lattice, the hole will be in the top of valence band, which in our model is at $\overline{J'}$ point, with energy $E^V(\overline{J'}) = E_n^V + 0.18$ev, as can be seen in Fig.2.2.

In the case that the hole is perfectly localized in one particular cell, say cell p, the adiabatic energy of (2N-1) electrons plus 2N atoms in the ground state equilibrium configuration is

$$\mathcal{E}^{unrel}_{2N-1} = \frac{r}{2}\sum_{n,i}(H_{n,i}-H_0)^2 + 2\cdot\sum_{n(\neq p)} E^{(V)}_n(H_{n,i}) + E^{(V)}_p(H_{p,i}) \qquad (2.33)$$

with $E^V_n(H_{n,i})$ given in eq.(2.15) and $H_{n,1}$=0.96A, $H_{n,2}$=0.68A.

After the lattice relaxed, the adiabatic energy becomes

$$\mathcal{E}^{rel}_{2N-1} = \frac{r}{2}\sum_{n,i}(H^{(h)}_{n,i}-H_0)^2 + 2\cdot\sum_{n(\neq p)} E^{(V)}_n(H^{(h)}_{n,i}) + E^{(V)}_p(H^{(h)}_{p,i}) \qquad (2.34)$$

The new equilibrium positions $H^h_{n,i}$ is determined by $\frac{\partial \mathcal{E}^{rel}_{2N-1}}{\partial H^{(h)}_{n,i}} = 0$.

It turns out that $H^h_{n,1}=H_{n,1}$=0.96A, $H^h_{n,2}=H_{n,2}$=0.68A (for $n\neq p$), and

$$h^{(h)}_{p,1} = \frac{c\alpha_1^2 H_0}{ra^2-\alpha_1^2 c} = 0.127\text{ A}$$

$$h^{(h)}_{p,2} = \frac{c\alpha_2^2 H_0}{ra^2-\alpha_2^2 c} = 0.019\text{ A}$$

$$E^{(V)}_0(H^{(h)}_{p,i}) = E_p - \frac{c}{2}\left[\alpha_1^2\frac{(H_0+h^{(h)}_{p,1})^2}{a^2} + \alpha_2^2\frac{(H_0+h^{(h)}_{p,2})^2}{a^2}\right] = E_p - 1.37\text{eV} \qquad (2.35)$$

The relaxation energy in this case is

$$\begin{aligned} E^{(h)}_R &= \mathcal{E}^{unrel}_{2N-1} - \mathcal{E}^{rel}_{2N-1} \\ &= \frac{r}{2}\left(h^2_{p,1} + h^2_{p,2} - h^{(h)\,2}_{p,1} - h^{(h)\,2}_{p,2}\right) + E^{(V)}_p(H_{p,i}) - E^{(V)}_p(H^{(h)}_{p,i}) \\ &= 0.36\text{ eV} \end{aligned} \qquad (2.36)$$

E^h_R is much larger than the energy 0.18ev that the system would gain if the hole would spread over the whole frozen lattice. The hole will therefore prefer to be localized, as in the case of the electron, with negligible spreadto the nearest neighbor cells even when the transfer is switched on.

The effective force constants of the atoms of the cell in which the hole is perfectly localized can be calculated in the way similar to the case of electron-polaron. It turns out that

$$\begin{aligned} r^{(h)}_1 a^2 &= ra^2 - c\alpha_1^2 = 308.2\text{ eV} \\ r^{(h)}_2 a^2 &= ra^2 - c\alpha_2^2 = 359.2\text{ eV} \end{aligned} \qquad (2.37)$$

The corresponding phonon energies are

$$\hbar\omega^{(h)}_1 = 0.056\text{eV}\ ,\ \hbar\omega^{(h)}_2 = 0.060\text{ eV} \qquad (2.38)$$

and the Huang-Rhys factor at T=0°K for the hole-polaron is

$$S^h=6.4$$

The energy levels of electron-polaron and hole-polaron are schematically shown in Fig.2.2.

2.2.4 Electron-hole Pair

When a conduction electron and a hole are localized on the same cell, say cell 0, then the electronic distribution is just that of the ideal 1x1 surface, e.g., one electron per atomic site. After relaxation, the atomic positions of that cell take the ideal surface values, 0.79A. The relaxation energy E_R^{e-h} is therefore given by

$$E_R^{(e-h)} = \frac{\gamma}{2}\left[h_{0,1}^2+h_{0,2}^2-2\times(0.79-0.64)^2\right]+E_n^{(V)}+E_n^{(C)}-2\cdot\left[E_p-\frac{c}{2}\left(\frac{0.79A}{a}\right)^2\right]$$
$$= 0.38\ \mathrm{eV} \qquad (2.39)$$

The energy level of the e-h pair in the same cell is also shown in Fig.2.2.

2.3 EXCITON

Denote the creation and the annihilation operators of the conduction band Wannier state $|n^c\rangle$ of spin σ by $a_{n,\sigma}^{c+}$ and $a_{n,\sigma}^{c}$, respectively. While $a_{n,\sigma}^{v+}$ and $a_{n,\sigma}^{v}$ denote the corresponding operators of the valence band Wannier state $|n^v\rangle$ of spin σ. Introduce the hole operators by definition

$$d_{n,\sigma}^{+} = a_{n,\bar{\sigma}}^{(v)} \quad , \quad d_{n,\sigma} = a_{n,\bar{\sigma}}^{(v)+}$$

The optically generated singlet state (total spin=0) exciton with the electron in the (n)th cell and the hole in the (m)th cell will then be described by the following wave function

$$\frac{1}{\sqrt{2}}\left[a_{n,\frac{1}{2}}^{(c)+}\, d_{m,-\frac{1}{2}}^{+} + a_{n,-\frac{1}{2}}^{(c)+}\, d_{m,\frac{1}{2}}^{+}\right]|0\rangle$$

Where $|0\rangle$ denotes the electronic ground state.

As shown in many text-books(11), the Coulomb and exchange interaction between the electron and the hole in singlet strongly localized exciton state is given by

$$E_{e-h}=-\left[W\left(\begin{smallmatrix} n & n & n & n \\ v & c & c & v\end{smallmatrix}\right)-2W\left(\begin{smallmatrix} n & n & n & n \\ v & c & v & c\end{smallmatrix}\right)\right] \qquad (2.40)$$

Where the screened Coulomb interaction is

$$W\left(\begin{smallmatrix} n & n & n & n \\ v & c & c & v\end{smallmatrix}\right)=\int a_n^{(v)*}(\vec{r}_1)\,a^{(e)*}(\vec{r}_2)\frac{e^2}{\epsilon|\vec{r}_1-\vec{r}_2|}\,a_n^{(c)}(\vec{r}_2)\,a_n^{(v)}(\vec{r}_1)\,d\vec{r}_1\,d\vec{r}_2$$
$$=\int\Big\{\alpha_1^2\alpha_2^2\left[|\varphi_1(\vec{r}_1-\vec{R}_{n,1})|^2|\varphi_1(\vec{r}_2-\vec{R}_{n,1})|^2+|\varphi_2(\vec{r}_1-\vec{R}_{n,2})|^2|\varphi_2(\vec{r}_2-\vec{R}_{n,2})|^2\right]+$$
$$+\alpha_1^4|\varphi_1(r_1-R_{n,1})|^2|\varphi_2(r_2-R_{n,2})|^2+\alpha_2^4|\varphi_2(r_1-R_{n,2})|^2|\varphi_1(r_2-R_{n,1})|^2\Big\}\frac{e^2}{\epsilon|\vec{r}_1-\vec{r}_2|}\,d\vec{r}_1\,d\vec{r}_2$$
$$=\alpha_1^2\alpha_2^2\,\mathcal{E}_{self}+(\alpha_1^4+\alpha_2^4)\,\mathcal{E}_{coul} \qquad (2.41)$$

and the screened exchange interaction is

$$W\left(\begin{smallmatrix} n & n & n & n \\ v & c & v & c\end{smallmatrix}\right)=\int a_n^{(v)*}(\vec{r}_1)\,a_n^{(c)*}(\vec{r}_2)\frac{e^2}{\epsilon|\vec{r}_1-\vec{r}_2|}\,a_n^{(v)}(\vec{r}_2)\,a_n^{(c)}(\vec{r}_1)\,d\vec{r}_1\,d\vec{r}_2$$
$$=\int\alpha_1^2\alpha_2^2\Big[|\varphi_1(\vec{r}_1-\vec{R}_{n,1})|^2|\varphi_1(\vec{r}_2-\vec{R}_{n,1})|^2+|\varphi_2(\vec{r}_1-\vec{R}_{n,2})|^2|\varphi_2(\vec{r}_2-\vec{R}_{n,2})|^2-$$
$$-|\varphi_2(\vec{r}_1-\vec{R}_{n,2})|^2|\varphi_1(\vec{r}_2-\vec{R}_{n,1})|^2-|\varphi_1(\vec{r}_1-\vec{R}_{n,1})|^2|\varphi_2(\vec{r}_2-\vec{R}_{n,2})|^2\Big]\frac{e^2}{\epsilon|\vec{r}_1-\vec{r}_2|}\,d\vec{r}_1\,d\vec{r}_2$$
$$=\alpha_1^2\alpha_2^2\,\mathcal{E}_{self}-2\alpha_1^2\alpha_2^2\,\mathcal{E}_{coul}$$

Because of the large separation(3.85A) between surface atoms and because of the well-localized nature of the DB orbitals as can be seen from Table 1, the Coulomb interaction $\mathcal{E}_{coul}$ between two electrons centered at two atoms can well be approximated by the interaction of two point charges centered at each atom sites. This is confirmed by Kotani's table(12). The surface dielectric constant ϵ takes into account the screening of back bonds and bulk electrons, and is estimated to be $(\epsilon_b+1)/2$ (5), where ϵ_b is the bulk dielectric constant, e.g. $\epsilon=6$. It turns out that $\mathcal{E}_{coul}=0.62$ev.

To calculate the DB state Coulomb self-energy $\mathcal{E}_{self}$, we use Table 1 data and take the DB orbitals corresponding to the ideal (1x1) surface configuration, e.g. $H_{n,i}=0.79$A. It turns out that $\mathcal{E}_{self}=4.16$ev.

Finally, we get the e-h interaction energy E_{e-h}

$$E_{(e-h)} = \alpha_1^2\alpha_2^2\,\mathcal{E}_{self} - (1+2\alpha_1^2\alpha_2^2)\,\mathcal{E}_{coul} = -0.25\,eV \qquad (2.43)$$

e.g. the binding energy of the strongly localized exciton is 0.25ev.

2.4 EXCITONIC POLARON

When the electron-lattice coupling is switched on, as pointed out in sec.2.2.4, the atoms of the cell in which an exciton is localized will relax to the positions of the ideal 1x1 surface, $H_{n,i}$=0.79A, and the relaxation energy E_R^{e-h} is given there to be 0.38ev.

The effective force constants of the atoms of cell in which the exciton is localized can also be evaluated as

$$\gamma_1^{(e-h)}a^2 = \gamma_2^{(e-h)}a^2 = \gamma a^2 - C = 298\,eV \qquad (2.44)$$

and the corresponding phonon energies are

$$\hbar\omega_1^{(e-h)} = \hbar\omega_2^{(e-h)} = 0.055\,eV$$

The S factor at T=0°K for exciton-polaron is calculated as S^{e-h}=6.98. This means that the exciton-phonon coupling is strong in our model. The exciton will be practically immobile and the exciton-polaron bandwidth is extremely narrow.

2.5 EXPECTED OPTICAL ABSORPTION LINE SHAPE

In the adiabatic and Condon approximation, the normalized line shape function, for transistion from electronic ground state (g) to exciton state (ex) as shown schematically in Fig.2.4, can be written as(13,14)

$$I_{g,ex}(E) = \underset{k}{Av}\sum_{l} |\langle g,k|ex,l\rangle|^2\,\delta(\mathcal{E}_{ex,l} - \mathcal{E}_{g,k} - E) \qquad (2.45)$$

Where $\langle g,k|$ and $\langle ex,l|$ are the vibrational wave functions for the electronic ground and exciton states, respectively, and satisfy:

$$\left[T_N + \mathcal{E}_i^{adia}(Q)\right]\psi_{ip}(Q) = \mathcal{E}_{ip}\,\psi_{ip}(Q) \qquad (2.46)$$

$$T_N = \sum_{n,i} -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial Q_{n,i}^2} \qquad (2.47)$$

Where(i,p)stands for either(g,k)or(ex,l). T_N is the atomic kinetic energy operator.Q represents the atomic coordinate. $\underset{k}{Av}$ stands for a thermal average over initial vibrational states and $\sum_{\ell}$ for a sum over final vibrational states. $\mathcal{E}_i^{adiab}$ is the adiabatic potential corresponding to the electronicstate i.

For the electronic ground state $\mathcal{E}_g^{adiab}$ is given by eq.(2.22) and $\psi_{g,k}$ is given by

$$\psi_{g,k}(Q) = \prod_{n,i} \chi_{k_{n,i}}^{(g)}(Q_{n,i} - h_{n,i}) \qquad (2.48)$$

Where the harmonic oscillator wave function $\chi_{k_{n,i}}^{(g)}(Q_{n,i}-h_{n,i})$ is given by

$$\chi_k^{(g)}(Q_{n,i} - h_{n,i}) = \left(\frac{M\omega_i^{(g)}}{\pi\hbar}\right)^{1/4} \frac{e^{-\frac{M\omega_i^{(g)}}{2\hbar}(Q_{n,i}-h_{n,i})^2}}{(2^k\cdot(k!))^{1/2}} H_k\left[\left(\frac{M\omega_i^{(g)}}{\hbar}\right)^{1/2}(Q_{n,i}-h_{n,i})\right] \qquad (2.49)$$

$H_n(\rho)$ is a Hermite polynomial.

