Condensed Matter Physics

PHY 5111

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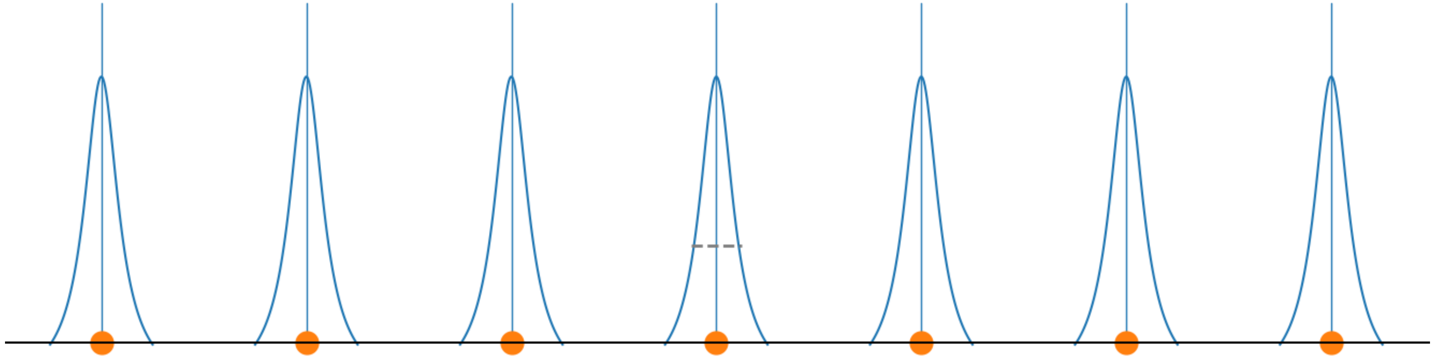
Nearly Free and Tightly Bound Electrons

