

Construction of the Hamiltonian Matrix

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This section describes our calculation of the Hamiltonian matrix.

1 Basis

Our lattice vectors are $\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$, $\mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{z}})$, and $\mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}})$ where a is the cubic lattice spacing. The basis consists of a Ga atom located at $\mathbf{0}$ and an As atom at $\mathbf{d}_1 = \frac{a}{4}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$.

The Ga atom's nearest neighbours are at \mathbf{d}_1 , $\mathbf{d}_2 = \frac{a}{4}(\hat{\mathbf{x}} - \hat{\mathbf{y}} - \hat{\mathbf{z}})$, $\mathbf{d}_3 = \frac{a}{4}(-\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$, and $\mathbf{d}_4 = \frac{a}{4}(-\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}})$. The As atom's nearest neighbours are at $\mathbf{0}$, \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 .

We will use the s and p orbitals of the Ga and As atoms in each primitive cell to approximate the crystal wavefunction. We expect these 8 orbitals to play a significant role in bonding.

2 Nearest Neighbour Interactions

The nearest neighbour interactions are

$$\begin{aligned} E_{ss} &= \langle \phi_{sc}(\mathbf{0}) | H | \phi_{sa}(\mathbf{d}_1) \rangle \\ E_{sp} &= \langle \phi_{sc}(\mathbf{0}) | H | \phi_{p_x a}(\mathbf{d}_1) \rangle \\ E_{xx} &= \langle \phi_{p_x c}(\mathbf{0}) | H | \phi_{p_x a}(\mathbf{d}_1) \rangle \\ E_{xy} &= \langle \phi_{p_x c}(\mathbf{0}) | H | \phi_{p_y a}(\mathbf{d}_1) \rangle \end{aligned}$$

where H is the crystal Hamiltonian and ϕ_{ij} is an i type eigenfunction of the Hamiltonian of an isolated atom of type j where $j \in \{\text{anion}, \text{cation}\}$.

These interactions can be simplified to

$$\begin{aligned} E_{ss} &= V_{ss\sigma} \\ E_{sp} &= \frac{1}{\sqrt{3}} V_{sp\sigma} \\ E_{xx} &= \frac{1}{3} V_{pp\sigma} + \frac{2}{3} V_{pp\pi} \\ E_{xy} &= \frac{1}{3} V_{pp\sigma} - \frac{1}{3} V_{pp\pi} \end{aligned}$$

by applying

$$\langle \phi_{s1} | H | \phi_{p2} \rangle = \hat{\mathbf{d}} \cdot \hat{\mathbf{b}} V_{sp\sigma}$$

and

$$\langle \phi_{p1} | H | \phi_{p2} \rangle = (\hat{\mathbf{d}} \cdot \hat{\mathbf{b}}_1)(\hat{\mathbf{d}} \cdot \hat{\mathbf{b}}_2) V_{pp\sigma} + [\hat{\mathbf{b}}_1 - \hat{\mathbf{d}}(\hat{\mathbf{b}}_1 - \hat{\mathbf{d}})] \cdot [\hat{\mathbf{b}}_2 - \hat{\mathbf{d}}(\hat{\mathbf{b}}_2 \cdot \hat{\mathbf{d}})] V_{pp\pi}$$

where $\hat{\mathbf{d}}$ is the unit vector from the atom in the bra to the atom in the ket and $\hat{\mathbf{b}}$ is the unit vector from negative to the positive lobe of the p orbital.

We only need these nearest neighbour interactions listed above because of the symmetry of the crystal.