The energy eigenvalue of $\psi_{g,k}(Q)$ is

$$\mathcal{E}_{g,k} = \sum_n \sum_i (k_{n,i} + \tfrac{1}{2})\hbar\omega_i^{(g)} + E_0 \qquad (2.50)$$

For the strongly binding exciton localized at cell m,the adiabatic potential can be written as

$$\begin{aligned}\mathcal{E}_{ex}^{adia} &= \frac{1}{2}\sum_{n(\neq m)}\sum_i \gamma_i^{(g)}(Q_{n,i}-h_{n,i})^2 + \frac{1}{2}\sum_i \gamma_i^{(e-h)}(Q_{m,i}-h_{m,i}^{(e-h)})^2 + E_0 + E_n^{(c)}(h_{n,i}) - E_n^{(v)}(h_{n,i}) - \\ &\qquad - E_R^{(e-h)} + E_{(e-h)} \\ &= \frac{1}{2}\sum_{n(\neq m)}\sum_i \gamma_i^{(g)}(Q_{n,i}-h_{n,i})^2 + \frac{1}{2}\sum_i \gamma_i^{(e-h)}(Q_{m,i}-h_{m,i}^{(e-h)})^2 + E_0 + 0.15\,eV \qquad (2.51)\end{aligned}$$

Where $E_n^C(h_{n,i})$ and $E_n^V(h_{n,i})$ are the ground state conduction band and valence band Wannier states energies,respectively,as given by eqs.(2.15) and (2.16). E_R^{e-h} is the relaxation energy for e-h pair and is given by eq.(2.39). E_{e-h} is the interaction energy between the electron and the hole,as given by eq.(2.43).

The corresponding vibrational wave function is given by

$$\psi_{ex,\ell} = \prod_{i=1}^{2} \chi_{\ell_{m,i}}^{(ex)}(Q_{m,i} - h_{m,i}^{(e-h)}) \prod_{n(\neq m)} \prod_{i=1}^{2} \chi_{\ell_{n,i}}^{(g)}(Q_{n,i} - h_{n,i}) \qquad (2.52)$$

Where χ_ℓ^g is given by eq.(2.49), while χ_ℓ^{ex} is given by

$$\chi_\ell^{(ex)}(Q_{m,i}-h_{m,i}^{(ex)}) = \left(\frac{M\omega_i^{(ex)}}{\pi\hbar}\right)^{1/4} \frac{e^{-\frac{M\omega_i^{(ex)}}{2\hbar}(Q_{m,i}-h_{m,i}^{(ex)})^2}}{(2^\ell\cdot \ell!)^{1/2}} H_\ell\left(\left(\frac{M\omega_i^{(ex)}}{\hbar}\right)^{1/2}(Q_{m,i}-h_{m,i}^{(e-h)})\right) \quad (2.53)$$

The eigenvalue of $\psi_{ex,\ell}$ is

$$\mathcal{E}_{ex,\ell} = \sum_i (\ell_{m,i}+\tfrac{1}{2})\hbar\omega_i^{(ex)} + \sum_{n(\neq m)}\sum_i (\ell_{n,i}+\tfrac{1}{2})\hbar\omega_i^{(g)} + E_0 + 0.15\,eV$$

At temperature T, an oscillator with frequency ω is excited to its (k)th excited state with probability

$$P(k,\hbar\omega) = e^{-k\hbar\omega/k_BT}\left(1-e^{-\hbar\omega/k_BT}\right)$$

So that the line shape function (2.45) has the following form

$$I_{g.ex}(E) = \sum_{k_{m,i}}\sum_{\ell_{m,i}} \prod_{i=1}^{2} P(k_{m,i},\hbar\omega_i^{(g)}) \left|\langle \chi_{k_{m,i}}^{(g)}(Q_{m,i}-h_{m,i}) | \chi_{\ell_{m,i}}^{(ex)}(Q_{m,i}-h_{m,i}^{(e-h)})\rangle\right|^2 \cdot$$
$$\cdot\,\delta\left[(\ell_{m,1}+\ell_{m,2})\hbar\omega^{(ex)} - k_{m,1}\hbar\omega_1^{(g)} - k_{m,2}\hbar\omega_2^{(g)} + 0.15\,eV - E\right] \quad (2.54)$$

Where m labels the particular unit in which the exciton is localized.

We have calculated numerically the line shape function $I_{g,ex}$ for T equals 2,152,302 and 452 K with cut-off in summation over $k_{m,i}$ up to 5 and with separation in energy step=0.02ev. The probability of our oscillator($\hbar\omega$=0.05ev) at its (6)th excited state at T=452, P(6,0.05), is about 5.5×10^{-4}. This justify our cut-off procedure.

The results is plotted in Fig.2.5.

It is found that the position of the peak does not move with temperature, while its heigh lowered when T increases. As shown in Table 2, its half-maximum width obeys quite well the $\left[\mathrm{Coth}\left(\frac{\hbar\omega}{2k_BT}\right)\right]^{1/2}$ formula, as mentioned by Chiarotti in his lecture notes(14).

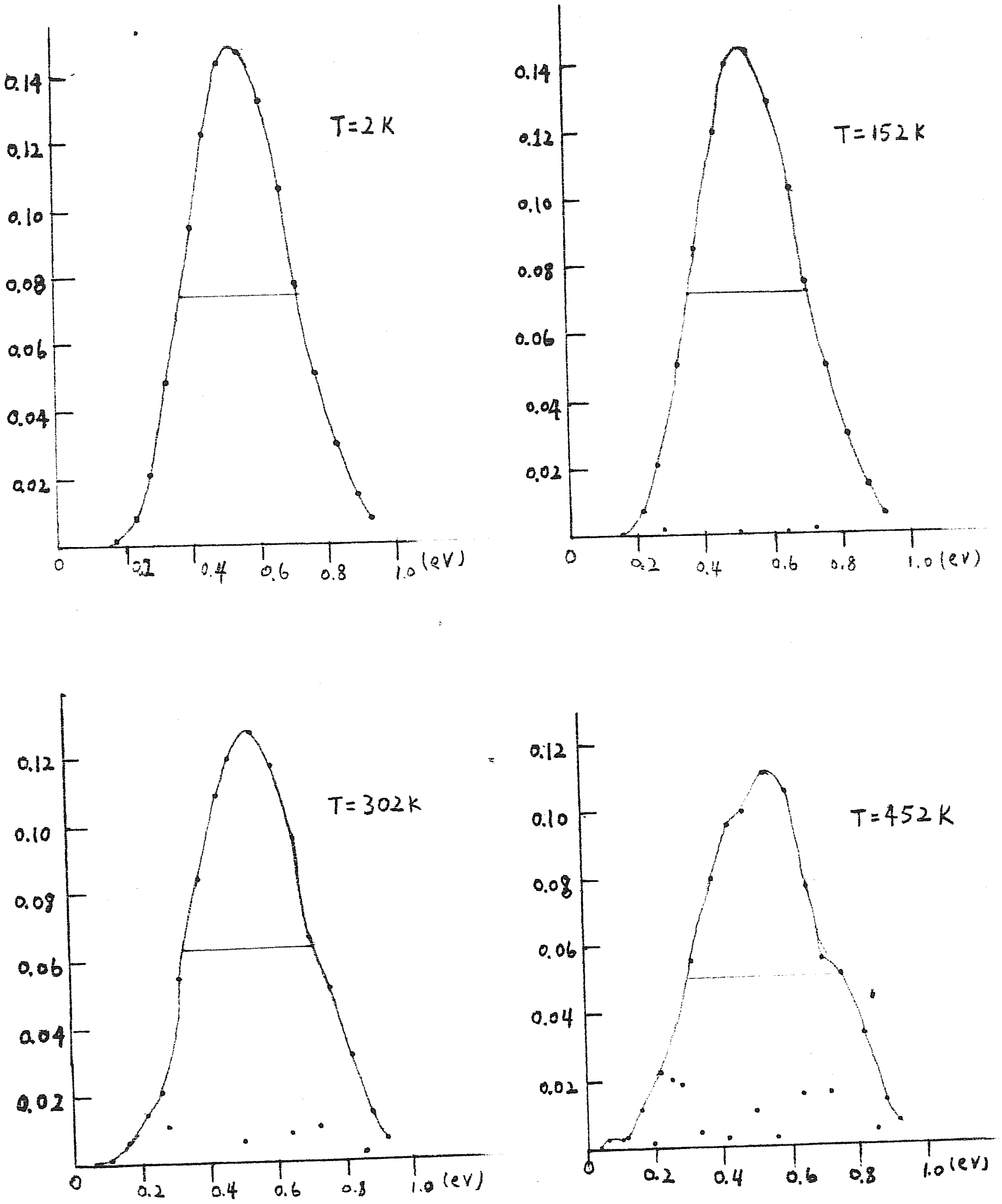


Fig.2.5 Expected optical absorption line shape of Si(111)2x1 surface states in buckling model at 2 K, 152 K, 302 K, and 452 K.

Table 2. $\hbar\omega_p = 0.055$ev. H: Half-maximum width.

T	2	76	302	452
H(ev)	0.35	0.35	0.39	0.44
H/H	1.00	1.00	1.11	1.26
$(\mathrm{Cth}\frac{\hbar\omega_p}{2kT})^{1/2}$	1.000	1.000	1.128	1.283

3. π-BONDED CHAIN MODEL

3.1 THE MODEL AND THE PARAMETERS

In the π-bonded chain model proposed by Pandey(4), the surface atoms are each bonded to two other surface atoms and form zig-zag chains similar in bonding topology to the Si(110) surface. The chain structure can be obtained easily from the ideal bonding topology by moving the type 2 atoms(Fig.3.1) from the subsurface layer into the surface layer and at the same time moving the type 3 atoms from the surface layer into the subsurface layer. An important feature of this chain model geometry is that the surface atoms are nearest neighbor(d=2.35A) to each other. This feature is responsible to the large dispersion along $\bar{\Gamma}\bar{J}$(the chain direction).

A lot of elaborate works have been done on the surface state energy band structure for this chain model. For our purpose, it is much simpler to isolate the top surface layer from the bulk underneath it and calculate the band structure by tight-binding method.

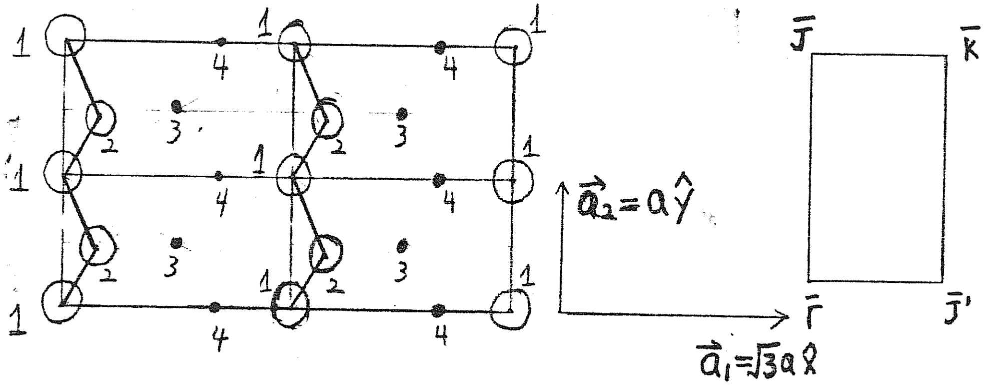


Fig.3.1 Surface geometry of Si(111)2x1 dimerized π-bonded chain model. Also shown are the primitive surface vectors and the surface Brillouin zone. O: Surface atom. ● : Subsurface atom.

The surface has a rectangle as its unit cell which contains type 1 atoms and type 2 atoms each. After dimerization,the longer bond alternates with the shorter ones along a chain,as shown in Fig.3.1.

Denote the DB atomic orbitals,which are mostly p_z orbitals, of type 1 atom and that of type 2 atom in unit cell n by $|n,1\rangle$ and $|n,2\rangle$,respectively. The Bloch state of wave vector $\vec{k}$ can be expressed as a linear combination of Bloch sums with the same wave vector $\vec{k}$,

$$\begin{aligned}\Psi_{\vec{k}}(\vec{r}) &= \frac{\alpha_1(\vec{k})}{\sqrt{N}}\sum_n e^{i\vec{k}\cdot\vec{R}_n}|n,1\rangle + \frac{\alpha_2(\vec{k})}{\sqrt{N}}\sum_n e^{i\vec{k}\cdot\vec{R}_n}|n,2\rangle \\ &= \alpha_1(\vec{k})\Phi_{\vec{k},1} + \alpha_2(\vec{k})\Phi_{\vec{k},2} \end{aligned} \qquad (3.1)$$

The matrix elements of the one-electron Hamiltonian H between Bloch sums are then

$$\begin{aligned} H_{1,1} &= (\Phi_{\vec{k},1}|H|\Phi_{\vec{k},2}) = \frac{1}{N}\sum_n\sum_m e^{-i\vec{k}\cdot(\vec{R}_n-\vec{R}_m)}\langle n,1|H|m,1\rangle \\ &= \langle n,1|H|n,1\rangle \equiv \varepsilon \\ H_{2,2} &= H_{1,1} = \varepsilon \\ H_{1,2} &= (\Phi_{\vec{k},1}|H|\Phi_{\vec{k},2}) = \frac{1}{N}\sum_n\sum_m e^{-i\vec{k}\cdot(\vec{R}_n-\vec{R}_m)}\langle n,1|H|m,2\rangle \\ &= \langle n,1|H|n,2\rangle + e^{-i\vec{k}\cdot\vec{a}_2}\langle n,1|H|n-1,2\rangle = t_1 + t_2 e^{-i\vec{k}\cdot\vec{a}_2} \\ H_{2,1} &= (H_{1,2})^* \end{aligned} \qquad (3.2)$$

Here we take into account only hopping integral between nearest neighbor atoms and ε denotes the atomic orbital energy; t_1 and t_2 stand for the hopping integrals between atoms connected by short bond and that connected by long bond,respectively.

