

CHAPTER 4

Results on Energy Gap for ZnS_xSe_{1-x} ($0 \leq x \leq 1$): A Simple Theory

4.1 THE SPINLESS $\vec{k}\cdot\vec{p}$ PERTURBATION

Consider the time independent Schrödinger equation,

$$\left(\frac{\hbar^2}{2m_0}\right)\nabla^2\psi + [E - V(r)]\psi = 0 . \quad (4.1)$$

An electron exists in a periodic potential $V(r)$ yields different bands that are separated from each other by an energy gap. The top of the lower band (valence band) is the highest occupied molecular orbital (HOMO) and the bottom of the upper band (conduction band) is the lowest unoccupied molecular orbital (LUMO). The difference in energy HOMO and LOMO is the band gap. For semiconductors the wave functions of the electrons at the band edges within a few $k_B T$ from the LUMO and HOMO extremes are sufficiently described by atomic s and p orbitals [Altarelli, 1985; Bastard, 1981; Bastard and Brum, 1986]. For states slightly away from the LUMO and HOMO extremes the $\vec{k}\cdot\vec{p}$ perturbation theory proves to be a very useful approximation for the wave function of the electron. The $\vec{k}\cdot\vec{p}$ perturbation theory [Kane, 1966; Wang 1966; Nag, 1980] is based on the fact that the cell periodic functions for the electrons for any wave vector \mathbf{k} in different bands form a complete set and the expression of the wave functions for electrons are in terms of the functions for the minima and maxima (i.e., HOMO and LUMO bands).

Consider the wave function for electrons having a value \mathbf{k} near the minima (i.e., in Brillouin zone) in the n^{th} band. For simplicity, the minima is assumed to be located at $\mathbf{k}=0$. The wave function is given by

$$\psi = u_{nk}(\vec{r}) \exp(i\vec{k} \cdot \vec{r}) = \left[\sum_m C_m u_{m0}(\vec{r}) \right] \exp(i\vec{k} \cdot \vec{r}) \quad (4.2)$$

where n is the band index and k is the wave vector, C_m is the coefficient over m where $m = 1, 2, \dots, n$.

Substituting Eqn. (4.2) into Eqn. (4.1) gives

$$\begin{aligned} & \left[-(\hbar^2/2m_0) \nabla^2 + V(\vec{r}) \right] e^{ik \cdot r} u_{nk}(\vec{r}) = E_n(\vec{k}) e^{ik \cdot r} u_{nk}(\vec{r}) \Rightarrow \\ & -(\hbar^2/2m_0) \left[e^{ik \cdot r} \nabla^2 u_{nk}(\vec{r}) + 2i k e^{ik \cdot r} \nabla u_{nk}(\vec{r}) - k^2 e^{ik \cdot r} u_{nk}(\vec{r}) \right] + V(\vec{r}) e^{ik \cdot r} u_{nk}(\vec{r}) \\ & = E_n(\vec{k}) e^{ik \cdot r} u_{nk}(\vec{r}) \end{aligned} \quad (4.3)$$

After factoring out $e^{ik \cdot r}$ and replacing $p = -i\hbar \nabla$ gives

$$\left[-\frac{\hbar^2}{2m_0} \nabla^2 + \frac{\hbar}{m_0} \vec{k} \cdot \vec{p} + \frac{\hbar^2 k^2}{2m_0} + V(\vec{r}) \right] u_{nk}(\vec{r}) = E_n(\vec{k}) u_{nk}(\vec{r}) \quad (4.4)$$

However u_{m0} is the wave function for $k=0$ in the n^{th} band satisfying the equation

$$\left[-\frac{\hbar^2}{2m_0} \nabla^2 + V(\vec{r}) \right] u_{m0}(\vec{r}) = E_m(0) u_{m0}(\vec{r}) \quad (4.5)$$

Substituting Eqn. (4.2) in Eqn. (4.4) and using Eqn. (4.5), the potential energy due to the electron-electron interaction is obtained as

$$\sum C_m \left[E_m(0) + \frac{\hbar^2}{2m_0} k^2 + \frac{\hbar}{m_0} k \cdot p \right] u_{m0}(r) = \sum C_m E_n(k) u_{m0}(r) \quad (4.6)$$

Multiplying both sides of Eqn. (4.5) by $u_{l0}^*(r)$ and integrating over the unit cell (V_c), the following set of linear homogeneous equations is obtained

$$C_l \left[E_n(k) - E_l(0) - \frac{\hbar^2 k^2}{2m_0} \right] - \sum_m C_m \frac{\hbar}{m_0} (k \cdot P_{lm}) = 0 \quad (4.7)$$

where $P_{lm} = \int_{V_c} u_{l0}^*(r) p u_{m0}(r) dr$. By giving l successive integer values one obtains the full set of equations.

