The Tight-Binding Model

Previously, we have treated nearly free electrons subject to a *weak* periodic potential. The *tight-binding model* deals with the opposite limit in which the wave function is close to that of the atomic wave function, but there is enough overlap of the atomic wave functions that corrections to the picture of isolated atoms are required. The approximation is most useful for describing the <u>energy bands that arise from the low-lying core states</u>, partially filled d-shells of transition metal atoms and for describing the electronic structure of insulators.
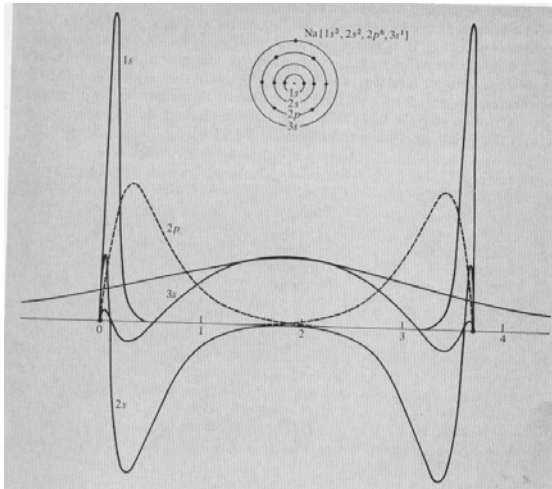

Fig. 6.1 (from A&M) Calculated electron wave functions for the levels of atomic sodium, plotted about two nuclei separated by the nearest-neighbor distance in metallic sodium, 3.7 Å. The solid curves are $r\psi(r)$ for the 1s, 2s, and 3s levels. The dashed curve is r times the radial wave function for the 2p levels. Note how the 3s curves overlap extensively, the 2s and 2p curves overlap only a little, and the 1s curves have essentially no overlap. The scale on the r-axis is in Å.

6.1 General Formulation

Denote the single atom Hamiltonian by H_{at} and a bound state eigenfunction by ψ_n and the corresponding energy eigen value by E_n:

$$H_{at}\psi_n = E_n\psi_n. \tag{6.1}$$

We suppose that $\psi_n(\mathbf{r})$ is small when r exceeds a distance of the order of the lattice constant. Further, we denote the full crystal Hamiltonian by H, and suppose that it begins to differ from H_{at} only in regions far removed from the lattice point where $\psi_n(\mathbf{r}) \approx 0$. Then the atomic wave function, $\psi_n(\mathbf{r})$, will be an excellent approximation to the actual crystal wave function, $\psi(\mathbf{r})$. We denote the actual crystal energy eigenvalue problem by:
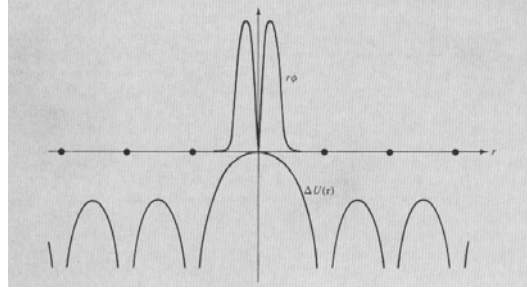
$$H\psi(\mathbf{r}) = \varepsilon_k\psi(\mathbf{r}),$$

To find the corrections, writes H as:

$$H = H_{at} + \Delta U(\mathbf{r}), \tag{6.2}$$

where $\Delta U(\mathbf{r})$ contains all the corrections required to produce the full periodic potential of the crystal (see Figure 6.2). Given our assumptions, $\Delta U(\mathbf{r}) \approx 0$ where $\psi_n(\mathbf{r})$ is not and vice

The Tight-Binding Model

Fig. 6.2 (from A&M)
The lower curve depicts the function $\Delta U(\mathbf{r})$ drawn along a line of atomic sites. When $\Delta U(\mathbf{r})$ is added to a single atomic potential localized at the origin, the full periodic potential $U(\mathbf{r})$ is recovered. The upper curve represents r times an atomic wave function localized at the origin. When $r\phi(\mathbf{r})$ is large, $\Delta U(\mathbf{r})$ is small, and vice versa.