Solve the Schrodinger equation $H\Psi_k(\mathbf{r})=E(k)\Psi_k(\mathbf{r})$, and get

$$\begin{aligned} E(\vec{k}) &= E \pm |t_1 + t_2 e^{-i\vec{k}\cdot\vec{a}_2}| \\ &= E \pm (t_1^2 + t_2^2 + 2t_1t_2 \,\mathrm{Cos}\, \vec{k}\cdot\vec{a}_2)^{1/2} \end{aligned} \qquad (3.3)$$

The Bloch state then has the following form:

$$\Psi_{\vec{k}}^{(\mu)}(\vec{r}) = \frac{1}{\sqrt{N}}\sum_n e^{i\vec{k}\cdot\vec{R}_n}\left[\alpha_1^{(\mu)}(\vec{k})|n,1\rangle + \alpha_2^{(\mu)}(\vec{k})|n,2\rangle\right] \qquad (3.4)$$

(μ : v or c)

with the relation between $\alpha_1^{(\mu)}(\vec{k})$ and $\alpha_2^{(\mu)}(\vec{k})$ as

$$\frac{\alpha_2^{(\mu)}(\vec{k})}{\alpha_1^{(\mu)}(\vec{k})} = \pm \frac{t_1 + t_2 e^{-i\vec{k}\cdot\vec{a}_2}}{\left|t_1 + t_2 e^{-i\vec{k}\cdot\vec{a}_2}\right|} = \pm e^{-i\theta(\vec{k})} \quad \left(\pm : \text{for } {v \atop c}\right)$$

where $\theta(\vec{k}) = \tan^{-1}\left(\frac{t_2 \sin \vec{k}\cdot\vec{a}_2}{t_1 + t_2 \cos \vec{k}\cdot\vec{a}_2}\right) = \theta(k_y)$

To construct Wannier functions it is necessary to choose a suitable phase for Bloch states. W.Kohn(15) suggested to choose the phase such that

$\Psi_k(0)$=Real and positive

If we put the origin of the coordinate on the middle point of $|0,1\rangle$ site and $|0,2\rangle$ site, the Bloch state in the following form will then has the required property,

$$\Psi_{\vec{k}}^{(v)}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_n e^{i\vec{k}\cdot\vec{R}_n} \alpha\cdot\left(e^{i\theta(\vec{k})/2}|n,1\rangle + e^{-i\theta(\vec{k})/2}|n,2\rangle\right)$$

$$\Psi_{\vec{k}}^{(c)}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_n e^{i\vec{k}\cdot\vec{R}_n} \frac{\alpha}{i}\left(e^{i\theta(\vec{k})/2}|n,1\rangle - e^{-i\theta(\vec{k})/2}|n,2\rangle\right)$$

The Wannier function can be constructed as

$$a^{(v)}(\vec{r}-\vec{R}_l) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}_l} \Psi_{\vec{k}}^{(v)}(\vec{r})$$

$$= \frac{\alpha}{N} \sum_n \sum_{\vec{k}} \left[e^{-i(\vec{k}\cdot(\vec{R}_l-\vec{R}_n) - \theta(\vec{k})/2)} |n,1\rangle + e^{-i(\vec{k}\cdot(\vec{R}_l-\vec{R}_n) + \theta(\vec{k})/2)} |n,2\rangle \right.$$

$$= \sum_n \alpha \left[c(l-n)|n,1\rangle + d(l-n)|n,2\rangle \right]$$

$$= \sum_n \alpha \left\{ \frac{c(l-n)+d(l-n)}{2}\left(|n,1\rangle + |n,2\rangle\right) + \frac{c(l-n)-d(l-n)}{2}\left(|n,1\rangle - |n,2\rangle\right) \right]$$

Where

$$c(l-n) = \frac{1}{N} \sum_{\vec{k}} e^{-i(\vec{k}(\vec{R}_l-\vec{R}_n) - \theta(\vec{k})/2)}$$

$$= \frac{1}{N} \sum_{k_y} e^{-i[k_y(y_l-y_n) - \theta(k_y)/2]} \cdot \sum_{k_x} e^{-ik_x(x_l-x_n)}$$

$$= \frac{1}{(2M+1)} \sum_{k_y} e^{-i[k_y(y_l-y_n) - \theta(k_y)/2]}$$

$$= \frac{1}{(2M+1)} \sum_{j=-M}^{M} e^{-i\left[\frac{2\pi j(l-n)}{2M+1} - \frac{1}{2}\tan^{-1}\left(\frac{t_2 \sin\frac{2\pi j}{2M+1}}{t_1 + t_2\cos\frac{2\pi j}{2M+1}}\right)\right]}$$

$$= \frac{1}{(2M+1)} \left\{ 1 + 2\sum_{j=1}^{M} \cos\left[\frac{2\pi j(l-n)}{2M+1} - \frac{1}{2}\tan^{-1}\left(\frac{t_2 \sin\frac{2\pi j}{2M+1}}{t_1 + t_2\cos\frac{2\pi j}{2M+1}}\right)\right]\right\}$$

and

$$d(l-n) = \frac{1}{(2M+1)} \left\{ 1 + 2\sum_{j=1}^{M} \cos\left[\frac{2\pi j(l-n)}{2M+1} + \frac{1}{2}\tan^{-1}\left(\frac{t_2 \sin\frac{2\pi j}{2M+1}}{t_1 + t_2\cos\frac{2\pi j}{2M+1}}\right)\right]\right\}$$

Where (2M+1) is the number of unit cell along a chain.

We have calculated $c(\ell)$ and $d(\ell)$ for M=100, means 201 unit cells along the chain, using $t_1=-0.89$ev and $t_2=-0.49$ev. The result is shown in Table 3. It turns out that the Wannier state $a^v(r)$ is almost entirely composed of the bonding state on the same cell with about 1.8% antibonding state on each nearest neighboring cells along the chain direction. While the conduction band Wannier state

$$a^c(\vec{r}-\vec{R}_\ell)=\sum_n \frac{\alpha}{\lambda}\left[c(\ell-n)|n,1\rangle - d(\ell-n)|n,2\rangle\right]$$

$$=\sum_n \frac{\alpha}{\lambda}\left\{\frac{c(\ell-n)+d(\ell-n)}{2}\left[|n,1\rangle-|n,2\rangle\right]+\frac{c(\ell-n)-d(\ell-n)}{2}\left[|n,1\rangle+|n,2\rangle\right]\right\}$$

as opposed to $a^v(r)$, is almost entirely composed of the antibonding state on the same cell with about 1.8% bonding state on each nearest neighboring cells along the chain direction.

It is therefore a good approximation to consider $a^v(r)$ and $a^c(r)$ as the bonding and antibonding states on the same cell, respectively:

$$a^v(\vec{r}-\vec{R}_n)=\alpha\left(|n,1\rangle+|n,2\rangle\right) \tag{3.5}$$

$$a^c(\vec{r}-\vec{R}_n)=\frac{\alpha}{\lambda}\left(|n,1\rangle-|n,2\rangle\right) \tag{3.6}$$

The overlap integral between atomic orbitals $|n,1\rangle$ and $|n,2\rangle$ belonged to the same cell is estimated from Kotani's Table(12),

$$\langle n,1|n,2\rangle \cong 0.08$$

While that between $|n,1\rangle$ and $|n-1,2\rangle$ is more less than 0.08, because of the longer bond length due to dimerization. For simplicity, we neglect all overlap integrals, putting $\alpha=1/\sqrt{2}$. The orthonormality of the approximate Wannier function then is preserved.

The energy of electron in the valence band Wannier state $a^v(r-R_n)$ is

$$E_n^v=\langle a^v(\vec{r}-\vec{R}_n)|H|a^v(\vec{r}-\vec{R}_n)\rangle$$

Table.3 The bonding component $[c(j)+d(j)]/2$ and anti-bonding component $[c(j)-d(j)]/2$ at j-th cell of a Wannier state $a_0^v(r)$ centered at o-th cell.

j	0	1	2	3	4	5
$[c(j)+d(j)]/2$	0.981	0.006	0.007	-0.004	0.002	-0.001
$[c(j)-d(j)]/2$	0.0	-0.136	-0.037	0.014	-0.006	0.003

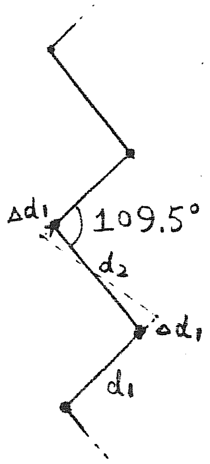


Fig.3.2 The geometry of dimerized chain model.

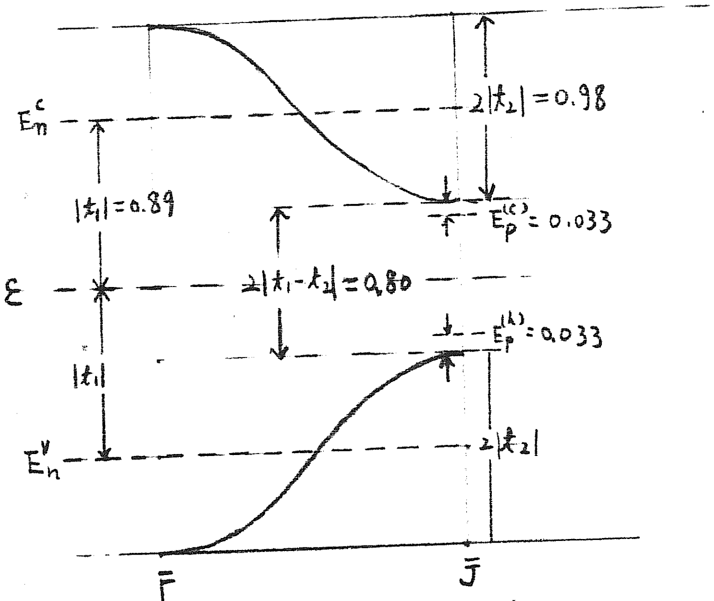


Fig.3.3 The simplified surface state energy bands of the chain model along $\bar{\Gamma}\bar{J}$ direction. Also shown are the electron-polaron and hole-polaron energy levels, E_p^c and E_p^h.

$$= \alpha^2 \left[\langle n,1|H|n,1\rangle + \langle n,2|H|n,2\rangle + \langle n,1|H|n,2\rangle + \langle n,2|H|n,1\rangle\right]$$

$$= \frac{1}{2}\left[2\varepsilon + 2t_1(n)\right] = \varepsilon + t_1(n) \qquad (3.7)$$

While that of electron in the conduction band Wannier state $a^c(r-R_n)$ is

$$E_n^c = \langle a^c(r-R_n)|H|a^c(r-R_n)\rangle$$

$$= \alpha^2 \left[\langle n,1|H|n,1\rangle + \langle n,2|H|n,2\rangle - \langle n,1|H|n,2\rangle - \langle n,2|H|n,1\rangle\right]$$

$$= 1/2\left[2\varepsilon - 2t_1(n)\right] = \varepsilon - t_1(n) \qquad (3.8)$$

Where ε is the atomic orbital energy; $t_1(n)$ is the hopping integral between atoms separated by short bond $d_{n,1}$ in the (n)th cell.

From the slab calculation of Si(111)2x1 by Selloni(16), as far as the dimerization is not too large, say $\left|(d_{n,1}-d_o)/d_o\right| < 0.15$, $t_1(n)$ can be represented quite well by

$$t_1 = t_o \cdot \exp(-\beta(d_{n,1}-d_o)) = t_o \cdot \exp(-\beta \Delta d_{n,1}) \qquad (3.9)$$

$$\Delta d_{n,1} = d_{n,1} - d_o \qquad (3.10)$$

Where d_o is the un-dimerized bond length.

Similarly, the hopping integral between atoms of different type separated by long bond $d_{n,2}$, can be expressed as

$$t_2 = t_o \cdot \exp(-\beta \Delta d_{n,2}) \qquad (3.11)$$

where $$\Delta d_{n,2} = d_{n,2} - d_o \qquad (3.12)$$

Consider now the equilibrium ground state of the surface. The system consists of 2N (N being the number of unit cells) surface atoms and 2N electrons. Simulating the interaction on the atoms along the bond direction by a force constant γ and neglecting the inter-chain interaction, the elastic energy of the lattice is then

$$\varepsilon_{elastic} = \gamma/2 \sum_n \left[(\Delta d_{n,1})^2 + (\Delta d_{n,2})^2\right] \qquad (3.13)$$

The summation is over all unit cells.

In the ground state, the 2N electrons will fill the valence band fully and leave the conduction band empty. Within Born-Oppenheimer adiabatic approximation, the adiabatic potential energy then equals the lattice energy plus the electronic energy which depends on the atomic configuration,

$$\mathcal{E}_{2N}^{adib}=\mathcal{E}^{latt}+\mathcal{E}_{2N}^{elect}(d_{n,i}) \qquad (3.14)$$

The electronic Hamiltonian can be expressed in terms of the second quantization language as

$$H_{elec}=2\sum_{n,\mu}E_n^{\mu}a_n^{\mu+}a_n^{\mu}+\sum_{\substack{n,\mu\\ m}}t_2/2(a_n^{V+}a_m^{V}-a_n^{C+}a_m^{C}) \qquad (3.15)$$

m: the neighboring cells of n along chain direction

Where n labels the unit cell; μ labels the band; The factor of 2 takes care of the spin. $a_n^{\mu+}$ and a_n^{μ} are the creation and the annihilation operators of μ band Wannier state, respectively.

$\pm t_2/2$ is the hopping integral between Wannier states of neighboring unit cells along chain direction, as can be verified as follows:

$$\langle a^V(r-R_n)|H|a^V(r-R_{n+1})\rangle$$

$$=\alpha^2\Big[\langle n,1|H|(n+1),1\rangle+\langle n,1|H|(n+1),2\rangle+\langle n,2|H|(n+1),1\rangle+$$

$$+\langle n,2|H|(n+1),2\rangle\Big]$$

$$=1/2\,\langle n,2|H|(n+1),1\rangle=t_2/2$$

Remember that t_2 is the hopping integral between atoms connected by long bond and that we neglect the hopping beyond nearest neighbor.

Denote the ground electronic state by $|\Phi_0\rangle$ with the well-known properties:

$$a_n^C|\Phi_0\rangle=0\ ,\text{and}\quad a_n^{V+}|\Phi_0\rangle=0.$$

The electronic energy in the ground state is then

$$\mathcal{E}_{2N}^{elec}=\langle\Phi_0|H_{elec}|\Phi_0\rangle=2\sum_n E_n^V \qquad (3.16)$$

From eqs.(3.7),(3.9),(3.13) and (3.16),eq.(3.14) can be expressed as

$$\mathcal{E}_{2N}^{adiab} = \gamma/2\sum_{n}\left[(\Delta d_{n,1})^2+(\Delta d_{n,2})^2\right] +2\sum_{n}\left[\mathcal{E}+t_0\exp(-\beta\Delta d_{n,1})\right] \tag{3.17}$$

$\Delta d_{n,1}$ and $\Delta d_{n,2}$ are not independent to each other in dimerized π-bonded chain model. In Fig.3.3,it is shown that the bond angle is 109.5° in the case of undimerized chain and this angle will not change much as long as the dimerization is not too large.

