Tight-binding method in a nutshell

Consider first, for the sake of simplicity, a solid built up from atoms of the same type. A tight binding variational wavefunction is given by

$$\psi(\mathbf{r}) = \sum_{inlm} a_{inlm}\phi_{nlm}(\mathbf{r} - \mathbf{R}_i)\,, \tag{1}$$

where $\phi_{nlm}(\mathbf{r})$ are the atomic orbitals, the index i refers to atoms of the lattice, $\mathbf{R}_i$ is the position vector of the i-th nucleus. The values of the coefficients a_{inlm} are to be found by using the variational method. In the following, we consider a simple crystal lattice with one atom per unit cell. We may thus restrict our attention to functions satisfying the Bloch theorem,

$$\psi(\mathbf{r} + \mathbf{R}_q) = e^{i\mathbf{k}\mathbf{R}_q}\psi(\mathbf{r}) \ \forall \ \mathbf{R}_q$$

of the crystal lattice. By inserting the expression on the r. h. s. of Eq. (1) we obtain

$$\sum_{inlm} a_{inlm}\phi_{nlm}[\mathbf{r} - (\mathbf{R}_i - \mathbf{R}_q)] = e^{i\mathbf{k}\mathbf{R}_q}\sum_{inlm} a_{inlm}\phi_{nlm}(\mathbf{r} - \mathbf{R}_i)\,. \tag{2}$$

By comparing the expressions on the left and the right hand side of the above equation (the coefficients associated with the wave function $\phi_{nlm}(\mathbf{r})$ "at the origin") we find that

$$a_{qnlm} = a_{0nlm}e^{i\mathbf{k}\mathbf{R}_q}\,. \tag{3}$$

The expansion of Eq. (1) then becomes

$$\psi(\mathbf{r}) = \sum_{nlm} a_{0nlm}\sum_q e^{i\mathbf{k}\mathbf{R}_q}\phi_{nlm}(\mathbf{r} - \mathbf{R}_q) =$$

$$= \sum_{nlm} a_{nlm}\varphi_{k,nlm}(\mathbf{r})\,, \tag{4}$$

where $a_{nlm} = a_{0nlm}\sqrt{N}$,

$$\varphi_{k,nlm} = \frac{1}{\sqrt{N}}\sum_q e^{i\mathbf{k}\mathbf{R}_q}\phi_{nlm}(\mathbf{r} - \mathbf{R}_q)\,, \tag{5}$$

and N is the number of unit cells in the Born Kármán region. The factor $1/\sqrt{N}$ is introduced because of normalization: if the set of the atomic orbitals is orthonormal then the wavefunctions defined by Eq. (5) are normalized. For any $\mathbf{k}$, the number of basis wavefunctions $\varphi_{k,nlm}$, and also the corresponding number of equations to be solved, is the same as the number of atomic orbitals considered!

It remains to find the equations determining the coefficients $a_{nlm}(\mathbf{k})$ (the argument has been added, the coefficients are $\mathbf{k}$-dependent) of Eq. (4). The strategy is the same as in the studies of the electronic structure of simple molecules; the variational condition leads to the following set of equations:

$$\sum_{nlm} a_{nlm}(\mathbf{k})[\langle\varphi_{k,n'l'm'}|h|\varphi_{k,nlm}\rangle - \epsilon(k)\langle\varphi_{k,n'l'm'}|\varphi_{k,nlm}\rangle] = 0\,. \tag{6}$$

The matrix elements in the above equation are then expressed in terms of those between the atomic orbitals: $\langle\phi_{n'l'm}(\mathbf{r} - \mathbf{R}_i)|h|\phi_{nlm}(\mathbf{r} - \mathbf{R}_j)\rangle$ and $\langle\phi_{n'l'm}(\mathbf{r} - \mathbf{R}_i)|\phi_{nlm}(\mathbf{r} - \mathbf{R}_j)\rangle$.

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Frequently it is assumed that the only relevant matrix elements of h are
(a) the "on-site matrix elements", $\langle \phi_{nlm}(\mathbf{r} - \mathbf{R}_i)|h|\phi_{nlm}(\mathbf{r} - \mathbf{R}_i)\rangle = \epsilon_{nlm}$, and
(b) the "hopping matrix elements" corresponding to "nearest neighbours"
$\langle \phi_{n'l'm'}(\mathbf{r} - \mathbf{R}_i)|h|\phi_{nlm}(\mathbf{r} - \mathbf{R}_j)\rangle = t_{ij,n'l'm',nlm}$ (i, j nearest neighbours).
The values of the on-site matrix elements and the hopping-matrix elements may be
estimated according to various semiempirical rules. The overlap matrix
$\langle \phi_{n'l'm'}(\mathbf{r}-\mathbf{R}_i)|\phi_{nlm}(\mathbf{r}-\mathbf{R}_j)\rangle$ is frequently approximated by the unit matrix $\delta_{ij}\delta_{n'l'm';nlm}$.

For crystals with several atoms per unit cell, we obtain an analogue of Eq. (6),
where the sum runs, in addition to n,l,m, over the atoms.