versa, and $\varepsilon \approx E_n$ and $\psi(\mathbf{r}) \approx \psi_n(\mathbf{r})$. If so, each atomic level $\psi_n(\mathbf{r})$ should lead to N levels in the periodic potentials, with the corresponding N wave functions being approximately just $\psi_n(\mathbf{r} - \mathbf{R})$, the atomic wave function at each of the N sites $\mathbf{R}$ in the lattice. As discussed before, $\psi(\mathbf{r})$ must fulfill the Bloch theorem: $\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r})$. Consider the following wavefunction:

$$\psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \psi_n(\vec{r} - \vec{R}), \tag{6.3}$$

where $\mathbf{k}$ takes on the N values in the first Brillouin zone as discussed before. The Bloch condition is verified for the wave functions (6.3) by noting that

$$
\begin{aligned}
\psi(\mathbf{r} + \mathbf{R}) &= \sum_{\mathbf{R}'} e^{i\mathbf{k}\cdot\mathbf{R}'}\psi_n(\mathbf{r} + \mathbf{R} - \mathbf{R}') \\
&= e^{i\mathbf{k}\cdot\mathbf{R}}\left[\sum_{\mathbf{R}'} e^{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})}\psi_n(\mathbf{r} - (\mathbf{R}' - \mathbf{R}))\right] \\
&= e^{i\mathbf{k}\cdot\mathbf{R}}\left[\sum_{\overline{\mathbf{R}}} e^{i\mathbf{k}\cdot\overline{\mathbf{R}}}\psi_n(\mathbf{r} - \overline{\mathbf{R}})\right] \\
&= e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r}).
\end{aligned}
\tag{6.4}
$$

Let's adopt a more general form of the wavefunction as follows:

$$\psi(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \phi(\vec{r} - \vec{R}), \tag{6.5}$$

with $\phi(\mathbf{r} - \mathbf{R})$ being a general function to be determined. Because of the requirement that $\Delta U(\mathbf{r})\phi(\mathbf{r} - \mathbf{R}) \approx 0$ except near $\mathbf{r} = \mathbf{R}$, we still expect $\phi(\mathbf{r} - \mathbf{R}) \approx \psi_n(\mathbf{r} - \mathbf{R})$ or those that are degenerate with it. It is then natural to seek for $\phi(\mathbf{r})$ that can be expanded in a small number of localized atomic wave functions:

$$\phi(\mathbf{r}) = \sum_n b_n \psi_n(\mathbf{r}). \tag{6.6}$$

The Tight-Binding Model

Recall that the crystal Schrödinger equation is

$$H\psi(\mathbf{r}) = (H_{at} + \Delta U(\mathbf{r}))\psi(\mathbf{r}) = \varepsilon(\mathbf{k})\psi(\mathbf{r}). \tag{6.7}$$

Now multiply eqn. 6.7 by the atomic wavefunction $\psi_m^*(\mathbf{r})$, integrate over all $\mathbf{r}$, and use the fact that

$$\int \psi_m^*(\mathbf{r})H_{at}\psi(\mathbf{r})\, d\mathbf{r} = \int (H_{at}\psi_m(\mathbf{r}))^*\psi(\mathbf{r})\, d\mathbf{r} = E_m \int \psi_m^*(\mathbf{r})\psi(\mathbf{r})\, d\mathbf{r}, \tag{6.8}$$

one then obtains

$$(\varepsilon(\mathbf{k}) - E_m)\int \psi_m^*(\mathbf{r})\psi(\mathbf{r})\, d\mathbf{r} = \int \psi_m^*(\mathbf{r})\, \Delta U(\mathbf{r})\psi(\mathbf{r})\, d\mathbf{r}. \tag{6.9}$$