In the general case, the set of equations has a non-trivial solution if the determinant of the coefficients is zero, namely if $l=2$ and $m=1, 2$ then $\begin{vmatrix} C_2 & C_1 \\ C_2 & C_2 \end{vmatrix} = 0$ when $C_1=C_2$.

This condition gives the energy eigenvalues $E_n(k)$ in terms of the quantities $E_m(0)$ and P_{lm} . The relative values of the expansion coefficient C_m is then obtained using the values $E_n(k)$. The absolute values of C_m are obtained by imposing normalization condition on the wave function ψ . Therefore, the energy eigenvalues near a characteristic point $k = 0$ can be expressed as

$$E_n(k) = E_n(0) + \frac{\hbar^2 k^2}{2m_0} + \frac{\hbar^2}{m_0^2} \sum'_{l,n} \frac{[k \cdot P_{ln}(0)]^2}{E_n(0) - E_l(0)} \quad (4.8)$$

where the prime at the sum indicates summation overall n and l with $n \neq l$.

The second and third terms in Eqn. (4.4) can be considered as small perturbations in the vicinity of the minima $\mathbf{k} = \mathbf{k}_0 \neq 0$. Therefore, Eqn. (4.4) can be written as

$$\left[-\frac{\hbar^2}{2m_0} \nabla^2 + \frac{\hbar}{m_0} (k - k_0) \cdot P_{ln} + \frac{\hbar^2 (k - k_0)^2}{2m_0} + V(r) \right] u_{nk}(r) = E_n u_{nk}(r) \quad (4.9)$$

and the energy eigenvalue in Eqn.(4.8) near a characteristic point \mathbf{k}_0 can be expressed as

$$E_n(k) = E_n(k_0) + \frac{\hbar^2 (k - k_0)^2}{2m_0} + \frac{\hbar^2}{m_0^2} \sum'_{l,n} \frac{[(k - k_0) \cdot P_{ln}(k_0)]^2}{E_n(k_0) - E_l(k_0)} \quad (4.10)$$

Eqn. (4.10) can be simplified when interactions between only two neighboring bands are of interest (e.g., the valence and conduction bands) and the energy difference between these is small compared to the difference with all other bands. Then

$$E_n(k) = E_n(k_0) + \frac{\hbar^2}{2} \sum_i^3 \frac{(k_i - k_{0i})^2}{m_i^*} \quad (4.11)$$

where $i = x, y, z$, and the effective mass m_i^* can be expressed as [Nag, 1980]

$$\frac{1}{m^*} = \frac{1}{m_0} \pm \frac{2|P_{ln}(k_0)|^2}{m_0^2 [E_n(k_0) - E_l(k_0)]} \quad (4.12)$$

with + or - for the upper or lower band, respectively. Eqn. (4.10) can be rewritten

$$\begin{aligned}
E_n(k) - E_n(k_0) &= -\frac{Eg}{2} + \frac{\hbar^2(k-k_0)^2}{2m_0} + \frac{Eg}{2} + \frac{\hbar^2}{m_0^2} \sum_{l,n} \frac{[(k-k_0) \cdot P_{ln}(k_0)]^2}{E_n(k_0) - E_l(k_0)} \\
&= -\frac{Eg}{2} + \frac{\hbar^2(k-k_0)^2}{2m_0} + \frac{1}{2} \left(Eg + \frac{\hbar^2}{m_0^2} (Eg)^{-1} \sum_{l,n} 2 [(k-k_0) \cdot P_{ln}(k_0)]^2 \right)
\end{aligned} \tag{4.13}$$

since the last term is so small so, the energy $E(k)$ near a critical point k_0 can be written

as

$$E(k-k_0) = -\frac{Eg}{2} + \frac{\hbar^2(k-k_0)^2}{2m_0} \pm \frac{1}{2} \sqrt{Eg^2 \pm \frac{4\hbar^2(k-k_0)^2 |P_{nl}(k_0)|^2}{m_0^2}} \tag{4.14}$$