Under uniform dimerization,the followin geometric relation holds:

$$\begin{aligned} d_2 &= 2\cdot\left[(d_0/2)^2+(\Delta d_1/2)^2-2\cdot(d_0/2)\ (|\Delta d_1|/2)\ \mathrm{Cos}109.5^\circ\right]^{1/2} \\ &\cong d_0(1+1/3\cdot|\Delta d_1|/d_0) \\ \Delta d_2 &= d_2-d_0=-1/3\,\Delta d_1 \end{aligned} \tag{3.18}$$

But notice that if we just change one particular bond length,say $d_{j,1}$, then

$$\frac{\partial\Delta d_{j,2}}{\partial\Delta d_{j,1}} = -1/6 = \frac{\partial\Delta d_{j-1,2}}{\partial\Delta d_{j,1}}$$

and all the other bond lengths remain unchanged. So that

$$\begin{aligned} \frac{\partial\mathcal{E}_{2N}^{adiab}}{\partial\Delta d_{n,1}} &= 0 = \gamma\left[\Delta d_{n,1}+\Delta d_{n,2}\frac{\partial\Delta d_{n,2}}{\partial\Delta d_{n,1}}+\Delta d_{n-1,2}\frac{\partial\Delta d_{n-1,2}}{\partial\Delta d_{n,1}}\right]+2\cdot\frac{\partial t_1}{\partial\Delta d_{n,1}} \\ &= 10/9\cdot\gamma\,\Delta d_{n,1}-2\cdot\beta t_0\cdot\exp(-\beta\Delta d_{n,1}) \end{aligned} \tag{3.19}$$

The above equation shows the dependence of dimerization parameter $\Delta d_{n,1}$ on γ, β and t_0.

It seems that we have a lot of parameters to be determined, but actually there are only three independent parameters in our model,either t_1, t_2 and γ or γ, β and t_0. Below we first determine t_1 and t_2 through the experimental curve obtained recently by Lüth(3),which is reproduced in Fig.3.4.

In his wavevector-resolved electron-energy-loss experiment,

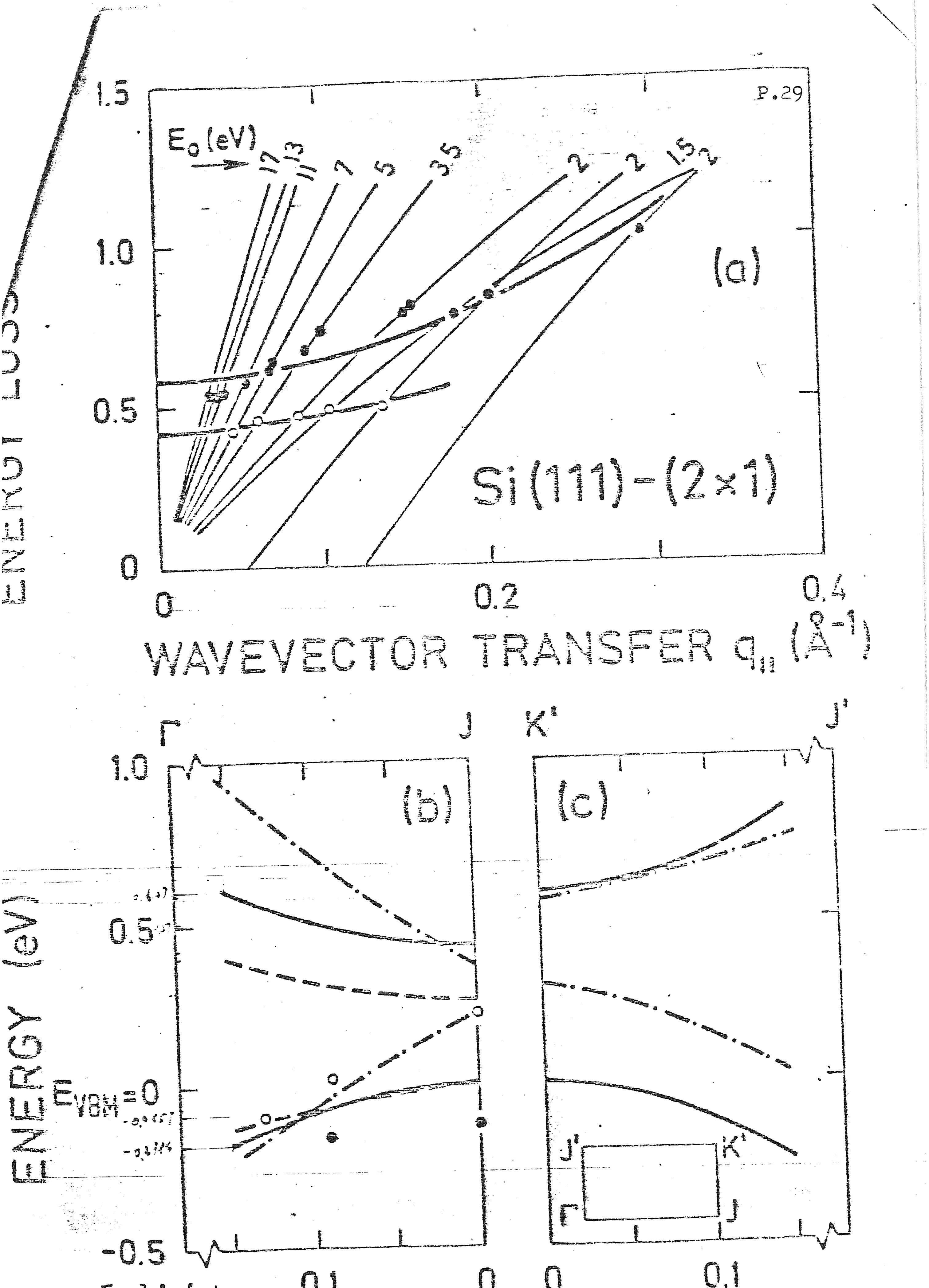


Fig. 3.4. Lüth experimental curves

Lüth obtained the band dispersion along $\overline{\Gamma J}$ and $\overline{J'K}$ directions and band gaps at $\overline{J}$ and $\overline{K}$ points, as shown in Fig.3.4 b and c, by assuming equal electron and hole effective masses. From Lüth's curve curvature, we obtain that $m_e = m_h \pm 0.48 m_o$. Compared with our model's dispersion, eq.(3.3), we obtain

$$\frac{t_1 t_2 a^2}{2\, t_1 - t_2} = \frac{\hbar^2}{2 m_e} \equiv \overline{C} = 8.095\ eV \cdot A^2$$

Not the same as Lüth's interpretation, we explain the "band gap" (0.43ev at $\overline{J}$ point and 0.59ev at $\overline{K}$ point) as the exciton excitation energy. Since 0.43ev is much closer to the Chiarotti's (2) optical absorption peak position (0.47ev) than 0.59ev, we take 0.43ev for our parameter determination. As will be calculated in sec. 3.3 and 3.2, the exciton binding energy is 0.34ev and the electron-polaron binding energy is about 0.03ev, the actual band gap at $\overline{J}$ point in our interpretation will then be about 0.8ev. In our notation, the band gap at $\overline{J}$ point is $2\,|t_1 - t_2|$, thus

$$2 \cdot |t_1 - t_2| = 0.8ev \tag{3.22}$$

Combining eqs.(3.21) and (3.22), one gets

$$t_1 = -0.89ev \tag{3.23}$$

$$t_2 = -0.49ev \tag{3.24}$$

From eqs.(3.9), (3.11) and (3.18), we get

$$t_1/t_2 = \exp\left[-\beta(\Delta d_{n,1} - \Delta d_{n,2})\right] = \exp(-\tfrac{4}{3}\beta \Delta d_{n,1}) \tag{3.25}$$

$$\beta \Delta d_{n,1} = -\tfrac{3}{4}\ln(t_1/t_2) = -0.448 \tag{3.26}$$

$$t_o = t_1 \exp(\beta \Delta d_{n,1}) = -(t_2^3 \cdot t_1)^{1/4} = -0.57ev \tag{3.27}$$

In recent paper, Pandey(4) showed the total energy dependence on intra-chain bond length that we reproduced in Fig.3.5. We estimate the curvature of the curve $\mathcal{C}$,

$$C = 3.29ev/A^2 = 48.8ev/a^2 \qquad (a = 3.85A) \tag{3.28}$$

In our notation, it corresponds to

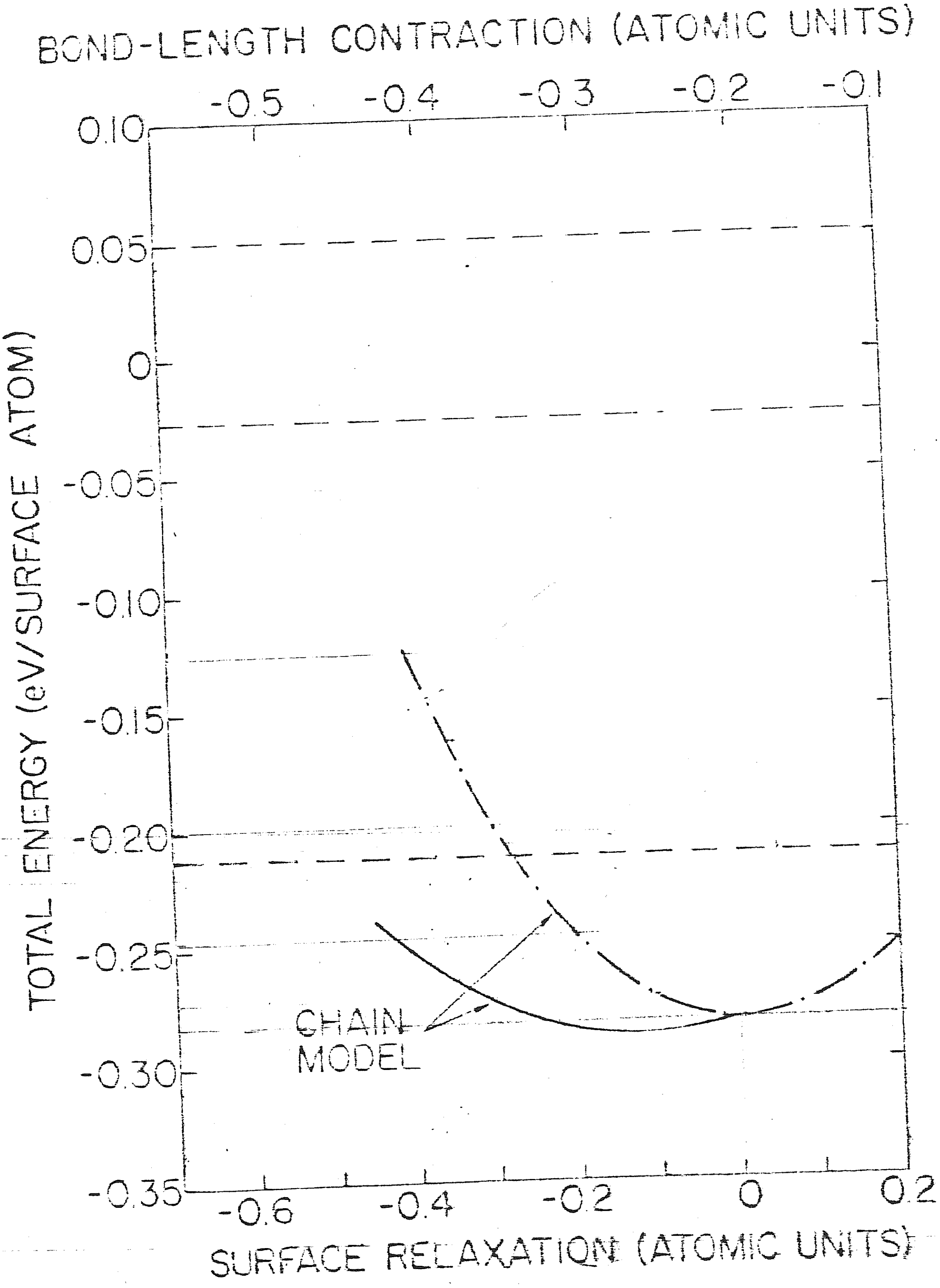


Fig.3.5 The total-energy dependence on intra-chain bond length(dash-dot line) (From K.C.Pandey (4)).

$$C=\gamma/2+t_0\beta^2/2$$

or $$\gamma a^2=2Ca^2-t_0\beta^2a^2 \qquad (3.29)$$

From eqs.(3.9) and (3.19),we get

$$10/9\,\gamma\beta\Delta d_{n,1}=2\beta^2t_1 \quad \text{or} \quad \beta^2a^2=\frac{5}{9}\gamma a^2(\beta\Delta d_{n,1})/t_1 \qquad (3.30)$$

Combined with eq.(3.29),finally we get

$$\gamma a^2=116\text{ev} \qquad (3.31)$$

$$\beta^2a^2=32.41 \quad \text{or} \quad \beta a=5.69 \qquad (3.32)$$

$$\Delta d_{n,1}=-0.303\text{A}=-0.0786a \qquad (3.33)$$

$$\Delta d_{n,2}=-\frac{1}{3}\Delta d_{n,1}=0.10\text{A}=0.026a \qquad (3.34)$$

The surface state energy band structure obtained is shown in Fig.3.4.

3.2 ELECTRON-POLARON AND HOLE-POLARON

3.2.1 Electron-polaron

As shown in sec.2.2.1,the localization or delocalization of an excess electron is roughly determined by the ratio E_R^e/B,where E_R^e is the relaxation energy due to the localization of the electron and B is half the conduction band width and equals to t_2 in the present model. If $E_R^e>B$,then the electron will be localized.

a) First we calculate the relaxation energy E_R^e in the case of an excess electron perfectly localized in one cell,say cell 0.