Condensed Matter Physics – Michael P. Marder

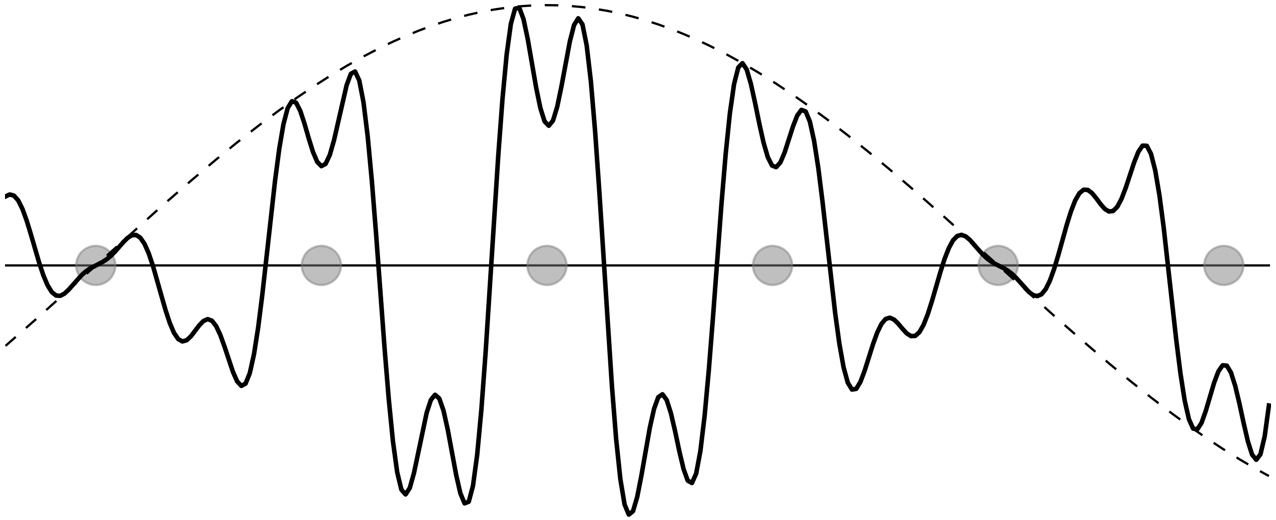
Chapter 8

Bloch's Theorem

$$U(\mathbf{r}+\mathbf{R}) = U(\mathbf{r})$$

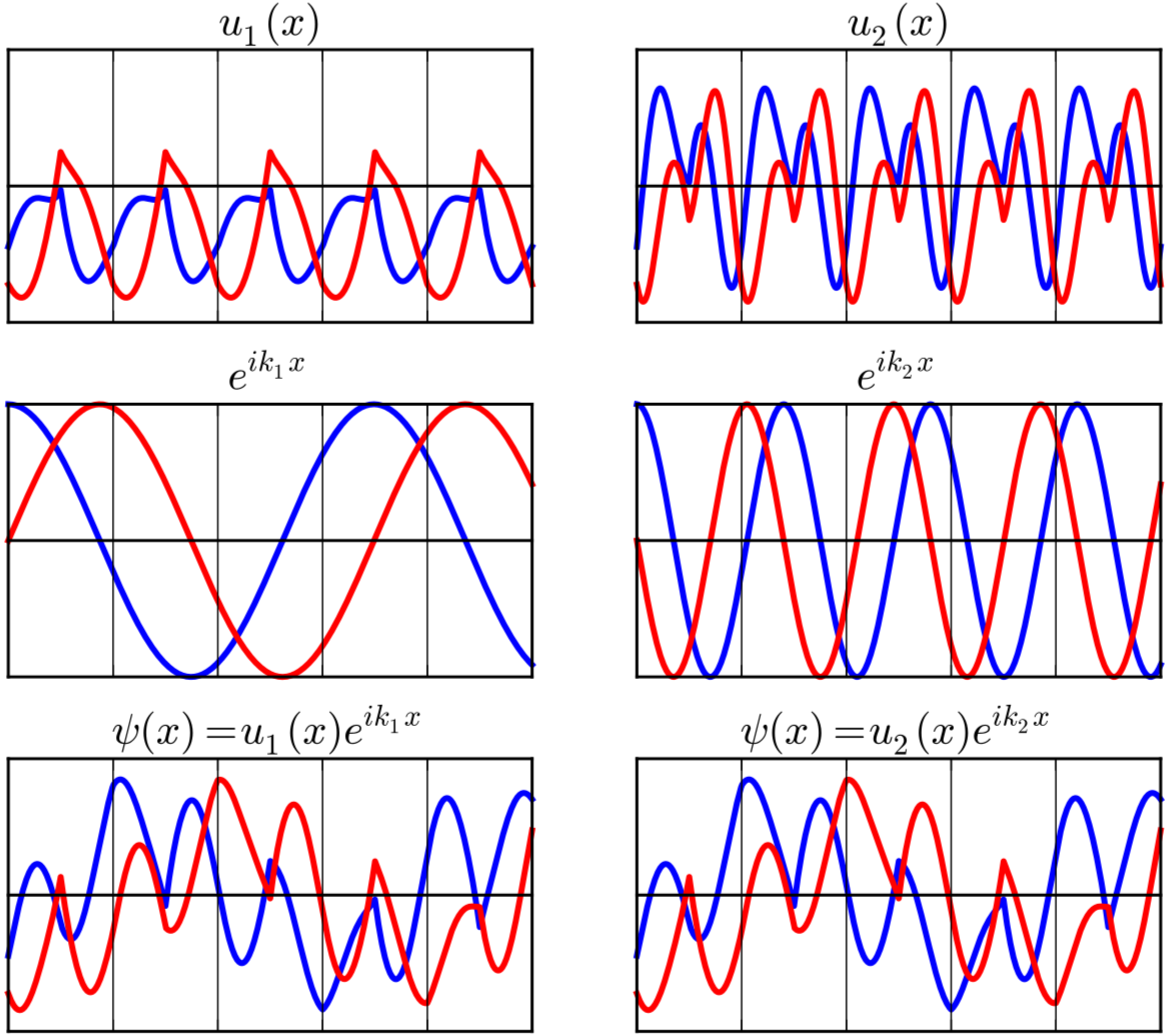


$$\psi(\mathbf{r}) = \mathrm{e}^{\mathbf{ik}\cdot\mathbf{r}}u(\mathbf{r})$$

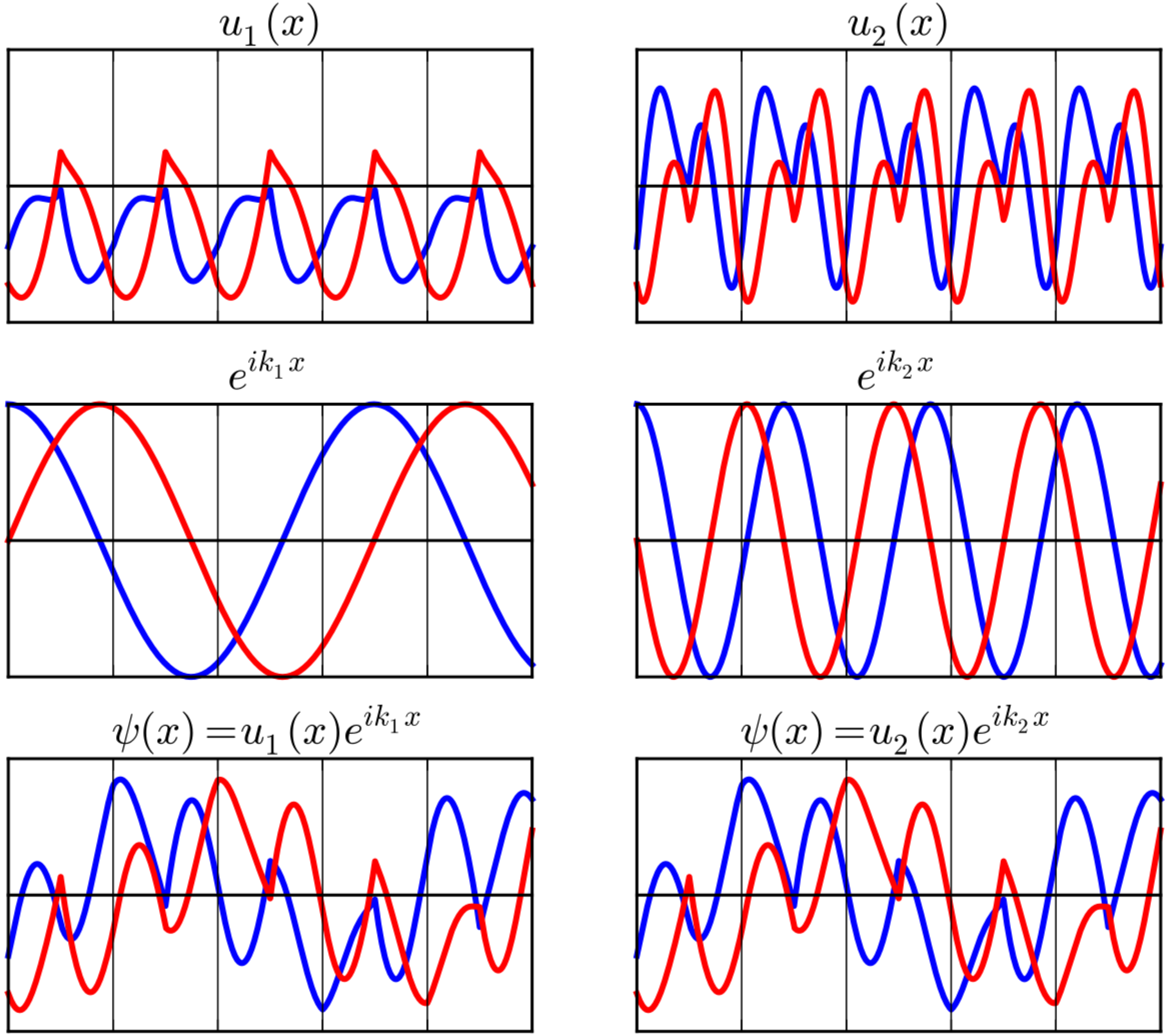


Bloch wave function

$$\psi(\mathbf{r}) = \mathrm{e}^{\mathbf{ik\cdot r}}u(\mathbf{r})$$



A Bloch wave function (bottom) can be broken up into the product of a periodic function (top) and a plane-wave (center). The left side and right side represent the same Bloch state broken up in two different ways, involving the wave vector k_1 (left) or k_2 (right). The difference ($k_1 - k_2$) is a reciprocal lattice vector. In all plots, blue is real part and red is imaginary part.



How strong is the interaction?

Nearly Free Electrons

Tightly Bound Electrons

Nearly Free Electrons

$$(\mathcal{E}^0_{\vec{q}} - \mathcal{E})\psi\,(\vec{q}) + \sum_{\vec{K}} U_{\vec{K}}\psi(\vec{q} - \vec{K}) = 0.$$

A formal means to treat the potential U as small is to define

$$U_{\vec{K}} = \Delta\ w_{\vec{K}}$$

Δ is the small parameter in terms of which perturbation theory will expand.

$$\psi(\vec{q}) = \psi^{(0)}\,(\vec{q}) + \psi^{(1)}\,(\vec{q})\,\Delta + \ldots; \quad \mathcal{E} = \mathcal{E}^{(0)} + \Delta\,\mathcal{E}^{(1)} + \ldots.$$

Nearly Free Electrons

Zeroth Order:

$$\boxed{\psi^{(0)}(\vec{q})\left[\mathcal{E}^0_{\vec{q}} - \mathcal{E}^{(0)}\right] = 0.}$$