By substituting Eqns. 6.5 and 6.6 in Eqn. 6.9, separating the $\mathbf{R} = 0$ terms from the $\mathbf{R} \neq 0$ terms, and using the orthonormality relation of the atomic wave functions,

i.e,
$$\int \psi_m^*(\mathbf{r})\psi_n(\mathbf{r})\, d\mathbf{r} = \delta_{nm}, \tag{6.10}$$

one obtains:

$$
\begin{aligned}
(\varepsilon(\mathbf{k}) - E_m)b_m = &-(\varepsilon(\mathbf{k}) - E_m)\sum_n \left(\sum_{\mathbf{R}\neq 0}\int \psi_m^*(\mathbf{r})\psi_n(\mathbf{r} - \mathbf{R})e^{i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{r}\right)b_n \\
&+ \sum_n \left(\int \psi_m^*(\mathbf{r})\,\Delta U(\mathbf{r})\psi_n(\mathbf{r})\, d\mathbf{r}\right)b_n \\
&+ \sum_n \left(\sum_{\mathbf{R}\neq 0}\int \psi_m^*(\mathbf{r})\,\Delta U(\mathbf{r})\psi_n(\mathbf{r} - \mathbf{R})\,e^{i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{r}\right)b_n.
\end{aligned} \tag{6.11}
$$

The first term on the RHS of Eqn. 6.11 contains integrals of the form

$$\int d\mathbf{r}\, \psi_m^*(\mathbf{r})\psi_n(\mathbf{r} - \mathbf{R}). \tag{6.12}$$

Due to the assumption that the atomic wave functions are localized, the above integral is $\ll 1$. Similarly, the other two terms on the RHS of Eqn. 6.11 should be $\ll 1$ as well. As a result, the RHS of Eqn. 6.11 and hence $(\varepsilon(\mathbf{k}) - E_m)b_m$ is always small. This is possible if

$$\varepsilon(\mathbf{k}) \approx E_0, \quad b_m \approx 0 \text{ unless } E_m \approx E_0. \tag{6.13}$$

where E_0 is an atomic energy level. This conclusion allows us to greatly reduce the sum of Eqn. 6.11 to those states where $\varepsilon(\mathbf{k}) = E_0$, and hence degenerate. If the atomic level corresponding to E_0 is non-degenerate, such as for an s-level, then Eqn. 6.11 reduces to a single equation giving an explicit expression for the energy of the band arising from this

The Tight-Binding Model

s-level. For bands arising from an atomic *p*-level, which is triply degenerate, Eqn. 6.11 gives a set of three homogeneous equations, whose eigenvalues give the $\varepsilon(\mathbf{k})$ for the three *p*-bands, and whose solutions $b(\mathbf{k})$ give the appropriate linear combinations of the atomic *p*-levels making up ϕ at the various $\mathbf{k}$'s in the Brillouin zone. This works similarly for the five *d*-bands. If the resultant eigenvalues $\varepsilon(\mathbf{k})$ turn out to be close to the energy of another atomic level, one may need to redo the calculation to include the terms involving wave functions of or degenerate with this other atomic level. This "hybridization" is often needed in calculating the band structure of transition metals, involving both the *s*- and *d*-levels.

6.2 Bands Arising From a Single Atomic s-Level

We apply the above formulation to the simplest example, i.e., calculation of an *s*-band. From the above discussion, all the coefficients b_n in Eqn. 6.11 are zero except for the single atomic *s*-level of concern. Equation 6.11 becomes:

$$\varepsilon(\vec{k}) - E_0 = -(\varepsilon(\vec{k}) - E_0) \underset{\vec{R} \neq 0}{\sum} e^{i\vec{k}\cdot\vec{R}} \underbrace{\int \psi_0^*(\vec{r}) \psi_0(\vec{r}-\vec{R}) d^3r}_{\alpha(\vec{R})}$$