From Eqn. (4.13), and Eqn. (4.14) can be written as

$$E(k-k_0) = -\frac{Eg}{2} + \frac{\hbar^2(k-k_0)^2}{2m_0} \pm \frac{Eg}{2} \sqrt{1 \pm \frac{2\hbar^2(k-k_0)^2}{Eg} \left(\frac{1}{m^*} - \frac{1}{m_0} \right)} \tag{4.15}$$

with m^* as the effective mass in the conduction (+) or valence (-) band. $Eg = E_c(\mathbf{k}_0) - E_v(\mathbf{k}_0)$ is the band gap energy. This illustrates the usefulness of the \vec{k}, \vec{p} method. If Eqn. (4.14) is written in terms of reduced mass μ^* where $[(\mu^*)^{-1} = (m_c)^{-1} + (m_v)^{-1}]$, and m_c being the effective electron mass at the edge of the conduction band (**CB**) and m_v the effective mass of the heavy hole at the top of the valence band (**VB**) in the absence of any field, then assuming that the conduction band minimum and the valence band maximum are at the zone center, it is possible to write

$$E_c(k) = -\frac{Eg_0}{2} + \frac{\hbar^2 k^2}{2m_0} + \frac{Eg_0}{2} \sqrt{1 + \frac{\hbar^2 k^2}{\mu^* Eg_0}} \quad (4.16)$$

and

$$E_v(k) = -\frac{Eg_0}{2} + \frac{\hbar^2 k^2}{2m_0} - \frac{Eg_0}{2} \sqrt{1 + \frac{\hbar^2 k^2}{\mu^* Eg_0}} \quad (4.17)$$

where Eg_0 is the band gap of a pure binary semiconducting alloy. Using the approximation

$$\frac{1}{\mu^*} \approx 2 \left(\frac{1}{m^*} - \frac{1}{m_0} \right) \quad (4.18)$$

which is deduced from the results given by Abo Hassan *et al.*, [2005a]. Eqn. (4.16) and Eqn. (4.17) give

$$\begin{aligned} E_c(k) - E_v(k) &= Eg_0 \sqrt{1 + \frac{\hbar^2 k^2}{\mu^* Eg_0}} \\ &= Eg_0 \left(1 + \frac{\hbar^2 k^2}{\mu^* Eg_0} \right)^{\frac{1}{2}} \\ &= Eg_0 + \frac{\hbar^2 k^2}{2\mu^*} \end{aligned} \quad (4.19)$$

neglecting higher order terms.

Hence we can write $Eg = Eg_0 + \Delta Eg$ where $\Delta Eg = \frac{\hbar^2 k^2}{2\mu^*}$.

From Abo Hassan *et al.*, [2005a], $\Delta Eg = \frac{2\hbar^2 \pi^2}{\mu^* D^2}$ implying that we may take k as $\frac{2\pi}{D}$

where D is the crystallite diameter. Hence the energy gap may be written as

$$Eg = Eg_0 + \frac{2\hbar^2 \pi^2}{\mu^* D^2} \quad (4.20)$$

From the results reported by Abo Hassan *et al.*, [2005a] as shown below in Table 4.1

TABLE 4.1: Shift in band gap ΔE_g caused by grain size effect and reduce effective mass μ^* for ZnS_xSe_{1-x} ($0 < x < 1$) thin films.

x	μ^*/m_c	E_{g_0} (eV)
0.12	0.14	2.5816
0.34	0.17	2.9514
0.35	0.17	2.9565
0.37	0.17	2.9573
0.41	0.17	2.9865
0.48	0.18	3.0521
0.78	0.22	3.2910
0.80	0.22	3.3023
0.82	0.22	3.3531
0.90	0.23	3.5469
0.96	0.24	3.5197
0.99	0.24	3.7351

the relationship between μ^*/m_c and the unperturbed energy gap E_{g_0} can be written as

$$\frac{\mu^*}{m_c} = (0.124E_{g_0})^{1.76} \quad (4.21)$$

Using the relationship given by Eqn. (4.21)

$$\Delta E_g = \frac{2\hbar^2\pi^2}{m_c D^2 (0.124E_{g_0})^{1.76}} \quad (4.22)$$

Substitute Eqn. (4.21) in Eqn. (4.20) gives

$$E_g = E_{g_0} + \frac{2\hbar^2\pi^2}{m_c D^2 (0.124E_{g_0})^{1.76}} \quad (4.23)$$

Eg_0 according to Abo Hassan *et al.* [2005a] is the energy gap of the stress free crystal. The values of Eg_0 are taken from the results of CASTEP.