Denote the dimerization parameters before lattice distortion by $d_{n,1}$, $d_{n,2}$,and those after lattice distortion by $d^e_{n,1}$, $d^e_{n,2}$. Within adiabatic approximation,the adiabatic potential energy before and after lattice relaxation are

$$\mathcal{E}^{\text{unrel}}_{2N+1}=\frac{\gamma}{2}\sum_n(\Delta d_{n,1}^2+\Delta d_{n,2}^2)+2\sum_n E_n^v(\Delta d_{n,1})+E_0^c(\Delta d_{0,1}) \qquad (3.35)$$

$$\mathcal{E}^{\text{rel}}_{2N+1}=\frac{\gamma}{2}\sum_n(\Delta d_{n,1}^{(e)2}+\Delta d_{n,2}^{(e)2})+2\sum_n E_n^v(\Delta d_{n,1}^{(e)})+E_0^c(\Delta d_{0,1}^{(e)}) \qquad (3.36)$$

Because of perfectly localization, the bond lengths that change after lattice relaxation are $d_{o,1}$, $d_{o,2}$ and $d_{o-1,2}$. $\Delta d^{(e)}_{o,1}$ can be determined by minimizing E^{rel}_{2N+1} with respect to $d^{e}_{o,1}$.

$$\frac{\partial \mathcal{E}^{rel}_{2N+1}}{\partial \Delta d^{(e)}_{0,1}} = 0 = \gamma\left[\Delta d^{(e)}_{0,1} + \Delta d^{e}_{0,2}\frac{\partial \Delta d^{e}_{0,2}}{\partial \Delta d^{e}_{0,1}} + \Delta d^{e}_{0-1,2}\frac{\partial \Delta d^{e}_{0-1,2}}{\partial \Delta d^{e}_{0,1}}\right] + \frac{\partial t_1(0)}{\partial \Delta d^{e}_{0,1}}$$

$$= \frac{10}{9}\gamma \Delta d^{e}_{0,1} - \beta t_0 e^{-\beta \Delta d^{e}_{0,1}} \tag{3.37}$$

$$\beta \Delta d^{e}_{o,1} = -0.17 \tag{3.38}$$

$$\Delta d^{e}_{o,1} = -0.115A = -0.03a \tag{3.39}$$

All other $\Delta d_{n,1}$ unchanged and are given by eq.(3.33).

$$\Delta d^{e}_{o,2} = \Delta d^{e}_{o-1,2} = -\frac{1}{6}(\Delta d^{e}_{o,1} + \Delta d^{e}_{o-1,1}) = 0.07A = 0.018a \tag{3.40}$$

The relaxation energy is given by

$$E^{e}_{R} = \mathcal{E}^{unrel}_{2N+1} - \mathcal{E}^{rel}_{2N+1}$$

$$= \frac{\gamma}{2}[\Delta d^{2}_{0,1} + \Delta d^{2}_{0,2} + \Delta d^{2}_{0-1,2}] - \frac{\gamma}{2}[\Delta d^{e\,2}_{0,1} + \Delta d^{e\,2}_{0,2} + \Delta d^{e\,2}_{0-1,2}] + t_0(e^{-\beta \Delta d_{0,1}} - e^{-\beta \Delta d^{e}_{0,1}})$$

$$= 0.13ev \tag{3.41}$$

While half conduction band width is $|t_2| = 0.49ev$. $E^{e}_{R} < |t_2|$, so that the excess electron will not be localized. Instead, the electron will spread over quite a large number of cells and forms a large polaron on surface.

b) Secondly, we consider the case when the excess electron on surface state forms a large electron-polaron.

Assuming the electronic wave function of the surface with one excess electron as

$$\Phi_c = \sum_n c_n a^{c+}_n |\Phi_o\rangle \tag{3.42}$$

Where $|\Phi_o\rangle$ is the ground state wave function with full valence band and empty conduction band. c_n is the amplitude probability of the excess electron being in cell n. The normalization condition then requires

$$\sum_n |c_n|^2 = 1 \tag{3.43}$$

The electronic energy of the system is

$$\mathcal{E}^{\mathrm{elec}}_{2N+1} = \langle \Phi_c | H_{\mathrm{elec}} | \Phi_c \rangle$$

$$= 2\sum_n E^V_n + \sum_n |c_n|^2 E^c_n - t_2/2 \sum_{\substack{n \\ m:\text{the n.n. of } n \text{ along chain}}} c^*_n c_m \qquad (3.44)$$

and the adiabatic potential of the system is

$$\mathcal{E}^{\mathrm{adia}}_{2N+1} = \mathcal{E}^{\mathrm{lat}} + \mathcal{E}^{\mathrm{elec}}_{2N+1}$$

$$= \frac{\gamma}{2}\sum_n \left[(\Delta d^e_{n,1})^2 + (\Delta d^e_{n,2})^2 \right] + (2N+1)\mathcal{E} + \sum_n (2 - |c_n|^2) t_1 -$$

$$- t_2/2 \sum_{\substack{n \\ m:\text{the n.n. of } n \text{ along chain}}} c^*_n c_m \qquad (3.45)$$

By minimizing E^{adia}_{2N+1} with respect to c_n, one would get the adiabatic potential $\mathcal{E}^{\mathrm{adia}}_{2N+1}[\Delta d^e_{n,i}]$ as a functional of $\Delta d^e_{n,i}$. As far as the extrema of the adiabatic potential are concerned, however, one can take a much simpler way by converting the order of extremization: For fixed c_n, one minimizes $\mathcal{E}^{\mathrm{adia}}_{2N+1}$ with respect to $\Delta d^e_{n,i}$.

$$\frac{\partial \mathcal{E}^{\mathrm{adia}}_{2N+1}}{\partial(\Delta d^e_{n,1})} = 0$$

$$= \gamma \frac{10}{9} \Delta d^e_{n,1} - \beta (2 - |c_n|^2) t_0 \exp(-\beta \Delta d^e_{n,1}) \qquad (3.46)$$

Remember $t^e_1 = t_0 \exp(-\beta \Delta d^e_{n,1})$.

We expand t^e_1 to successive powers in $|c_n|^2$ and keep to only the first order,

$$t^e_1 = t_0 \exp(-\beta \Delta d^e_{n,1}) = t_1 + A\,|c_n|^2 + \cdots$$

$$= t_0 \exp(-\beta \Delta d_{n,1}) + A |c_n|^2 \qquad (3.47)$$

then $$A = \left.\frac{\partial (t_0 e^{-\beta \Delta d^e_{n,1}})}{\partial(|c_n|^2)}\right|_{|c_n|^2=0} = \frac{\beta^2 (t_0 e^{-\beta \Delta d_{n,1}})^2}{\frac{10}{9}\gamma + 2\beta^2 t_0 e^{-\beta \Delta d_{n,1}}}$$

$$= \frac{\beta^2 t_1^2}{\frac{10}{9}\gamma + 2\beta^2 t_1} = 0.36\ \mathrm{eV} \qquad (3.48)$$

Where $\Delta d_{n,1}$, t_1 denote the dimerization parameter and intra-cell hopping integral without the excess electron, while $\Delta d^e_{n,1}$, t^e_1 denote those with the excess electron.

In principle,this $\Delta d^{e}_{n,1}$ as a function of $|c_n|^2$ should be put in the eq;and $\mathcal{E}^{adia}_{2N+1}$ should be minimized with respect to $|c_n|^2$. But it is too difficult to do that directly. instead,we follow Holstein's paper by considering the Schrödinger eq. of that excess electron in the distorted lattice,ignoring for the moment the presence of the valence electron. Since we neglect interchain hopping,the problem reduces to one chain problem.

The one-electron Hamiltonian and wave function of the excess electron are:

$$H^e = \sum_n |n^c\rangle E^c_n \langle n^c| + t_2/2 \sum_n \left[|(n+1)^c\rangle\langle n^c| + |(n-1)^c\rangle\langle n^c| \right]$$

$$\psi^c = \sum_n c_n |n^c\rangle \quad \text{and} \quad \sum_n |c_n|^2 = 1$$

From Schrödinger eq. $H^e \psi^e = \mathcal{E}^c_b \psi^c$,one get

$$E^c_n c_n + t_2/2\cdot(c_{n-1} + c_{n+1}) = \mathcal{E}^c_p c_n \qquad (3.49)$$

Substitude the difference by diffential

$$c_{n-1} + c_{n+1} - 2c_n \cong \frac{d^2 c_n}{dn^2}$$

and from eqs.(3.8) and (3.47) we have

$$E^c_n = \mathcal{E} - t^e_1 = \mathcal{E} - t_1 - A|c_n|^2 \quad ,$$

eq.(3.49) then becomes

$$(\mathcal{E}^c_p - \mathcal{E} + t_1 + A|c_n|^2 - t_2)\cdot c_n = t_2/2 \frac{d^2 c_n}{dn^2} \qquad (3.50)$$

By $(3.50)\times\frac{dc_n^*}{dn} + (3.50)^*\times\frac{dc_n}{dn}$, we get

$$(\mathcal{E}^c_p + A|c_n|^2)\frac{d|c_n|^2}{dn} = t_2/2 \frac{d}{dn}\left(\frac{dc_n}{dn}\frac{dc_n^*}{dn}\right) \qquad (3.51)$$

In eq.(3.51), energy is measured from the bottom of conduction band. (Note that $(\mathcal{E} - t_1 + t_2)$ is the unrelaxed energy of the bottom of conduction.) Integrating eq.(3.51), one obtains

$$(\mathcal{E}_p^c + \frac{A}{2}|C_n|^2)|C_n|^2 - t_2/2\left|\frac{dC_n}{dn}\right|^2 = \text{Const.} \qquad (3.52)$$

As discussed by Holstein(18), for localized solution, e.g. $C_n \longrightarrow 0, \left|\frac{dC_n}{dn}\right| \longrightarrow 0$ for $n \to \infty$, it is necessary that the constant in eq.(3.52) equals zero and C_n be all real. C_n therefore satisfy the following eq.

$$\frac{dC_n}{dn} = \pm C_n\left(\frac{2\mathcal{E}_p^c}{t_2} + \frac{A C_n^2}{t_2}\right)^{-1/2} \qquad (3.53)$$

$$C_n = \left(-\frac{2\mathcal{E}_p^c}{A}\right)^{1/2} \mathrm{Sech}\left[\sqrt{\frac{2\mathcal{E}_p^c}{t_2}}\,(n-n_0)\right] \qquad (3.54)$$

From the normalization condition, $\int_{-\infty}^{\infty} C_n^2\,dn = 1$, we have

$$\sqrt{\frac{2\mathcal{E}_p^c}{t_2}} = -\frac{A}{2t_2} = 0.37 \qquad (3.55)$$

$$\mathcal{E}_p^c = \frac{A^2}{8t_2} = -0.033\,eV \qquad (3.56)$$

The polaron radius is 1/0.37 ≅ 3 unit cells. The distribution of that excess electron is shown in Fig.3.6. The polaron binding energy is 0.033ev.

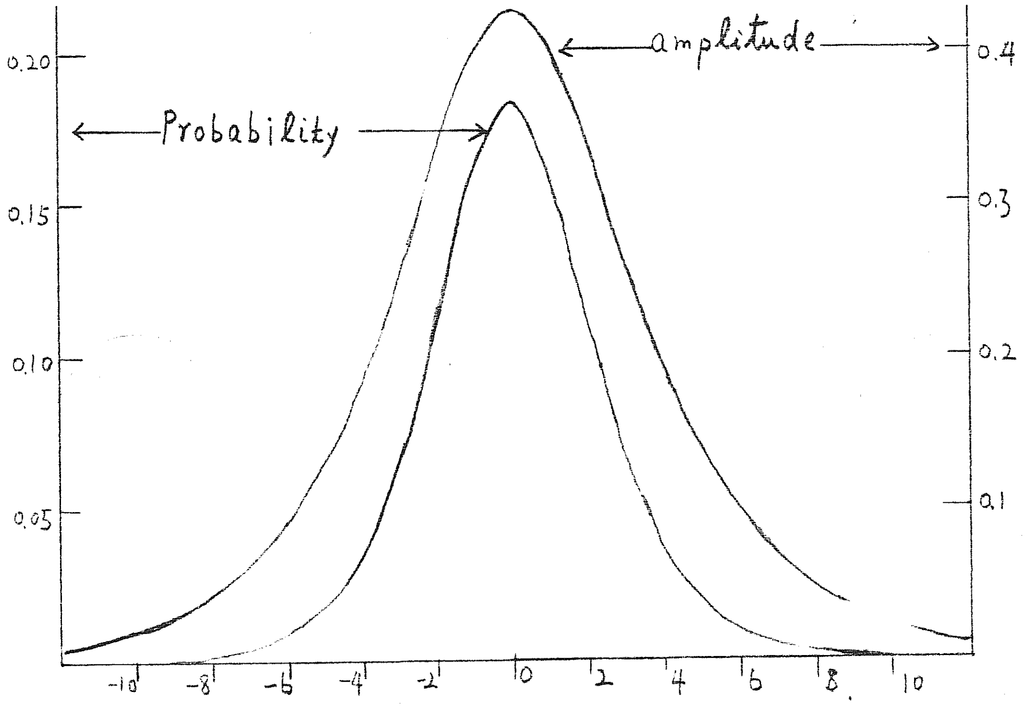


Fig.3.6. Distribution of electron in the electron-polaron.

Note that here we have neglected the changes due to lattice distortion in the elastic energy and in the total valence electron energy. By the lattice distortion (less dimerized) due to the excess electron, we loss some energy in the valence electron energy and at the same time gain some in elastic energy. These two almost cancel each other as can be seen below.

$$\mathcal{E}^{unrel}_{elastic} = \frac{\gamma}{2}\sum_{n,i}(\Delta d_{n,i})^2 = \frac{1}{2\gamma}\sum_{n}\frac{10}{9}(\gamma\Delta d_{n,1})^2 = \frac{5}{9\gamma}\sum_{n}(1.8\beta t_1)^2$$

$$\mathcal{E}^{rel}_{elastic} = \frac{\gamma}{2}\sum_{n,i}(\Delta d^{(e)}_{n,i})^2 = \frac{1}{2\gamma}\sum_{n}\frac{10}{9}(\gamma\Delta d_{n,1})^2 = \frac{5}{9\gamma}\sum_{n}\left[0.9\cdot(2-C_n^2)\beta t_1^{(e)}\right]^2$$

$$= \frac{5}{9\gamma}\sum_{n}(1.8\beta t_1)^2\left[1-(1-\frac{2A}{t_1})C_n^2\right]$$

The change in elastic energy

$$\Delta\mathcal{E}_{elastic} = \mathcal{E}^{unrel}_{elastic} - \mathcal{E}^{rel}_{elastic} = \frac{5}{9\gamma}(1.8\beta t_1)^2\sum_{n}(1-\frac{2A}{t_1})C_n^2$$

$$= 1.8\frac{\beta^2}{\gamma}t_1^2(1-\frac{2A}{t_1}) = 0.72\ eV$$

$$= 2A$$

For the valence electron energy part

$$\mathcal{E}^{unrel}_{v.e} = 2\cdot\sum_{n}(\epsilon + t_1)$$

$$\mathcal{E}^{rel}_{v.e} = 2\cdot\sum_{n}(\epsilon + t_1^{(e)})$$

The change in the v.e. energy

$$\Delta\mathcal{E}_{v.e.} = \mathcal{E}^{unrel}_{v.e} - \mathcal{E}^{rel}_{v.e} = -2\sum_{n}(t_1^{(e)} - t_1) = -2\sum_{n}A C_n^2 = -2A = {}^{-}0.72eV$$

and the total change $\Delta\mathcal{E}_{elastic} + \Delta\mathcal{E}_{v.e} \cong 0$.