Extended zone scheme:

$$\psi^{(0)}_{\vec{k}}(\vec{q}) = \delta_{\vec{k},\vec{q}}$$

$$\Rightarrow \psi^{(0)}_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}$$

$$\Rightarrow \mathcal{E}^{(0)} = \mathcal{E}^0_{\vec{k}}$$

Reduced zone scheme:

$$\psi^{(0)}_{n\vec{k}}(\vec{q}) = \delta_{\vec{K}_n+\vec{k},\vec{q}}$$

$$\Rightarrow \psi^{(0)}_{n\vec{k}}(\vec{r}) = e^{i(\vec{k}+\vec{K}_n)\cdot\vec{r}}$$

$$\Rightarrow \mathcal{E}^{(0)}_{nk} = \mathcal{E}^0_{\vec{k}+\vec{K}_n}.$$

Nearly Free Electrons

First Order:

$$[\mathcal{E}^0_{\vec q} - \mathcal{E}^0_{\vec k}]\psi^{(1)}_{\vec k}(\vec q) + \sum_{\vec K} w_{\vec K}\psi^{(0)}_{\vec k}(\vec q - \vec K) - \mathcal{E}^{(1)}\psi^{(0)}_{\vec k}(\vec q) = 0.$$

Taking $\psi^{(0)}_{\vec k}$ from previous solution and evaluation at $\vec q = \vec k$ gives $\mathcal{E}^{(1)} = w_0$.

$$\psi^{(1)}_{\vec k}(\vec q) = \left\{\sum_{\vec K \neq 0} w_{\vec K}\frac{\delta_{\vec k,\vec q-\vec K}}{\mathcal{E}^0_{\vec k} - \mathcal{E}^0_{\vec K+\vec k}}\right\}$$

$$\psi_{\vec k}(\vec q) \approx \delta_{\vec q\vec k} + \left\{\sum_{\vec K \neq 0} U_{\vec K}\frac{\delta_{\vec k,\vec q-\vec K}}{\mathcal{E}^0_{\vec k} - \mathcal{E}^0_{\vec K+\vec k}}\right\}$$

$$\mathcal{E}^0_{\vec k} = \mathcal{E}^0_{\vec K+\vec k}$$

Degenerate Perturbation Theory

One way to obtain a resolution of this problem is to recast Schrödinger's equation in variational form, as discussed in Appendix B. Solving the Schrödinger's equation is equivalent to finding extrema of the functional

$$\langle\psi|(\hat{\mathcal{H}}-\mathcal{E})|\psi\rangle.$$

$$|\psi\rangle = \sum_{i=1}^{l} C_i|\psi_i\rangle.$$

$$\sum_j \langle\psi_i|(\hat{\mathcal{H}}-\mathcal{E})|\psi_j\rangle C_j = 0,$$

$$\hat{\mathcal{H}}^{\mathrm{eff}}_{ij} = \langle\psi_i|(\hat{\mathcal{H}}-\mathcal{E})|\psi_j\rangle$$

Bloch's Theorem in Three Dimensions

$$(\mathcal{E}_{\vec{q}}^{0} - \mathcal{E})\psi(\vec{q}) + \sum_{\vec{K}} U_{\vec{K}}\psi(\vec{q} - \vec{K}) = 0.$$

$$\hat{\mathcal{H}} = \sum_{\vec{q}'} |\vec{q}'\rangle \mathcal{E}_{\vec{q}'}^{0} \langle \vec{q}'| + \sum_{\vec{q}'\vec{K}'} |\vec{q}'\rangle U_{\vec{K}'} \langle \vec{q}' - \vec{K}'|.$$

$$\langle \vec{q}|\hat{\mathcal{H}} - \mathcal{E}|\psi\rangle$$

Degenerate Perturbation Theory

In the present case, the plan is to restrict all attention to wave functions that are linear combinations of the two vectors $|\psi_1\rangle = |\vec{k}\rangle$ and $|\psi_2\rangle = |\vec{k}+\vec{K}\rangle$, but otherwise solve the Hamiltonian exactly.

$$\begin{vmatrix} \mathcal{E}^0_{\vec{k}} + U_0 - \mathcal{E} & U_{-\vec{K}} \\ U_{\vec{K}} & \mathcal{E}^0_{\vec{k}+\vec{K}} + U_0 - \mathcal{E} \end{vmatrix}$$

$$\boxed{\mathcal{E} = U_0 + \frac{\mathcal{E}^0_{\vec{k}} + \mathcal{E}^0_{\vec{k}+\vec{K}}}{2} \pm \sqrt{\frac{[\mathcal{E}^0_{\vec{k}} - \mathcal{E}^0_{\vec{k}+\vec{K}}]^2}{4} + |U_{\vec{K}}|^2}.}$$

Because $U(\vec{r})$ is real, $U_{-\vec{K}} = U^*_{\vec{K}}$.