4.2 RESULTS

Results for the band gap Eg of the alloys are depicted in Figure 4.1 upon applying the 1.7 correction factor and Figure 4.2 upon applying the 1.66 correction factor for Eg_0 . The theoretical values are compared with the experimental results of Abo Hassan *et al.* [2005a], Larach *et al.* [1957], and Ebina *et al.* [1974]. For $ZnSe$ ($x = 0$), the equation proposed by this work predicts that $Eg = 2.79$ eV. Published experimental works give the Eg for $ZnSe$ as 2.70 eV [Abrikosov *et al.*, 1969], 2.72 eV [Ebina *et al.*, 1974], 2.58 eV reported by Homann *et al.* [2006], and 2.77 eV reported by Swarnker *et al.* [2009]. For the calculation the value of Eg_0 is the band gap value for $ZnSe$ considered in order to find out the value for the energy band gap for $x=0.12$, and using Eqn. (4.23) again to find the energy gap for $x = 0.25$ the substitution of the energy band gap for $x = 0.12$ as Eg_0 was used. Following this procedure the energy band gaps for the remaining values for x were determined. Figure 4.3 shows the difference between the values for energy band gap from this work and the experimental results given by Larach *et al.* [1957] and Abo Hassan *et al.* [2005a]. It can be realized the results given by this work is in reasonable agreement with the experimental results.

The energy gap of the stress free crystal from chapter 3 applying the 1.7 correction factor can be fitted to the equation

$$Eg_0 = 0.4267 x^2 + 0.1905 x + 2.793. \quad (4.24)$$

For $x=1$ the energy gap from our work for ZnS is 3.41 eV. Ebina *et al.* [1974] obtained $E_g(ZnS)$ as 3.70 eV, Van de Walle (1989) 3.78 eV, Homann *et al.* [2006] as 3.68 eV using the linear combination of atomic orbitals (LCAO) method and Swarnkar *et al.* [2009] reported a value of $E_g(ZnS)=3.85$ eV and published results give E_g for ZnS as 3.60 eV [Abrikosov *et al.*, 1969]. The comparison for the results from this work with the results from the literature is shown in Figure 4.3. The D values are obtained from Abo Hassan *et al.*, [2005b] and given in Table 4.2.

Table 4.2: D values for ZnS_xSe_{1-x} [Abo Hassan *et al.*, 2005b].

x	Crystallite Diameter D (m)	x	Crystallite Diameter D (m)
0.12	662×10^{-10}	0.78	250×10^{-10}
0.34	593×10^{-10}	0.8	977×10^{-10}
0.35	383×10^{-10}	0.82	532×10^{-10}
0.37	480×10^{-10}	0.90	285×10^{-10}
0.41	342×10^{-10}	0.96	224×10^{-10}
0.48	158×10^{-10}	0.99	357×10^{-10}

In calculating E_g for ZnS_xSe_{1-x} for $x = 0.12, 0.25, 0.34, 0.35, 0.37, 0.41, 0.48, 0.5, 0.625, 0.75, 0.78, 0.8, 0.82, 0.875, 0.96, 0.99$, the results are listed in Table 4.3 upon applying the 1.7 correction factor and in Table 4.4 upon applying the 1.66 correction factor.

Table 4.3: Energy gap E_g from this work upon applying the 1.7 correction factor.

x	E_g (eV)	x	E_g (eV)
0.12	2.82	0.78	3.2
0.34	2.9	0.80	3.22
0.35	2.91	0.82	3.24
0.37	2.92	0.9	3.31
0.41	2.94	0.96	3.37
0.48	2.98	0.99	3.4

Table 4.4: Energy gap E_g from this work upon applying the 1.66 correction factor.

x	E_g (eV)	x	E_g (eV)
0.12	2.74	0.78	3.08
0.34	2.85	0.80	3.09
0.35	2.86	0.82	3.1
0.37	2.87	0.9	3.15
0.41	2.88	0.96	3.18
0.48	2.92	0.99	3.2

The value of E_g for each composition is calculated from Eqn. (4.23).