3.3.2 Hole-Polaron

A hole in the valence band can be considered as a carrier in the valence band with charge, momentum, spin, effective mass and especially energy as opposite to those of the electron in the same state.

For example, a hole perfectly localized in cell n will have energy $E^h_n = -E^v_n = -\epsilon + t_0\exp(-\beta\Delta d_{n,1})$,

apart from a constant, E^h_n has the same dependence on dimerization parameter $\Delta d_{n,1}$ as conduction Wannier state energy $E^c_n = \epsilon + t_0\exp(-\beta\Delta d_{n,1})$.

Therefore, a hole will have exactly the same effect as a conduction electron has,as far as the electron-lattice coupling is concerned,in our model. As an excess electron in conduction,a hole will not be self-trapped and will spread to the extend of about 3 unit cells with polaron binding energy 0.033ev.

The energy levels of electron-polaron and of hole-polaron are also shown schematically in Fig.3.4.

3.3 EXCITON

When an electron-hole pair is optically created on the surface states,the electron and hole will interact through the screened Coulomb force and bind together to form an exciton.

Denote the creation operators of a conduction electron and that of a hole in Bloch state at wave vector $\vec{k}$ with spin σ by $c^{c+}_{k,\sigma}$ and $d^{+}_{k,\bar{\sigma}}$,respectively,and the corresponding annihilation operators by $c^{c}_{k,\sigma}$ and $d_{k,\bar{\sigma}}$. Neglecting the terms representing interactions between conduction electrons and between holes which are irrelevant in our problem,the Hamiltonian including the screened Coulomb interaction can be expressed as

$$\begin{aligned}\mathcal{H}^{exit} &= \sum_{k,\sigma} E^{c}(\vec{k})\, c^{c+}_{k,\sigma} c_{k,\sigma} + \sum_{k,\sigma}(1 - d^{+}_{k,\sigma} d_{k\sigma}) E^{v}(\vec{k}) - \\ &- \sum_{\substack{k_1,k_2,k_3,k_4\\ \sigma_1,\sigma_2}} W\begin{pmatrix}\vec{k}_1\sigma_1 & \vec{k}_2\sigma_2 & \vec{k}_3\sigma_2 & \vec{k}_4\sigma_1\\ c & v & v & c\end{pmatrix} c^{c+}_{\vec{k}_1,\sigma_1} c^{c}_{\vec{k}_4,\sigma_1} d^{+}_{\vec{k}_3,\bar{\sigma}_2} d_{\vec{k}_2,\bar{\sigma}_2} + \\ &+ \sum_{\substack{k_1,k_2,k_3,k_4\\ \sigma_1,\sigma_2}} W\begin{pmatrix}\vec{k}_1\sigma_1 & \vec{k}_2\sigma_2 & \vec{k}_3\sigma_2 & \vec{k}_4\sigma_1\\ v & c & v & c\end{pmatrix} c^{c+}_{\vec{k}_2,\sigma_2} c^{c}_{k_4,\sigma_1} d^{+}_{k_3,\bar{\sigma}_2} d_{k_1,\bar{\sigma}_1} \qquad (3.57)\end{aligned}$$

Where $E^{c}(k)$ and $E^{v}(k)$ are the Bloch state energies given in eq. (3.3),and

$$W\begin{pmatrix}\vec{k}_1\sigma_1 & \vec{k}_2\sigma_2 & \vec{k}_3\sigma_2 & \vec{k}_4\sigma_1\\ j_1 & j_2 & j_3 & j_4\end{pmatrix} = \int \psi^{(j_1)*}_{\vec{k}_1}(\vec{r}_1)\, \psi^{(j_2)*}_{\vec{k}_2}(\vec{r}_2) \frac{e^2}{\epsilon|\vec{r}_1-\vec{r}_2|} \psi^{(j_3)}_{\vec{k}_3}(\vec{r}_2)\, \psi^{(j_4)}_{\vec{k}_4}(\vec{r}_1)\, d\vec{r}_1 d\vec{r}_2$$

In optical excitation,since we neglect inter-chain hopping the electron and the hole generated will be on the same chain. The generated exciton is a singlet state(total spin=0), $\Psi(k_h,k_e)$,

$$\Psi(\vec{k}_h,\vec{k}_e)=\frac{1}{\sqrt{2}}\left[c^{c+}_{\vec{k}_e,\frac{1}{2}}d^{+}_{\vec{k}_h,-\frac{1}{2}}+c^{c+}_{\vec{k}_e,-\frac{1}{2}}d^{+}_{\vec{k}_h,\frac{1}{2}}\right]|\Phi_0\rangle \tag{3.58}$$

with total momentum $\vec{K}=\vec{k}_e-\vec{k}_h$, which is a good quantum number. As shown in many textbooks(11), the matrx element of H^{exc} exists only between states of the same total momentum, and is given as

$$\begin{aligned}&(\Psi(\vec{k}-\vec{K},\vec{k})|\mathcal{H}^{excit}|\Psi(\vec{k}'-\vec{K},\vec{k}'))\\&=[\mathcal{E}_0+E^c(\vec{k})-E^v(\vec{k}-\vec{K})]\delta_{\vec{k}\vec{k}'}+2W\begin{pmatrix}\vec{k}&\vec{k}'-\vec{K}&\vec{k}'&\vec{k}-\vec{K}\\c&v&c&v\end{pmatrix}-W\begin{pmatrix}\vec{k}&\vec{k}'-\vec{K}&\vec{k}-\vec{K}&\vec{k}'\\c&v&v&c\end{pmatrix}\end{aligned} \tag{3.58}$$

Where $\mathcal{E}_0$ is the energy of the ground state with full valence band and empty conduction band. The Coulomb interaction between Bloch states can be transformed into that between Wannier states

$$\begin{aligned}W\begin{pmatrix}\vec{k}&\vec{k}'-\vec{K}&\vec{k}-\vec{K}&\vec{k}'\\c&v&v&c\end{pmatrix}&=\int\psi^{(c)*}_{\vec{k}}(\vec{r}_1)\psi^{(v)*}_{\vec{k}'-\vec{K}}(\vec{r}_2)\frac{e^2}{\epsilon|\vec{r}_1-\vec{r}_2|}\psi^{(v)}_{\vec{k}-\vec{K}}(\vec{r}_2)\psi^{(c)}_{\vec{k}'}(\vec{r}_1)d\vec{r}_1d\vec{r}_2\\&=\frac{1}{N^2}\sum_{l_1l_2l_3l_4}e^{-i[\vec{k}\cdot\vec{l}_1+(\vec{k}'-\vec{K})\vec{l}_2-(\vec{k}-\vec{K})\cdot\vec{l}_3-\vec{k}'\cdot\vec{l}_4]}\int a^{(c)*}(\vec{r}_1-\vec{l}_1)a^{(v)*}(\vec{r}_2-\vec{l}_2)\frac{e^2}{\epsilon|\vec{r}_1-\vec{r}_2|}a^{(v)}(\vec{r}_2-\vec{l}_3)a^{(c)}(\vec{r}_1-\vec{l}_4)\cdot\\&\qquad\cdot d\vec{r}_1d\vec{r}_2\end{aligned} \tag{3.60}$$

Neglecting the overlap between Wannier functions in different cells, the above equation becomes

$$\begin{aligned}W\begin{pmatrix}\vec{k}&\vec{k}'-\vec{K}&\vec{k}-\vec{K}&\vec{k}'\\c&v&v&c\end{pmatrix}&=\frac{1}{N^2}\sum_{l_1,l_2}e^{-i(\vec{k}-\vec{k}')\cdot(\vec{l}_1-\vec{l}_2)}\int|a^{(c)}(\vec{r}_1-\vec{l}_1)|^2|a^{(v)}(\vec{r}_2-\vec{l}_2)\frac{e^2}{\epsilon|\vec{r}_1-\vec{r}_2|}d\vec{r}_1d\vec{r}_2\\&=\frac{1}{N}\sum_{l}e^{-i(\vec{k}-\vec{k}')\cdot\vec{l}}\int|a^{(c)}(\vec{r}_1-\vec{l})|^2|a^{(v)}(\vec{r}_2)|^2\frac{e^2}{\epsilon|\vec{r}_1-\vec{r}_2|}d\vec{r}_1d\vec{r}_2\\&=\frac{1}{N}\sum_{l}e^{-i(\vec{k}-\vec{k}')\cdot\vec{l}}V(\vec{l})\end{aligned} \tag{3.61}$$

Where $V(\vec{l})$ is the screened Coulomb interaction between electron and hole in the Wannier states separated by $\vec{l}$.

Similarly, the exchange interaction of electron and hole in Bloch states can also be expressed in terms of Wannier states, in neglecting the overlap between different cell's Wannier function, as follows:

$$\begin{aligned}W\begin{pmatrix}\vec{k}&\vec{k}'-\vec{K}&\vec{k}'&\vec{k}-\vec{K}\\c&v&c&v\end{pmatrix}=\frac{1}{N}\Big[&\int a^{(c)*}(\vec{r}_1)a^{(v)}(\vec{r}_1)a^{(v)*}(r_2)a^{(c)}(r_2)\frac{e^2}{\epsilon|\vec{r}_1-\vec{r}_2|}d\vec{r}_1d\vec{r}_2+\\&+\sum_{\vec{l}\neq0}e^{i\vec{K}\cdot\vec{l}}\int a^{(c)*}(\vec{r}_1)a^{(v)}(\vec{r}_1)a^{(v)*}(\vec{r}_2-\vec{l})a^{(c)}(\vec{r}_2-\vec{l})\frac{e^2}{\epsilon|\vec{r}_1-\vec{r}_2|}d\vec{r}_1d\vec{r}_2\end{aligned}$$

$$=\frac{1}{N}\sum_{l} e^{i\vec{K}\cdot\vec{l}}\,X(\vec{l}) \qquad (3.62)$$

$X(\vec{l})$, which is of short range and of small value, is the exchange energy between electron and hole separated by $\vec{l}$.

We are interested in exciton state with total momentum K=0. Putting in K=0, the Coulomb and exchange energy terms then becomes:

$$2W\begin{pmatrix}\vec{k} & \vec{k}' & \vec{k}' & \vec{k}\\ c & v & c & v\end{pmatrix} - W\begin{pmatrix}\vec{k} & \vec{k}' & \vec{k} & \vec{k}'\\ c & v & v & c\end{pmatrix}$$

$$=-\frac{1}{N}\Big[V(0)-2\sum_{l'}X(\vec{l}')+\sum_{l(\neq 0)}e^{-i(\vec{k}-\vec{k}')\cdot\vec{l}}\,V(\vec{l})\Big]$$

$$=-W(\vec{k}-\vec{k}') \qquad (3.63)$$

Where W(k) is the Fourier transform of $V(\vec{l})$ with V(0) modified to $[V(0)-2\sum_{l'}X(\vec{l}')]$.

The exciton wave function with total momentum $\vec{K}=0$, $\Phi(\vec{K}=0)$, can be written in general as the combination of $\Psi(\vec{k},\vec{k})$:

$$\Phi(\vec{K}=0)=\sum_{k}C(\vec{k})\,\Psi(\vec{k},\vec{k}) \qquad (3.64)$$

the coefficients C(k) are to be determined from the set of eqs.:

$$\sum_{k'}\big(\Psi(\vec{k},\vec{k})\big|H^{excit}\big|\Psi(\vec{k}',\vec{k}')\big)C(\vec{k}')=\mathcal{E}\,C(\vec{k})$$

or

$$\big[(\mathcal{E}_0-\mathcal{E}+E^{(c)}(\vec{k})-E^{v}(\vec{k}))\delta_{\vec{k}\vec{k}'}+W(\vec{k}-\vec{k}')\big]C(\vec{k}')=0 \qquad (3.65)$$

It is better for our purpose to represent the exciton wave function in "Exciton representation" which is related to the Bloch state representation by the simple unitary transformation,

$$\Psi(\vec{K},\vec{l})=\frac{1}{\sqrt{N}}\sum_{k}e^{-i\vec{k}\cdot\vec{l}}\,\Psi(\vec{k}-\vec{K},\vec{k}) \qquad (3.66)$$

Then,

$$\Phi(\vec{K}=0)=\sum_{l}d(\vec{l})\,\Psi(\vec{K}=0,\vec{l}) \qquad (3.67)$$

with

$$d(\vec{l})=\frac{1}{\sqrt{N}}\sum_{k}e^{i\vec{k}\cdot\vec{l}}\,c(\vec{k}) \qquad (3.68)$$

Below we calculate first W(k), and then solve eq.(3.65).

$$X(\vec{l})=\int a^{(c)*}(\vec{r}_1)\,a^{(v)}(\vec{r}_1)\,a^{(v)*}(\vec{r}_2-\vec{l})\,a^{(c)}(\vec{r}_2-\vec{l})\frac{e^2}{\epsilon|\vec{r}_1-\vec{r}_2|}\,d\vec{r}_1\,d\vec{r}_2$$

$$
\begin{aligned}
&= \int [-i\alpha\varphi(\vec{r}_1-\vec{R}_{0,1})+i\alpha\varphi(\vec{r}_1-\vec{R}_{0,2})]^{*}[\alpha\varphi(\vec{r}_1-\vec{R}_{0,1}+\alpha\varphi(\vec{r}_1-\vec{R}_{0,2}]\frac{e^2}{\epsilon|r_1-r_2|}\,* \\
&\quad [\alpha\varphi(\vec{r}_2-\vec{R}_{\ell,1})+\alpha\varphi(\vec{r}_2-\vec{R}_{\ell,2})]^{*}[-i\alpha\varphi(\vec{r}_2-\vec{R}_{\ell,1})+i\alpha\varphi(\vec{r}_2-\vec{R}_{\ell,2})]\,d\vec{r}_1\,d\vec{r}_2 \\
&= \alpha^4\int [|\varphi(\vec{r}_1-\vec{R}_{01})|^2|\varphi(\vec{r}_2-\vec{R}_{\ell,1})|^2+|\varphi(\vec{r}_1-\vec{R}_{0,2})|^2|\varphi(\vec{r}_2-\vec{R}_{\ell,2})|^2-|\varphi(r_1-R_{0,1})|^2|\varphi(r_2-R_{\ell,2})|^2- \\
&\qquad -|\varphi(\vec{r}_1-\vec{R}_{0,2})|^2|\varphi(\vec{r}_2-\vec{R}_{\ell,1})|^2]\frac{e^2}{\epsilon|r_1-r_2|}\,d\vec{r}_1\,d\vec{r}_2 \qquad (3.69)
\end{aligned}
$$

It turns out that, for $\vec{\ell} \neq 0$, $X(\vec{\ell})$ is the combination of the Coulomb interactions between atomic orbitals centered at various sites. The atomic orbital of DB is mostly P_z(16). It is mostly $3P_z$ Slater orbital as can be seen from Table 1. Its decay factor is not less than 1.4284 a.u.. While nearest neighbor sites are separated by 3.84 a.u.(2.03A) in dimerized chain model. It is therefore a good approximation to consider the atomic orbitals as point charges centered at each sites as far as inter-site Coulomb interaction is concerned. It is also confirmed by Molecular table tabulated by Kotani et al(12).