Thus far, we have assumed that the overlap matrix is the identity matrix. We have also assumed that the atomic wavefunctions of an isolated Ga atom are the same as the atomic wavefunctions of an isolated As atom even though though an As atom has two more protons than a Ga atom. For example, we are assuming that

$$\langle \phi_{sc}(\mathbf{0}) | H | \phi_{p_x a}(\mathbf{d}_1) \rangle = -\langle \phi_{sa}(\mathbf{d}_1) | H | \phi_{p_x a}(\mathbf{0}) \rangle$$

even though one electron atomic wavefunctions depend on the number of protons in the nucleus. For example, the the 1s wavefunction for a one electron atom with Z protons in the nucleus is

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$$

There is nothing wrong with this assumption. We can do a finite basis approximation with whatever basis we wish. Of course, we cannot expect good solutions if our basis set is not close to the actual wavefunctions we are approximating. We expect that our basis set is reasonably good.

Given this assumption, we can say that

$$\langle \phi_{sc}(\mathbf{0}) | H | \phi_{sc}(\mathbf{0}) \rangle = \langle \phi_{sa}(\mathbf{d}_1) | H | \phi_{sa}(\mathbf{d}_1) \rangle$$

3 Hamiltonian Matrix

If we arrange $\vec{\epsilon}$ according to

$$\vec{\epsilon} = \begin{pmatrix} \epsilon_{s1} \\ \epsilon_{p_x1} \\ \epsilon_{p_y1} \\ \epsilon_{p_z1} \\ \epsilon_{s2} \\ \epsilon_{p_x2} \\ \epsilon_{p_y2} \\ \epsilon_{p_z2} \end{pmatrix}$$

where Ga is denoted by a subscript 1 and As is denoted by subscript 2, then the Hamiltonian matrix is

$$\begin{pmatrix} A_1 & B \\ B^* & A_2 \end{pmatrix}$$

where

$$A_i = \begin{pmatrix} E_{si} & 0 & 0 & 0 \\ 0 & E_{pi} & 0 & 0 \\ 0 & 0 & E_{pi} & 0 \\ 0 & 0 & 0 & E_{pi} \end{pmatrix}$$

$$B = \begin{pmatrix} E_{ss}g_0 & E_{sp}g_1 & E_{sp}g_2 & E_{sp}g_3 \\ -E_{sp}g_1 & E_{xx}g_0 & E_{xy}g_3 & E_{xy}g_2 \\ -E_{sp}g_2 & E_{xy}g_3 & E_{xx}g_0 & E_{xy}g_1 \\ -E_{sp}g_3 & E_{xy}g_2 & E_{xy}g_1 & E_{xx}g_0 \end{pmatrix}$$

and

$$\begin{aligned}
g_0 &= 1 + e^{-i\mathbf{k}\cdot\mathbf{R}_2} + e^{-i\mathbf{k}\cdot\mathbf{R}_3} + e^{-i\mathbf{k}\cdot\mathbf{R}_4} \\
g_1 &= 1 + e^{-i\mathbf{k}\cdot\mathbf{R}_2} - e^{-i\mathbf{k}\cdot\mathbf{R}_3} - e^{-i\mathbf{k}\cdot\mathbf{R}_4} \\
g_2 &= 1 - e^{-i\mathbf{k}\cdot\mathbf{R}_2} + e^{-i\mathbf{k}\cdot\mathbf{R}_3} - e^{-i\mathbf{k}\cdot\mathbf{R}_4} \\
g_3 &= 1 - e^{-i\mathbf{k}\cdot\mathbf{R}_2} - e^{-i\mathbf{k}\cdot\mathbf{R}_3} + e^{-i\mathbf{k}\cdot\mathbf{R}_4}
\end{aligned}$$

$$\begin{aligned}
\mathbf{R}_2 &= -\mathbf{a}_1 \\
\mathbf{R}_3 &= -\mathbf{a}_2 \\
\mathbf{R}_4 &= -\mathbf{a}_3
\end{aligned}$$