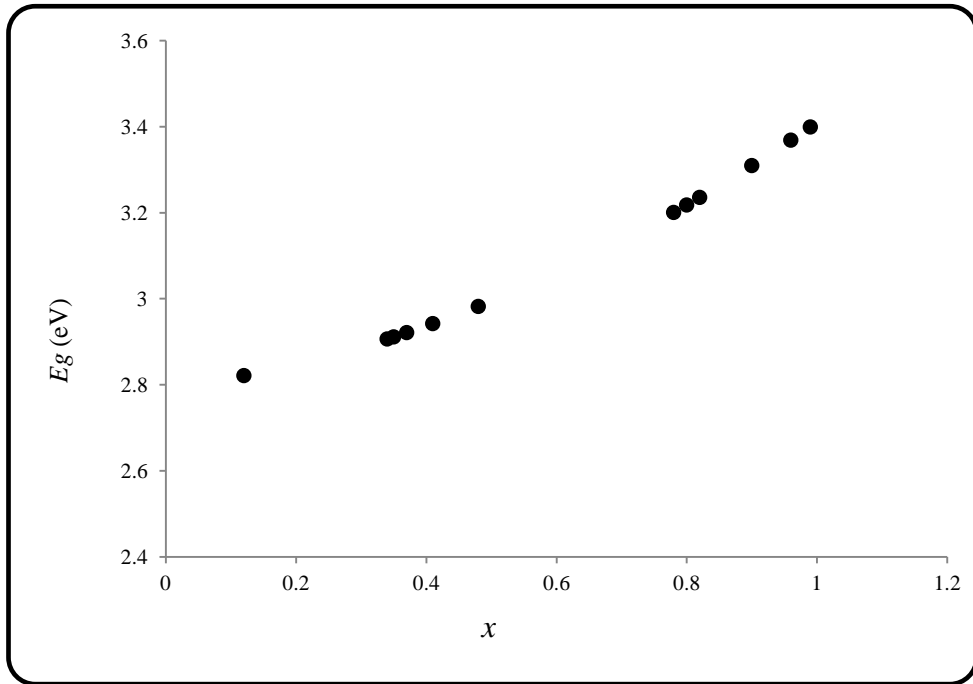


Figure 4.1: E_g as a function of x upon applying the 1.7 correction factor.

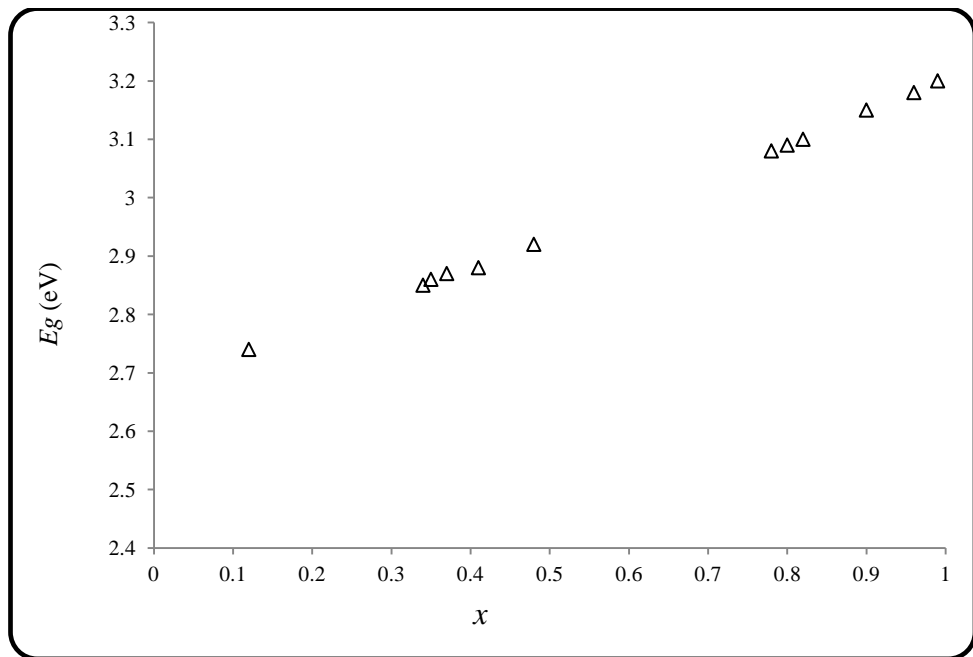


Figure 4.2: E_g as a function of x upon applying the 1.66 correction factor.