$$+ \underbrace{\int \psi_0^*(\vec{r}) \Delta u(\vec{r}) \psi_n(\vec{r}) d^3r}_{-\beta} + \underset{\vec{R} \neq 0}{\sum} e^{i\vec{k}\cdot\vec{R}} \underbrace{\int \psi_0^*(\vec{r}) \Delta u(\vec{r}-\vec{R}) \psi_0(\vec{r}-\vec{R}) d^3r}_{-\gamma(\vec{R})}$$

$$\therefore \left(1 + \underset{\vec{R} \neq 0}{\sum} e^{i\vec{k}\cdot\vec{R}} \alpha(\vec{R})\right)(\varepsilon(\vec{k}) - E_0) = -\beta - \underset{\vec{R} \neq 0}{\sum} e^{i\vec{k}\cdot\vec{R}} \gamma(\vec{R}) .$$

This gives the Bloch energy:

$$\varepsilon(\mathbf{k}) = E_s - \frac{\beta + \Sigma\gamma(\mathbf{R})e^{i\mathbf{k}\cdot\mathbf{R}}}{1 + \Sigma\alpha(\mathbf{R})e^{i\mathbf{k}\cdot\mathbf{R}}},$$

(6.14)

where E_s is the energy of the atomic *s*-level. The coefficients $\alpha(\mathbf{R})$, β and $\gamma(\mathbf{R})$ can be simplified by:

(1) Making use of some symmetry properties: Since ϕ is an *s*-level, $\phi(\mathbf{r})$ is real and depends only on the magnitude r. Furthermore, by the inversion symmetry of the Bravais lattice, $\Delta U(-\mathbf{r}) = \Delta U(\mathbf{r})$, one may show that $\gamma(\mathbf{R}) = \gamma(\mathbf{R})$:

General Features of Tight-Binding Levels

$$\gamma(-\vec{R}) = -\int d\vec{r}\, \phi(\vec{r}) \Delta u(\vec{r}) \phi(\vec{r}+\vec{R}) \qquad (\because \phi(\vec{r}) = \phi(\vec{r}))$$

$$= -\int d\vec{r}\, \phi(-\vec{r}) \Delta u(-\vec{r}) \phi(-\vec{r}-\vec{R})$$

$$= -\int d\vec{r}\, \phi(\vec{r}) \Delta u(\vec{r}) \phi(\vec{r}-\vec{R}) = \gamma(\vec{R}).$$

(2) One may ignore the terms in α in the denominator of Eqn. 6.14 since they are much smaller than 1. (3) A final simplication comes from assuming that only nearest-neighbor separations give appreciable overlap integrals. Putting all these together, Eqn. 6.14 may be simplified to:

The Tight-Binding Model

$$\mathcal{E}(\mathbf{k}) = E_s - \beta - \sum_{n.n.} \gamma(\mathbf{R}) \cos \mathbf{k} \cdot \mathbf{R}, \tag{6.18}$$

where the sum runs only over those $\mathbf{R}$ in the Bravais lattice that connect the origin to its nearest neighbors.

Let's apply Eqn. 6.18 to a fcc crystal. The 12 nearest neighbors of the origin are at

$$\mathbf{R} = \frac{a}{2}(\pm 1, \pm 1, 0), \quad \frac{a}{2}(\pm 1, 0, \pm 1), \quad \frac{a}{2}(0, \pm 1, \pm 1). \tag{6.19}$$

Writing $\mathbf{k} = (k_x, k_y, k_z)$, then the 12 values of $\mathbf{k} \cdot \mathbf{R}$ are

$$\vec{k} \cdot \vec{R} = \frac{a}{2}(\pm k_i \pm k_j), \qquad i, j = x, y; y, z; z, x. \tag{6.20}$$

