Supplemental Problems for Chapter 9

1) Consider a ring of N atoms, where N is a large number. There are two types of atoms (A and B) and they occupy alternate positions along the ring. If one uses the LCAO method, includes one s orbital on each atom, and assumes only nearest neighbor overlaps, the dispersion of states is given by the following equation:

$$\varepsilon = \bar{\varepsilon}_s \pm \sqrt{V_3^2 + 4V_{ss\sigma}^2 \cos^2(ka/2)}$$

where $\bar{\varepsilon}_s$ is the average of the s-electronic energy levels on each atom before the compound is formed, V_3 is the polar energy, a is the periodic repeat distance, k is a wave vector, and $V_{ss\sigma}$ has its usual meaning.
(i) Demonstrate how one arrives at the equation above.
(ii) Describe what happens to the bandgap and bandwidth as the number of atoms (N) gets smaller.
(iii) Use the result given above to explain the following data:

Crystal	Band Gap (eV)
AlN	6.3
GaN	3.37
InN	1.87
GaP	2.25
GaAs	1.43
GaSb	0.7

2) In class, it was shown that for atoms with s-electrons in a two-dimensional square lattice, the dispersion of energy levels is given by:

$$\varepsilon = \varepsilon_s - 2V_2(\cos(\vec{k}\cdot\vec{r}_1) + \cos(\vec{k}\cdot\vec{r}_3)) \quad (1)$$

where $\vec{r}_1$ and $\vec{r}_3$ are vectors directed along the x and y axes, respectively.

(i) Find an analogous relationship for the same atoms in a primitive cubic structure.
(ii) Correct eqn. 1, above, for next nearest neighbor interactions.
(iii) How does the width of the lowest energy band change as the spacing between the atoms shrinks?

3) Ionically bound compounds are often transparent. This property suggests that there is a large gap between the occupied and unoccupied electronic states of the crystal (the "band gap"). Conversely, covalent materials such as Si, Ge, and GaAs are not transparent, suggesting that these materials have a smaller band gap. Within the framework of the LCAO model, explain why the separation of occupied and unoccupied states in an ionic crystal is usually greater than in a covalent crystal.