4 The Hamiltonian at Γ

At Γ , the Hamiltonian matrix is equal to

$$\begin{pmatrix}
E_{s1} & 0 & 0 & 0 & 4E_{ss} & 0 & 0 & 0 \\
0 & E_{p1} & 0 & 0 & 0 & 4E_{xx} & 0 & 0 \\
0 & 0 & E_{p1} & 0 & 0 & 0 & 4E_{xx} & 0 \\
0 & 0 & 0 & E_{p1} & 0 & 0 & 0 & 4E_{xx} \\
4E_{ss} & 0 & 0 & 0 & E_{s2} & 0 & 0 & 0 \\
0 & 4E_{xx} & 0 & 0 & 0 & E_{p2} & 0 & 0 \\
0 & 0 & 4E_{xx} & 0 & 0 & 0 & E_{p2} & 0 \\
0 & 0 & 0 & 4E_{xx} & 0 & 0 & 0 & E_{p2}
\end{pmatrix}$$

with eigenvalues

$$\begin{aligned}
\lambda_{s1} &= \frac{E_{s1} + E_{s2} - \sqrt{E_{s1}^2 - 2E_{s1}E_{s2} + E_{s2}^2 + 64E_{ss}^2}}{2} \\
\lambda_{s2} &= \frac{E_{s1} + E_{s2} + \sqrt{E_{s1}^2 - 2E_{s1}E_{s2} + E_{s2}^2 + 64E_{ss}^2}}{2} \\
\lambda_{p1} &= \frac{E_{p1} + E_{p2} - \sqrt{E_{p1}^2 - 2E_{p1}E_{p2} + E_{p2}^2 + 64E_{xx}^2}}{2} \\
\lambda_{p2} &= \frac{E_{p1} + E_{p2} + \sqrt{E_{p1}^2 - 2E_{p1}E_{p2} + E_{p2}^2 + 64E_{xx}^2}}{2}
\end{aligned}$$

λ_{p1} and λ_{p2} both have a degeneracy of 3. The corresponding eigenvectors are

$$\vec{\epsilon}_{s1} = \begin{pmatrix} \frac{-(-E_{s1} + E_{s2} + \sqrt{E_{s1}^2 - 2E_{s1}E_{s2} + E_{s2}^2 + 64E_{ss}^2})}{8E_{ss}} \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\begin{aligned}
\vec{\epsilon}_{s2} &= \begin{pmatrix} \frac{-(-E_{s1}+E_{s2}-\sqrt{E_{s1}^2-2E_{s1}E_{s2}+E_{s2}^2+64E_{ss}^2})}{8E_{ss}} \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \\
\vec{\epsilon}_{p_x1} &= \begin{pmatrix} 0 \\ \frac{-(-E_{p1}+E_{p2}+\sqrt{E_{p1}^2-2E_{p1}E_{p2}+E_{p2}^2+64E_{xx}^2})}{8E_{xx}} \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \\
\vec{\epsilon}_{p_x2} &= \begin{pmatrix} 0 \\ \frac{-(-E_{p1}+E_{p2}-\sqrt{E_{p1}^2-2E_{p1}E_{p2}+E_{p2}^2+64E_{xx}^2})}{8E_{xx}} \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}
\end{aligned}$$

We have not listed the p_y, p_z orbitals to save space but they are similar.

The low energy $\vec{\epsilon}_{s1}$ wavefunction corresponds to s wavefunctions which are in phase from unit cell to unit cell. The high energy $\vec{\epsilon}_{s2}$ wavefunction corresponds to s wavefunctions which are out of phase from unit cell to unit cell. Similarly with $\vec{\epsilon}_{p_x1}$ and $\vec{\epsilon}_{p_x2}$.

Putting numbers in for the eigenvalues yields values in eV of

$$\begin{aligned}
\lambda_{s1} &= -12.5325 \\
\lambda_{s2} &= 0 \\
\lambda_{p1} &= 2.9065 \\
\lambda_{p2} &= 6.2640
\end{aligned}$$

which are in fair agreement with literature values from Harrison's text:

$$\begin{aligned}
\lambda_{s1} &\approx -12.6 \\
\lambda_{s2} &\approx 0 \\
\lambda_{p1} &\approx 2.3 \\
\lambda_{p2} &\approx 4.7
\end{aligned}$$