Now $\Delta U(\mathbf{r}) = \Delta U(x, y, z)$ has the full cubic symmetry of the lattice, and is therefore unchanged by permutation of x, y, z, or changes in their signs. This, together with the fact that the s-level wave function $\phi(\mathbf{r})$ depends only on the magnitude of $\mathbf{r}$, implies that $\gamma(\mathbf{r})$ is the same constant γ for all 12 of the vectors in (6.19). With the aid of Eqn. 6.20 and that

$$\cos(\pm k_i \pm k_j)\frac{a}{2} = \cos\frac{\pm k_i a}{2}\cos\frac{\pm k_j a}{2} - \sin\frac{\pm k_i a}{2}\sin\frac{\pm k_j a}{2},$$

the sum in Eqn. 6.18 gives:

$$\mathcal{E}(\mathbf{k}) = E_s - \beta - 4\gamma(\cos \tfrac{1}{2}k_x a \cos \tfrac{1}{2}k_y a \\ + \cos \tfrac{1}{2}k_y a \cos \tfrac{1}{2}k_z a + \cos \tfrac{1}{2}k_z a \cos \tfrac{1}{2}k_x a), \tag{6.21}$$

where

$$\gamma = -\int d\mathbf{r}\, \phi^*(x, y, z)\, \Delta U(x, y, z)\, \phi(x - \tfrac{1}{2}a, y - \tfrac{1}{2}a, z). \tag{6.22}$$

Eqn. 6.21 reveals a characteristic feature of tight-binding energy bands: The bandwidth is proportional to the small overlap integral γ (see Fig. 6.3). This also means that the tight-binding bands are always narrow. In the limit of vanishing overlap, the bandwidth also vanishes, and the band becomes N-fold degenerate, with electrons bearing atomic wave functions localized to the atoms that are essentially isolated.

The Tight-Binding Model
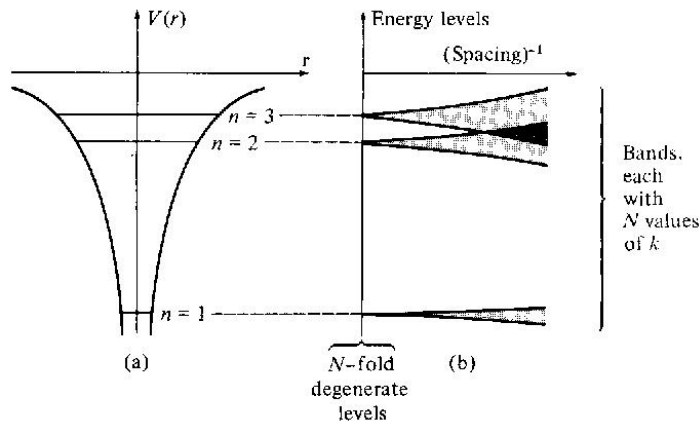
Fig. 6.3 (from A&M) (a) Schematic representation of nondegenerate electronic levels in an atomic potential. (b) The energy levels for N such atoms in a periodic array, plotted as a function of mean inverse interatomic spacing. When the atoms are far apart (small overlap integrals) the levels are nearly degenerate, but when the atoms are closer together (larger overlap integrals), the levels broaden into bands.

In the limit of small ka, Eqn. 6.21 reduces to

$$\mathcal{E}(\mathbf{k}) = E_s - \beta - 12\gamma + \gamma k^2 a^2. \tag{6.23}$$

This is independent of the direction of $\mathbf{k}$. This means that the constant energy surfaces are spherical in the vicinity of $\mathbf{k} = \mathbf{0}$.

6.3 General Features of the Tight-Binding Levels

1. It is apparent from the above that the bandwidth comes only from γ since it is the only term that varies with $\mathbf{k}$. A general feature of the tight-binding method can in fact be stated about the relation between the bandwidth and the overlap integrals

$$\gamma_{ij}(\mathbf{R}) = - \int d\mathbf{r}\ \phi_i^*(\mathbf{r})\ \Delta U(\mathbf{r})\phi_j(\mathbf{r} - \mathbf{R}). \tag{6.24}$$

If the γ_{ij} are small, the bandwidth is correspondingly small. As a rule of thumb, when the energy of a given atomic level decreases (i.e, the binding energy increases) so does the spatial extent of its wave function. Hence, the low-lying bands in a solid should be very narrow. As the average band energy increases, the bandwidth gets bigger. In metals the highest band(s) are very broad, since the spatial ranges of the highest atomic levels are comparable to a lattice constant. For this latter case, the tight-binding method would be inapplicable.