For $\vec{\ell}=0$, $X(0)$ is a self-interaction term which we calculate directly using Clementi's atomic data(see Table 1). One point to be pointed out is that the dielectric constant ϵ is taken to be $(\epsilon_{bulk}+1)/2=6$ (5) for inter-site interaction while for intra-site self-interaction, we take $\epsilon=3$ by considering central-cell correction. $X(\vec{\ell})$ is tabulated in Table 4.

ℓ	0	± 1	± 2	$\sum_{\ell} X(\ell)$
$X(\vec{\ell})$ (ev)	1.205	-0.03	-0.008	1.13

Table 4. The exchange energy between electron and hole separated by ℓ.

Similarly, for Coulomb interaction between electron and hole in Wannier states separated by ℓ, $V(\ell)$, we have

$$V(\ell) = \int |a^{(c)}(\vec{r}_1-\vec{\ell})|^2 |a^{(v)}(\vec{r}_2)|^2 \frac{e^2}{\epsilon|\vec{r}_1-\vec{r}_2|}\, d\vec{r}_1\, d\vec{r}_2$$

$$= \alpha^4 \int \Big[|\varphi(r_1-R_{\ell,1})|^2 |\varphi(r_2-R_{0,1})|^2 + |\varphi(r_1-R_{\ell,2})|^2 |\varphi(r_2-R_{0,2})|^2 +$$

$$+ |\varphi(\vec{r}_1-\vec{R}_{\ell,1})|^2 |\varphi(r_2-R_{0,2})|^2 + |\varphi(\vec{r}_1-\vec{R}_{\ell,2})|^2 |\varphi(r_2-R_{01})|^2 \Big] \frac{e^2}{\epsilon|\vec{r}_1-\vec{r}_2|}\, d\vec{r}_1\, d\vec{r}_2 \quad (3.70)$$

We get V(0)= 2.38ev, and $V(0)-2\sum_{\ell} X(\ell)=$ 0.12ev. We plot in Fig. 3.7 the Coulomb and exchange energy in R space $V(\ell)$ (with V(0) replaced by $V(0)-2\sum_{\ell} X(\ell)$).

Solving the Schrödinger eq. (3.65), we obtain C(k) and transform it to $d(\ell)$, which is shown in Fig.3.8, according to eq.(3.68). The exciton binding energy obtained is 0.34ev which is closed to 0.4ev obtained by Del Sole and Tosatti(5).

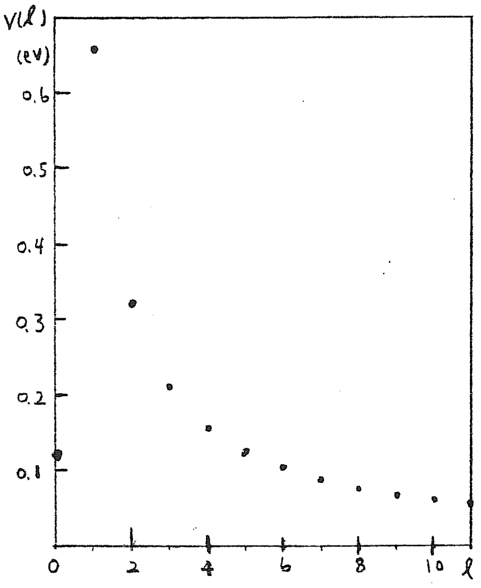


Fig.3.7 The Coulomb and exchange interaction between electron and hole in a singlet state exciton with total momentum K=0.

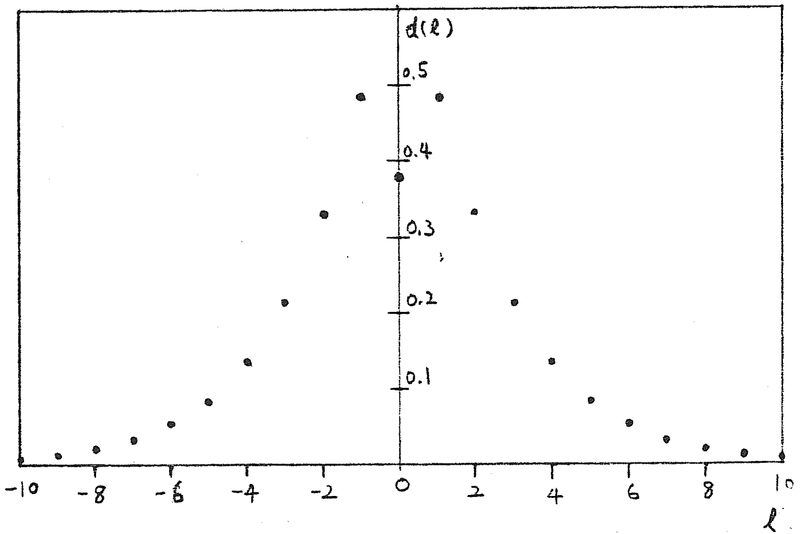


Fig.3.8 The coeffients of the exciton wave function in the " exciton representation".

3.4 EXCITONIC POLARON (tentative)

Unlike the case of the strongly localized exciton in the buckling model,the surface exciton in the chain model is a Wannier exciton which can transfers throughout the chain. The Wannier exciton also interacts with the lattice as the localized excitation does;However,this instantaneous interaction will more or less be averaged out because of the translational motion of the excitation. It can easily be shown that the electon or the hole in the exciton has the same probability to stay in any cell,and thus no local distortion on the lattice occured .Of course,there is still exciton-phonon interaction,as will be derived below.

As shown in sec.3.1,the band gap depends on the dimerization parameters $\Delta d_{n,i}$. If we denote the equilibrium values of the dimerization parameters and the band gap by $\Delta d_{n,1}$, $\Delta d_{n,2}$ and E_g^0,respectively,and denote the variation of $\Delta d_{n,i}$ by $q_{n,i}$,then

$$\begin{aligned} E_g &= 2\,|t_1' - t_2'| = 2\,|t_0 e^{-\beta(\Delta d_{n,1}+q_{n,1})} - t_0 e^{-\beta(\Delta d_{n,2}+q_{n,2})}| \\ &= 2\,|t_1 e^{-\beta q_{n,1}} - t_2 e^{-\beta q_{n,2}}| \cong 2\,|t_1(1-\beta q_{n,1}) - t_2(1-\beta q_{n,2})| \\ &= 2\,|t_1 - t_2 - \beta(t_1 q_{n,1} - t_2 q_{n,2})| = 2\,|t_1 - t_2 - \beta q_{n,1}(t_1 + \tfrac{1}{3}t_2)| \\ &= E_g^0 - 2\beta\,|t_1 + \tfrac{1}{3}t_2| \cdot q_{n,1} \end{aligned}$$

Remember that from the geometry consideration, $q_2 = -\frac{1}{3}q_1$ (see Fig.3.2).

By quantization

$$q_{n,1} = \sqrt{\frac{\hbar}{2N\mu\omega_0}} \sum_{\vec{k}} (b_{\vec{k}} + b^{+}_{-\vec{k}})\, e^{i\vec{k}\cdot\vec{R}_n}$$

Where b_k and b_k^+ are the phonon creation and annihilation operators,respectively; μ is the reduced mass of atoms and equals

M/2,M is the atom mass. Here the optical phonon is assumed to be as Einstein model with frequency ω_0. ω_0 can be determined by the following relation

$$\mu\omega_0^2 = \gamma = \frac{116\,eV}{a^2}$$

and $\hbar\omega_0 = 0.048$ev.

The excitation energy of the exciton with total momentum $\vec{K}$ is

$$\mathcal{E}_{\vec{K}}^{ex} = (E_g^0 - E_b^{ex}) + \frac{\hbar^2K^2}{2m_{ex}} \equiv \mathcal{E}_0^{ex} + \frac{\hbar^2K^2}{2m_{ex}}$$

Where E_b^{ex} =0.34ev,is the exciton binding energy as calculated in sec.3.3. m_{ex} is the exciton mass and $m_{ex} = m_e + m_h = 0.96m_0$,as determined from Luth's electron-energy-loss experiment curve(see sec.3.1).

If we denote the exciton state with total momentum $\vec{K}$ by $|\vec{K}\rangle$,then the exciton-phonon interaction Hamiltonian H' can be expressed as

$$H' = \sum_{\vec{K}\vec{K}'} |\vec{K}\rangle H'_{KK'} \langle\vec{K}'|$$

where $$H'_{kk'} = V_{\vec{K}\vec{K}'}\,(b^+_{-\vec{K}+\vec{K}'} + b_{\vec{K}-\vec{K}'})$$

with $$V_{\vec{K}\vec{K}'} = -2\beta\left|t_1 + \frac{1}{3}t_2\right|\sqrt{\frac{\hbar}{2N\mu\omega_0}} = \frac{-1}{\sqrt{N}}\cdot 0.175\,eV$$

projecting on the subspace of one-electron excitation,the exciton Hamiltonian can be expressed as

$$H_{ex} = \sum_{\vec{K}} |\vec{K}\rangle \mathcal{E}_K^{ex} \langle\vec{K}|$$

and the Hamiltonian of the phonon field is

$$H_L = \sum_{\vec{K}} \hbar\omega_0 b^+_{\vec{K}} b_{\vec{K}}$$

To sum up,the Hamiltonian of the interacting exciton-phonon system can be written as

$$H = H_{ex} + H_L + H'$$

3.5 EXPECTED OPTICAL ABSORPTION LINE SHAPE (tentative)

As derived by Toyozawa(18) with single exciton band assumption, the line shape function of our model will be of the Lorentzian form given by

$$I(E) \propto \frac{\Gamma_0}{(E-\varepsilon_p^{ex}-\Delta_0)^2+\Gamma_0^2}$$

The polaron shift Δ_0 is given by

$$\Delta_0=\sum_{\vec{k}}|V_{\vec{k}0}|^2\left\{[n(\hbar\omega_{-\vec{k}})+1]\frac{P}{\varepsilon_0^{ex}-\varepsilon_{\vec{k}}^{ex}-\hbar\omega_{-\vec{k}}}+n(\hbar\omega_{\vec{k}})\frac{P}{\varepsilon_0^{ex}-\varepsilon_{\vec{k}}^{ex}+\hbar\omega_{\vec{k}}}\right\}$$

Where P stands for the principal part of the integral; $n(\hbar\omega_K)$ $=\frac{1}{e^{\hbar\omega_{\vec{k}}/k_BT}-1}$,is the thermal average number of phonon $\hbar\omega_K$ at temperature T.

Very roughly, we replace the summation over K by $\sum_{\vec{k}}\rightarrow\frac{Na}{2\pi}\int_{-\infty}^{\infty}dk$ (remember that we neglect the inter-chain transfer, so that the problem reduces to the one-dimensional ones), and get

$$\Delta_0=-0.137\cdot\left(\frac{1}{e^{\hbar\omega_0/k_BT}-1}+1\right)\quad eV$$

The polaron shift for various temperature is listed in Table 5.

The half-maximum width is given as

$$2\Gamma_0=2\pi\sum_{\vec{k}}|V_{\vec{k}0}|^2\left\{[n(\hbar\omega_{-\vec{k}})+1]\delta(\varepsilon_0^{ex}-\varepsilon_{\vec{k}}^{ex}-\hbar\omega_{-\vec{k}})+n(\hbar\omega_{\vec{k}})\delta(\varepsilon_0^{ex}-\varepsilon_{\vec{k}}^{ex}+\hbar\omega_{\vec{k}})\right\}$$

By replacing $\sum_{\vec{k}}\longrightarrow\frac{Na}{2\pi}\int_{-\infty}^{\infty}dk$,we get approximately

$$2\Gamma_0=0.274\,\frac{1}{e^{\hbar\omega_0/k_BT}-1}$$

The values of $2\Gamma_0$ at various temperature are also listed in Table 5.

Table 5. The polaron shift Δ_0 and the half-maximum width $2\Gamma_0$ of the absorption spectrum at T= 2K, 150K, 300K, 450K and 600K.

T	2	150	300	450	600
Δ_0(ev)	-0.137	-0.140	-0.163	-0.194	-0.227
$2\Gamma_0$(ev)	0.	0.007	0.051	0.113	0.181

4. DISCUSSIONS,AND OUTLINE OF FUTURE WORK

We can summarize the conclusions of the work done so far as follows:

a) In the buckling model of Si(111)2x1,the electron-polaron, the hole-polaron and the e-h polaron are all small polarons with $S^{e}=4.25$, $S^{h}=6.4$ and $S^{e-h}=6.98$.

b) In the chain model,the electron-lattice coupling is substantially weaker,with electron-polaron binding energy just about 0.033ev.

c) The comparison of the results of the two models with optical absorption experiments at room temperature is not conclusive.

d) The main test should be the study of the temperature-dependent shift of the absorption. In the buckling model,one expect no shift due to polaron effect(though there may of course be a shift due to the thermal lattice relaxation). In the chain model ,we expect a polaron red shift with temperature.

The works in sec.3.4 on excitonic polaron and in sec.3.5 on optical absorption line shape were done tentatively and very roughly. They should be improved by considering multi exciton bands and by doing the summation more precisely. By doing so,it is expected that the energy shift Δ_0 will not be so large in magnitude,the half-maximum width $2\Gamma_0$ will be wider and the line shape obtained will be comparable with experimental curves(2). The same is for the line shape calculation in the buckling model . By using some proper Gaussian to replace the histogram used, the line shape will be more smooth. These works are to be done in the near future.

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APPENDIX A

Dependence of Dangling Bond Orbital and Energy on Vertical Position of Top Atom

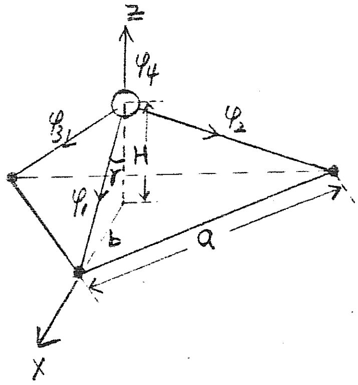

Fig.A1. The circle denotes the top atom, dots denote the second layer atoms. $\varphi_1, \varphi_2, \varphi_3$ are 3 back-bonds. φ_4 is the dangling bond.

