

Tight Binding Approximation to Electronic Bandstructure

We now take a very different approach to energy band structure, relative to that seen in the *nearly free electron approximation*. We recognize that the low lying core levels of a free atom are strongly localized in space. When free atoms are brought together, the core electronic levels *remain strongly localized*, and thus we don't anticipate large changes in the energy eigenstates as we go from atom to solid. Thus we might expect that the *electronic wavefunction in the solid* can be expressed as a superposition of atomic wavefunctions, or *linear combination of atomic orbitals* (LCAO) as it is often termed.

Let's begin by assuming that solutions for the *atomic* eigenstates and eigenfunctions, i.e., the solutions to

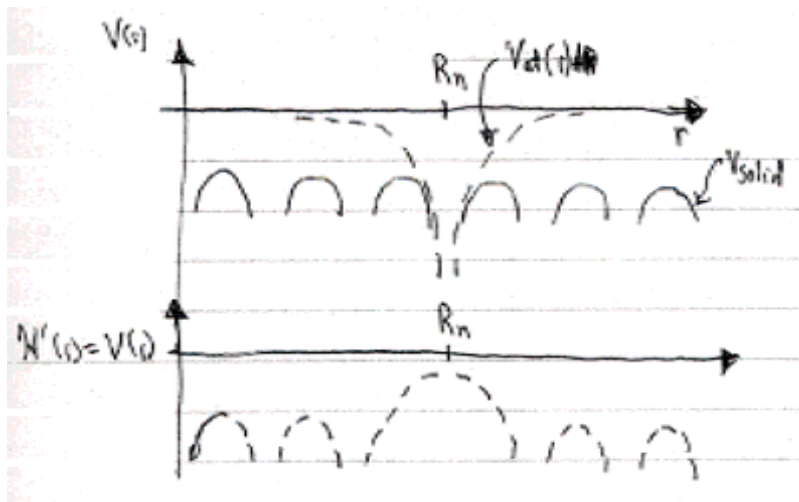
$$\mathcal{H}_{\text{at}}(\mathbf{r} - \mathbf{R}_n)\phi_i(\mathbf{r} - \mathbf{R}_n) = \mathcal{E}_i\phi_i(\mathbf{r} - \mathbf{R}_n)$$

are known. We then assume that these *atoms form a solid* where the atoms are arranged on a lattice with lattice vectors \mathbf{R}_n . The total potential of this Hamiltonian, which is the Hamiltonian of the solid expressed as a perturbed atomic Hamiltonian,

$$\mathcal{H}_{\text{solid}} = \mathcal{H}_{\text{at}} + \mathcal{H}' = -\frac{\hbar^2}{2m}\nabla^2 + V_{\text{at}}(\mathbf{r} - \mathbf{R}_n) + \mathcal{H}'(\mathbf{r} - \mathbf{R}_n)$$

The perturbation \mathcal{H}' is in this case the *difference between the atomic potential and the crystalline solid potential*. For an atom localized at \mathbf{R}_n ,

$$\mathcal{H}'(\mathbf{r} - \mathbf{R}_n) = \sum_{m \neq n} V_{\text{at}}(\mathbf{r} - \mathbf{R}_m)$$



Of course, what we ultimately seek are solutions to the Schrodinger equation in a crystalline solid which are Bloch waves, $\psi_{\mathbf{k}}(\mathbf{r})$, so that

$$\mathcal{H}_{\text{solid}}\psi_{\mathbf{k}}(\mathbf{r}) = \mathcal{E}(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r})$$

But multiplying by $\psi_{\mathbf{k}}^*$ and integrating yields $\mathcal{E}(\mathbf{k})$

$$\mathcal{E}(\mathbf{k}) = \frac{\int \psi_{\mathbf{k}}^* \mathcal{H}_{\text{solid}} \psi_{\mathbf{k}} d^3 r}{\int \psi_{\mathbf{k}}^* \psi_{\mathbf{k}} d^3 r}$$

The *variational principle* states that if one uses instead of the true wavefunction $\psi_{\mathbf{k}}$, a *trial wavefunction* $\phi_{\mathbf{k}}$, then one obtains an approximate energy $\mathcal{E}'(\mathbf{k})$ that is always *bigger than* $\mathcal{E}(\mathbf{k})$. IN this case, we try as an approximation solution a linear combination of atomic eigenfunctions

$$\psi_{\mathbf{k}} \simeq \phi_{\mathbf{k}} = \sum_n a_n \phi_i(\mathbf{r} - \mathbf{R}_n)$$

where the coefficient a_n are chosen so as to construct a Bloch wave:

$$a_n = e^{i\mathbf{k} \cdot \mathbf{R}_n}$$

This can be seen by noting

$$\phi_{\mathbf{k}+\mathbf{G}} = \sum_n e^{i\mathbf{k} \cdot \mathbf{R}_n} \underbrace{e^{i\mathbf{G} \cdot \mathbf{R}_n}}_1 \phi_i(\mathbf{r} - \mathbf{R}_n) = \phi_{\mathbf{k}}$$

Now let's find $\mathcal{E}'(\mathbf{k})$

$$\mathcal{E}'(\mathbf{k}) = \frac{\int \phi_{\mathbf{k}}^* \mathcal{H}_{\text{solid}} \phi_{\mathbf{k}} d^3 r}{\int \phi_{\mathbf{k}}^* \phi_{\mathbf{k}} d^3 r}$$

The denominator is:

$$\int \phi_{\mathbf{k}}^* \phi_{\mathbf{k}} d^3 r = \sum_{n,m} e^{i\mathbf{k} \cdot (\mathbf{R}_n - \mathbf{R}_m)} \int \phi_i^*(\mathbf{r} - \mathbf{R}_m) \phi_i(\mathbf{r} - \mathbf{R}_n) d^3 r$$

We now make our first physical approximation: we note that $\phi_i(\mathbf{r} - \mathbf{R}_n)$ only has significant value near \mathbf{R}_m ; thus we only retain terms with $n = m$, so

$$\int \phi_{\mathbf{k}}^* \phi_{\mathbf{k}} d^3 r = \sum_n \phi_i^*(\mathbf{r} - \mathbf{R}_n) \phi_i(\mathbf{r} - \mathbf{R}_n) d^3 r = N$$

where N is the number of atoms in the solids. Since we already know the atomic eigenstate \mathcal{E}_i , we write

$$\mathcal{E}(\mathbf{k}) \simeq \mathcal{E}'(\mathbf{k}) = \frac{1}{N} \sum_{n,m} e^{i\mathbf{k} \cdot (\mathbf{R}_n - \mathbf{R}_m)} \int \phi_i^*(\mathbf{r} - \mathbf{R}_m) [\mathcal{E}_i + \mathcal{H}'(\mathbf{r} - \mathbf{R}_n)] \phi_i(\mathbf{r} - \mathbf{R}_n) d^3 r$$

where in the sums on n, m to form \mathcal{H}' we sum over nearest neighbors for simplicity, and as before, for the term in \mathcal{E}_i nearest neighbor overlap is neglected.