Figure 4.3 shows the comparison between results from this work and the results given by Larach *et al.* [1957] and Abo Hassan *et al.* [2005a].

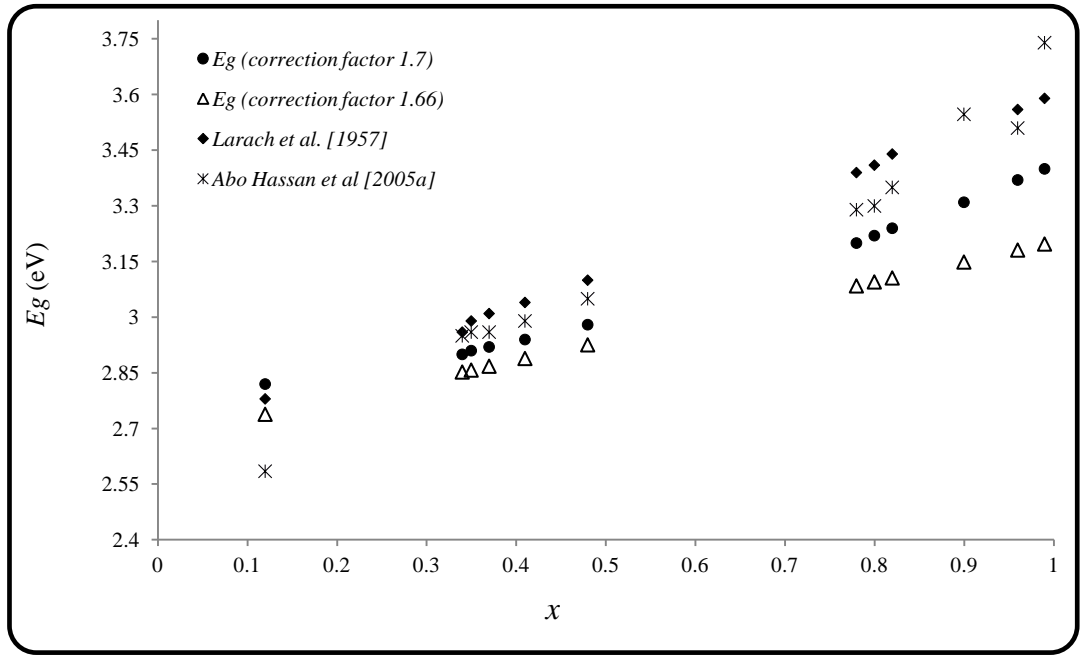


Figure 4.3: E_g as a function of x from Larach *et al.*, [1974], Abo Hassan *et al.*, [2005a], and the results for this work.

4.3 SUMMARY

The theoretical results were presented in Eqn. (4.19)

$$\begin{aligned}
 E_c(k) - E_v(k) &= E_{g_0} \sqrt{1 + \frac{\hbar^2 k^2}{\mu^* E_{g_0}}} \\
 &= E_{g_0} \left(1 + \frac{\hbar^2 k^2}{\mu^* E_{g_0}} \right)^{\frac{1}{2}} \\
 &= E_{g_0} + \frac{\hbar^2 k^2}{2\mu^*}
 \end{aligned}$$

and Eqn. (4.22)

$$E_g = E_{g_0} + \frac{2\hbar^2 \pi^2}{m_c D^2 \left((0.124 E_{g_0})^{1.76} \right)}$$

by using the approximation given in Eqn. (4.18)

$$\frac{1}{\mu^*} \approx 2 \left(\frac{1}{m^*} - \frac{1}{m_0} \right)$$

and the empirical relationship given in Eqn. (4.20)

$$\frac{\mu^*}{m_c} = (0.124 E g_0)^{1.76}.$$

$E g_0$ according to Abo Hassan *et al.*, [2005a] is the energy gap of the stress free crystal, and taken from the results of CASTEP.