As shown in Fig.A1, the 3 back-bonds are directed from the top surface atom to the other 3 second layer atoms underneath it, the dangling bond is directed outward perpendicular to the surface. To maintain the correct bond directions and the orthonormality condition among them, φ_1, φ_2, φ_3 and φ_4, should each be a proper hybridization of $|s\rangle$, $|p_x\rangle$, $|p_y\rangle$ and $|p_z\rangle$ orbitals:

$$\varphi_1 = \alpha_1|s\rangle + \beta_1[\sin\gamma\,|p_x\rangle - \cos\gamma\,|p_z\rangle]$$

$$\varphi_2 = \alpha_1|s\rangle + \beta_1\left[\sin\gamma\left(-\tfrac{1}{2}|p_x\rangle + \tfrac{\sqrt{3}}{2}|p_y\rangle\right) - \cos\gamma\,|p_z\rangle\right]$$

$$\varphi_3 = \alpha_1|s\rangle + \beta_1\left[\sin\gamma\left(-\tfrac{1}{2}|p_x\rangle - \tfrac{\sqrt{3}}{2}|p_y\rangle\right) - \cos\gamma\,|p_z\rangle\right]$$

$$\varphi_4 = \alpha_4|s\rangle + \beta_4\,|p_z\rangle$$

with the normality condition

$$\alpha_1^2 + \beta_1^2 = 1$$

$$\alpha_4^2 + \beta_4^2 = 1$$

and the orthogonality condition

$$\langle\varphi_1|\varphi_2\rangle = 0 = \alpha_1^2 + \beta_1^2\left(-\tfrac{1}{2}\sin^2\gamma + \cos^2\gamma\right)$$

$$\langle\varphi_1|\varphi_4\rangle = 0 = \alpha_1\alpha_4 - \beta_1\beta_4\cos\gamma$$

With the above condition, the remaining orthonormality conditions are automatically satisfied.

It is easy to obtain from the above eqs.

$$\alpha_4 = \sqrt{2}\,\cot\gamma = \sqrt{6}\,\frac{H}{a}$$

$$\beta_4 = \sqrt{1-\alpha_4^2}$$

Denote the atomic Hamiltonian by H^{atom} then

$$H^{atom}|s\rangle = E_s|s\rangle$$

$$H^{atom}|p_z\rangle = E_p|p_z\rangle$$

and the dangling bond orbital energy

$$E_{DB} = \langle\varphi_4|H^{atom}|\varphi_4\rangle = \alpha_4^2\ E_s + \beta_4^2\ E_p$$

$$\doteq E_p - 6(\tfrac{H}{a})^2\ (E_p - E_s)$$

$$= E_p - \tfrac{C}{2}\ (\tfrac{H}{a})^2$$

Where $C = 12\cdot(E_p - E_s)$.

APPENDIX B.

Perturbation Approach for Small Electron-Polaron

The excess conduction electron wave function can be expressed as

$$\psi^{(c)} = \sum_n a_n|n^c\rangle \qquad \text{(B.1)}$$

with normalization condition

$$\sum_n |a_n|^2 = 1 \qquad \text{(B.2)}$$

The one-electron model Hamiltonian is, as given by eq.(2.5),

$$H = \sum_n (|n^{(v)}\rangle E_n^{(v)}\langle n^{(v)}| + |n^{(c)}\rangle E_n^{(c)}\langle n^{(c)}|) + \sum_{n\neq m}[t_{nm}^{(v)}|n^{(v)}\rangle\langle m^{(v)}| + t_{nm}^{(c)}|n^{(c)}\rangle\langle m^{(c)}|] \qquad \text{(B.3)}$$

The schrodinger equation: $H\psi^{(c)} = E\psi^{(c)}$ gives

$$Ea_n = E_n^{(c)}a_n + \sum_{m(\neq n)} t_{nm}^{(c)}\cdot a_m \qquad \text{(B.4)}$$

and

$$E = \sum_n |a_n|^2 E_n^{(c)} + \sum_{n\neq m} t_{nm}^{(c)}\ a_n^*\ a_m \qquad \text{(B.5)}$$

$\{a_n\}$ is the eigenvector of real Hermite matrix and can always be chosen as real.

Assuming $t_{nm}^{(c)}$ small compared to the relevant energy(this is to be justified afterward) and use $a_n^{(i)}, E_n^{c(i)}$ and $E^{(i)}$ to denote the i-th order contribution to a_n, E_n^c and E, respectively, e.g.

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \cdots \tag{B.6}$$

$$E_n^{(c)} = E_n^{(c)(0)} + E_n^{(c)(1)} + E_n^{(c)(2)} + \cdots \tag{B.7}$$

$$a_n = a_n^{(0)} + a_n^{(1)} + a_n^{(2)} + \cdots \tag{B.8}$$

The normalization condition, eq.(B.2), requires:

$$\sum_n a_n^{(0)2} = 1 \tag{B.9}$$

$$\sum_n a_n^{(0)} \cdot a_n^{(1)} = 0 \tag{B.10}$$

$$\sum_n \left(2a_n^{(0)} a_n^{(2)} + a_n^{(1)2}\right) = 0 \tag{B.11}$$

Suppose the excess electron is essentially localized in cell 0, we then start from $a_n^{0} = \delta_{n,0}$, where $\delta_{n,0}$ is the Kronecker delta function.

Eq.(B.10) then gives: $a_0^{(1)} = 0$

Each order of eq.(B.4) can be expressed as

$$(E^{(0)} - E_n^{c(0)}) \cdot a_n^{(0)} = 0 \tag{B.12}$$

$$(E^{(1)} - E_n^{c(1)}) \cdot a_n^{(0)} + (E^{(0)} - E_n^{c(0)}) \cdot a_n^{(1)} = \sum_{m(\neq n)} t_{nm} \cdot a_m^{(0)} \tag{B.13}$$

$$(E^{(2)} - E_n^{c(2)}) \cdot a_n^{(0)} + (E^{(1)} - E_n^{c(1)}) \cdot a_n^{(1)} + (E^{(0)} - E_n^{c(0)}) \cdot a_n^{(2)} = \sum_{m(\neq n)} t_{nm} a_m^{(1)} \tag{B.14}$$

Eq.(B.12), because of $a_n^{(0)} = \delta_{n,0}$, gives $E^{(0)} = E_0^{c(0)}$.

Eq.(B.13), for n=0, gives $E^{(1)} = E_0^{c(1)}$, while for $n \neq 0$, gives

$$a_n^{(1)} = \frac{t_{n,0}}{E^{(0)} - E_n^{c(0)}} = \frac{t_{n,0}}{E_0^{c(0)} - E_n^{c(0)}}$$

Combined with eq.(B.11), we get $a_0^{(2)} = -\frac{1}{2}\sum_n a_n^{(1)2} = -\frac{1}{2}\sum_{n(\neq 0)} \frac{t_{n0}}{E_0^{c(0)} - E_n^{c(0)}}$

Using eq.(B.14) for n=0, $E^{(2)}$ is given by

$$E^{(2)} = E_0^{(c)(2)} + \sum_{m(\neq 0)} \frac{t_{0,m}\, t_{m,0}}{E_0^{c(0)} - E_m^{(c)(0)}}$$

while for $n \neq 0$, we get

$$a_n^{(2)} = \left[\sum_{m(\neq n)} t_{nm} a_m^{(1)} - (E_0^{c(1)} - E_n^{c(1)})\right] \Big/ (E_0^{c(0)} - E_n^{c(0)})$$

E_n^c and its various order contributions can be determined as follows. First minimization of the adiabatic energy

$$\mathcal{E}_{2N+1}^{adia}=\frac{r}{2}\sum_{n,i}(h_{n,i})^2+2\sum_{n}E_n^{v}+\sum_{n}a_n^2 E_n^{c}+\sum_{n\neq m}t_{nm}\,a_n a_m$$

with the normalization condition,eq.(B.2),yields

$$0=\frac{\partial\left(\mathcal{E}_{2N+1}^{adia}+\lambda\sum_{\ell}a_\ell^2\right)}{\partial h_{n,i}}=r h_{n,i}+2\frac{\partial E_n^{v}}{\partial h_{n,i}}+a_n^2\frac{\partial E_n^{c}}{\partial h_{n,i}}+2\sum_{\ell}\Big(E_\ell^{c}a_\ell+\sum_{m(\neq\ell)}t_{m\ell}a_m+\lambda a_\ell\Big)\cdot\frac{\partial a_\ell}{\partial h_{n,i}}$$

$$=r h_{n,i}+2\cdot\frac{\partial E_n^{v}}{\partial h_{n,i}}+a_n^2\frac{\partial E_n^{c}}{\partial h_{n,i}}$$

Where λ is the Lagrange's multiplier and we have made use of eq.(B.4) and eq.(B.2) to eliminate the last summation in the above eq. With E_n^V and E_n^C given in eqs.(2.6) and (2.7),we get

$$h_{n,1}=\frac{c(2\alpha_1^2+a_n^2\alpha_2^2)H_0}{ra^2-c(2\alpha_1^2+a_n^2\alpha_2^2)}=\frac{c\rho_{n,1}}{ra^2-c\rho_{n,1}}H_0$$

$$H_{n,1}=h_{n,1}+H_0=\frac{ra^2}{ra^2-c\rho_{n,1}}H_0$$

$$h_{n,2}=\frac{c(2\alpha_2^2+a_n^2\alpha_1^2)H_0}{ra^2-c(2\alpha_2^2+a_n^2\alpha_1^2)}=\frac{c\rho_{n,2}}{ra^2-c\rho_{n,2}}H_0$$

$$H_{n,2}=h_{n,2}+H_0=\frac{ra^2}{ra^2-c\rho_{n,2}}H_0$$

Where $\rho_{n,1}=2\alpha_1^2+a_n^2\cdot\alpha_2^2$

$\rho_{n,2}=2\alpha_2^2+a_n^2\alpha_1^2$

are the total amount of electrons on DB state of (n,1) and (n,2) atoms,respectively.

a_n^2, $\rho_{n,1}$ and $\rho_{n,2}$ can be expanded as a series of each order contributions

$$a_n^2=(a_n^{(0)2})+(2a_n^{(0)}a_n^{(1)})+(a_n^{(1)2}+2a_n^{(0)}a_n^{(2)})+\cdots$$

$$\rho_{n,1}=(2\alpha_1^2+a_n^{(0)2}\alpha_2^2)+(2a_n^{(0)}a_n^{(1)}\alpha_2^2)+[(a_n^{(1)2}+2a_n^{(0)}a_n^{(2)})\cdot\alpha_2^2]+\cdots$$

$$=\rho_{n,1}^{(0)}+\rho_{n,1}^{(1)}+\rho_{n.2}^{(2)}+\cdots$$

$$\rho_{n,2}=(2\alpha_2^2+a_n^{(0)2}\alpha_1^2)+(2a_n^{(0)}a_n^{(1)}\alpha_1^2)+\alpha_1^2(a_n^{(1)2}+2a_n^{(0)}\cdot a_n^{(2)})+\cdots$$

$$=\rho_{n,2}^{(0)}+\rho_{n,2}^{(1)}+\rho_{n.2}^{(2)}+\cdots$$

Finally,from

$$E_n^{c}=E_p-\frac{c}{2}\alpha_2^2\left(\frac{H_{n,1}}{a}\right)^2-\frac{c}{2}\alpha_1^2\left(\frac{H_{n,2}}{a}\right)^2$$

$$=E_p-\frac{c}{2}\left(\frac{H_0}{a}\right)^2\left[\alpha_2^2\left(\frac{ra^2}{ra^2-c\rho_{n,1}}\right)^2+\alpha_1^2\left(\frac{ra^2}{ra^2-c\rho_{n,2}}\right)^2\right]$$

we get

$$E_n^{c(0)}=E_p-\frac{c}{2}\left(\frac{H_0}{a}\right)^2\left[\alpha_2^2\left(\frac{ra^2}{ra^2-c\rho_{n,1}^{(0)}}\right)^2+\alpha_1^2\left(\frac{ra^2}{ra^2-c\rho_{n,2}^{(0)}}\right)^2\right]$$

$$E_n^{c(1)}=-\frac{c}{2}\left(\frac{H_0}{a}\right)^2\left\{\alpha_2^2\left(\frac{ra^2}{ra^2-c\rho_{n.1}^{(0)}}\right)^2\frac{2c\rho_{n,1}^{(1)}}{(ra^2-c\rho_{n.1}^{(0)})}+\alpha_1^2\left(\frac{ra^2}{ra^2-c\rho_{n,2}^{(0)}}\right)^2\frac{2c\rho_{n,2}^{(1)}}{ra^2-c\rho_{n,2}^{(0)}}\right]$$

$$E_n^{c(2)}=-\frac{c}{2}\left(\frac{H_0}{a}\right)^2\left\{\alpha_2^2\left(\frac{ra^2}{ra^2-c\rho_{n,1}^{(0)}}\right)^2\frac{2c\rho_{n.1}^{(2)}(ra^2-c\rho_{n.1}^{(0)})+3c^2\rho_{n,1}^{(1)2}}{(ra^2-c\rho_{n.1}^{(0)})^2}+\right.$$

$$\left.+\alpha_1^2\left(\frac{ra^2}{ra^2-c\rho_{n.2}^{(0)}}\right)^2\frac{2c\rho_{n.2}^{(2)}(ra^2-c\rho_{n.2}^{(0)})+3c^2\rho_{n,2}^{(1)2}}{(ra^2-c\rho_{n.1}^{(0)})^2}\right\}$$

From the above eqs.,we see

$$E^{(1)}=E_0^{c(1)}=0$$

and $E_0^{c(0)}$ is the energy of the conduction band Wannier state at the cell in which one conduction electron is perfectly localized ,as given by eq.(2.20). While $E_n^{c(0)}$,with $n\neq0$,is just the conduction band Wannier state energy in the ground state,as given by eq.(2.16),

$$E_0^{c(0)}-E_n^{c(0)}=(E_p-1.77\text{ev})-(E_p-1.29\text{ev})$$
$$=-0.48\text{ev}$$

In sec.2.1,we have estimated t=0.05ev. So that

$$\left|\frac{t_{1,0}}{E_0^{c(0)}-E_n^{c(0)}}\right|=0.104$$

This justify our perturbation method for small electron-polaron problem in our buckling model.