1 Bloch's theorem and an atomic orbital basis set (1s and 2s forming the basis)

Bloch's theorem states that

$$\psi(x+a) = e^{ika}\psi(x) \tag{1}$$

To talk about Bloch functions we need to first recognize that the types of atomic arrangements that we will be working with are infinite in extent, and perfectly periodic in nature. In other words, the atomic locations repeat themselves over and over again, with no variablity from one repeating unit to the next. With this in mind, we can state Bloch's theorem in words: The electronic wave function in one repeating unit can differ from the wavefunction in the adjacent repeating unit by no more than the multiplicative factor e^ika, where a is the distance between repeating units.

Let's consider an infinite one-dimensional chain of atoms, with spacing a. The first atom is located at d and subsequent atoms are located at $a + md$, where m is an integer. First, we must choose a basis with which to expand the wavefunction. For our case, we will use a basis consisting of a 1s orbital and a 2s orbital. Using this basis to expand the wavefunction gives:

$$|\psi\rangle = \sum_m \sum_n e^{ikx_m} c_n |mn\rangle \tag{2}$$

The index m indicates which atom the orbital is centered on, the index n indicates which type of orbital is centered there, and x_m is the location of the atom under consideration. The e^{ikx_m} term comes from Bloch's theorem. It is there to ensure that if we move to an atom in another repeating unit, we multiply the wavefunction by the term dictated by Bloch's theorem. Let's plug this expansion into the time-independent Schrodinger equation:

$$\mathbf{H}\sum_m \sum_n e^{ikx_m} c_n |mn\rangle = E\sum_m \sum_n e^{ikma} c_n |mn\rangle \tag{3}$$

Now, let's project onto the $|0n'\rangle$ state:

$$\sum_m \sum_n e^{ikx_m} c_n \langle 0n'|\mathbf{H}|mn\rangle = E\sum_m \sum_n e^{ikx_m} \langle 0n'|c_n|mn\rangle \tag{4}$$

The double sum on the right hand side collapses to one term, the term where $n' = n'$. On the left hand side, many terms are zero, but not all. We'll assume the nearest-neighbor hopping integrals are nonzero, but next-nearest neighbor hopping integrals are zero. This means that the terms on the left hand side are nonzero for $m = 0$ and $m = 1$ only. That's nice since we didn't want to have to sum over an infinite array of atoms right? Let's write out all of the terms explicitly to help you see:

$$e^{ikd}c_{1s}\langle 0,1s|\mathbf{H}|0,1s\rangle+e^{ikd}c_{2s}\langle 01s|\mathbf{H}|0,2s\rangle+e^{ik(d+a)}c_{1s}\langle 0,1s|\mathbf{H}|1,1s\rangle+e^{ik(d+a)}c_{2s}\langle 0,1s|\mathbf{H}|1,2s\rangle \tag{5}$$

Hopefully you can see the first row in a matrix here.

$$\begin{bmatrix} e^{ikd}\langle 0,1s|\mathbf{H}|0,1s\rangle + e^{ik(a+d)}\langle 0,1s|\mathbf{H}|1,1s\rangle & e^{ikd}\langle 01s|\mathbf{H}|0,2s\rangle + e^{ik(a+d)}\langle 0,1s|\mathbf{H}|1,2s\rangle \\ \cdots & \\ \cdots & \end{bmatrix} \begin{bmatrix} c_{1s} \\ c_{2s} \end{bmatrix} \tag{6}$$

We can find the second row by projecting onto the $|0,2s\rangle$ state. The Hamiltonian matrix becomes:

$$\begin{bmatrix} e^{ikd}\langle 0,1s|\mathbf{H}|0,1s\rangle + e^{ik(a+d)}\langle 0,1s|\mathbf{H}|1,1s\rangle & e^{ikd}\langle 01s|\mathbf{H}|0,2s\rangle + e^{ik(a+d)}\langle 0,1s|\mathbf{H}|1,2s\rangle \\ e^{ikd}\langle 0,2s|\mathbf{H}|0,1s\rangle + e^{ik(a+d)}\langle 0,2s|\mathbf{H}|1,1s\rangle & e^{ikd}\langle 02s|\mathbf{H}|0,2s\rangle + e^{ik(a+d)}\langle 0,2s|\mathbf{H}|1,2s\rangle \end{bmatrix} \begin{bmatrix} c_{1s} \\ c_{2s} \end{bmatrix} = E \begin{bmatrix} c_{1s} \\ c_{2s} \end{bmatrix} \tag{7}$$