2. Although the tight-binding wave function, $\psi(\mathbf{r})$, in (6.5) is constructed out of localized atomic levels $\phi(\mathbf{r})$, an electron in a tight-binding level will be found, with equal probability, in any cell at site $\mathbf{R}$ of the crystal, but with an added phase factor $e^{i\mathbf{k}\cdot\mathbf{R}}$ that changes with $\mathbf{R}$. This leads to a sinosoidal variation in the *real* or *imaginary* part of the wave function. Fig. 6.4 sketches the real (or imaginary) part of a characteristic tight-binding wave function.

A further indication that the tight-binding levels have a running wave character comes from the consideration of the mean velocity of an electron, $\mathbf{v}(\mathbf{k}) = (1/\hbar)(\partial \varepsilon / \partial \mathbf{k})$. As
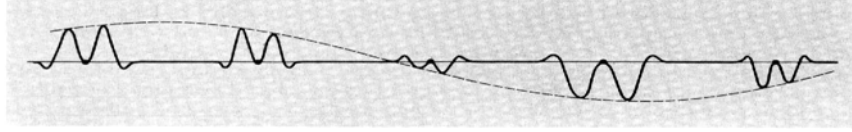
Fig. 6.4 Characteristic spatial variation of the real (or imaginary) part of the tight-binding

discussed in point no. 1, as long as there is finite amont of overlap between atomic wave functions in neighboring sites, there will be **k**-dependence in $\varepsilon(\mathbf{k})$ whereby $\mathbf{v}(\mathbf{k})$ is non-zero. The smaller the overlap, the smaller $\mathbf{v}(\mathbf{k})$ will be, but the motion of the electron through the crystal is not eliminated. One can view this motion as a quantum-mechanical tunneling from lattice site to lattice site.

3. In solids that are not monatomic Bravais lattice, the tight-binding approximation is more complicated. Formally, one can treat the basis as a molecule, whose wave functions are assumed to be known, and proceed as above, using molecular instead of atomic wave functions. Alternatively, one can proceed by continuing to construct linear combinations of atomic levels centered at the Bravais lattice points and at the basis points, generalizing Eqn. 6.5 to

$$\psi(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} (a\phi(\mathbf{r} - \mathbf{R}) + b\phi(\mathbf{r} - \mathbf{d} - \mathbf{R})),$$

(6.25)

where **d** is the separation of the two basis atoms.

6.4 Wannier Functions

The solution we wrote down in Eqn. 6.5 for the crystal Hamiltonian in the tight-binding approximation, is indeed of the general form of the Bloch function:

$$\psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{R}} \phi_n(\vec{r} - \vec{R}) e^{i\vec{k} \cdot \vec{R}}$$

(6.26)

where $\phi_n(\mathbf{r} - \mathbf{R})$ is known as Wannier functions. The form of Eqn. 6.26 is applicable to all kinds of bands (not just limited to the tight-binding kind). Clearly, the Wannier function is given by

$$\phi_n(\vec{r} - \vec{R}) = \frac{1}{v_0} \int dk \, e^{-i\vec{R} \cdot \vec{k}} \psi_{n\vec{k}}(\vec{r}),$$

(6.27)

where v_0 is the volume of the Brillouin zone. Unlike the tight-binding atomic functions, the Wannier functions at different sites or with different band indices are orthogonal. Since the complete set of Bloch functions can be written as linear combintions of the Wannier functions, the Wannier functions $\phi_n(\mathbf{r} - \mathbf{R})$ for all n and **R** form a complete orthogonal set. They therefore offer an alternative basis for an exact description of the independent electron levels in the presence of a crystal potential.