Degenerate Perturbation Theory

At the point where $\mathcal{E}^0_{\vec{k}+\vec{K}} = \mathcal{E}^0_{\vec{k}}$ is exactly satisfied, one obtains

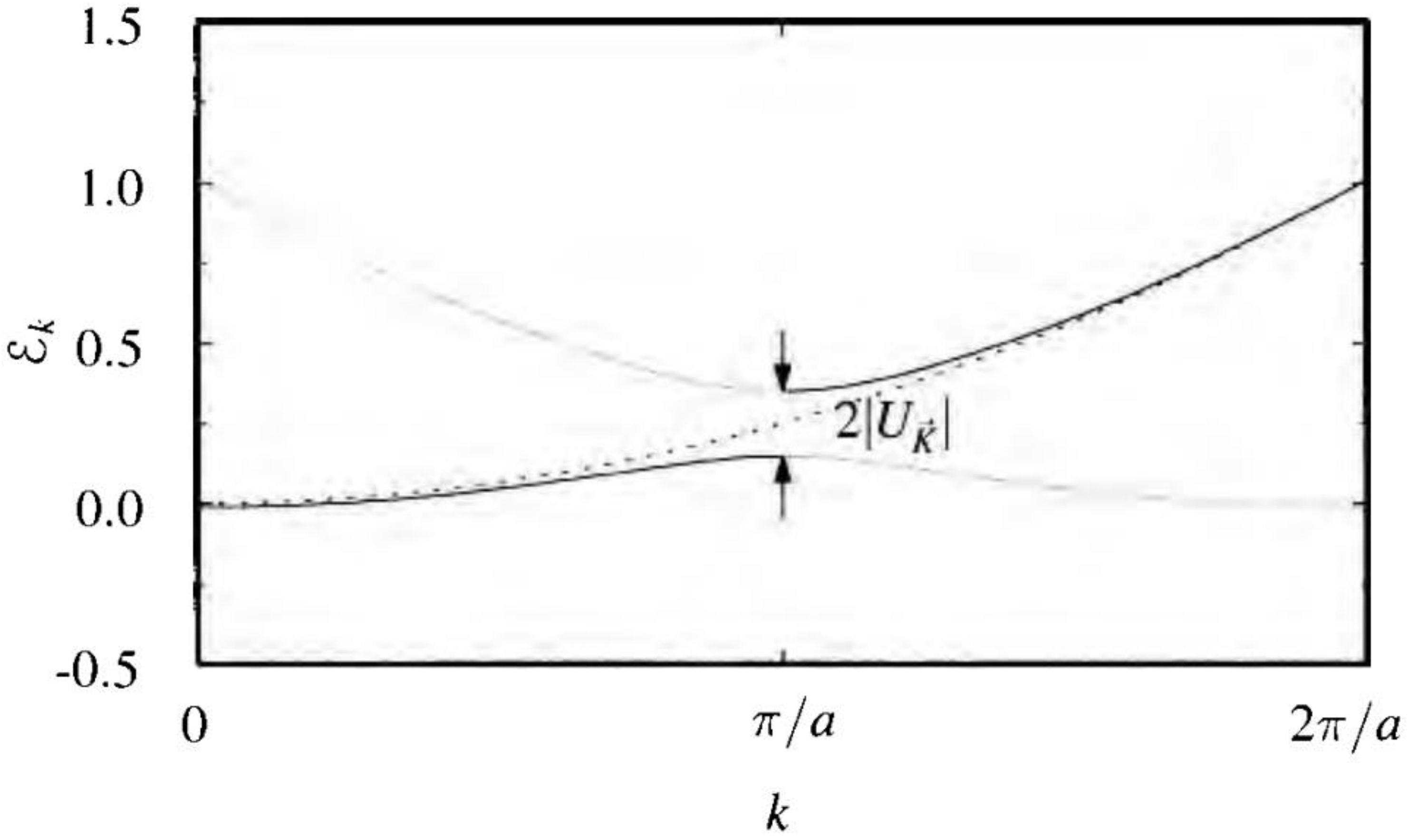
$$\mathcal{E} = \mathcal{E}^0_{\vec{k}} + U_0 \pm |U_{\vec{K}}|.$$

Thus the *energy gap* $\mathcal{E}_g$ between bands is

$$\mathcal{E}_g = 2|U_{\vec{K}}|.$$

Degenerate Perturbation Theory (1D)

$$\mathcal{E}_g = 2|U_{\vec{K}}|$$



Brillouin Zones

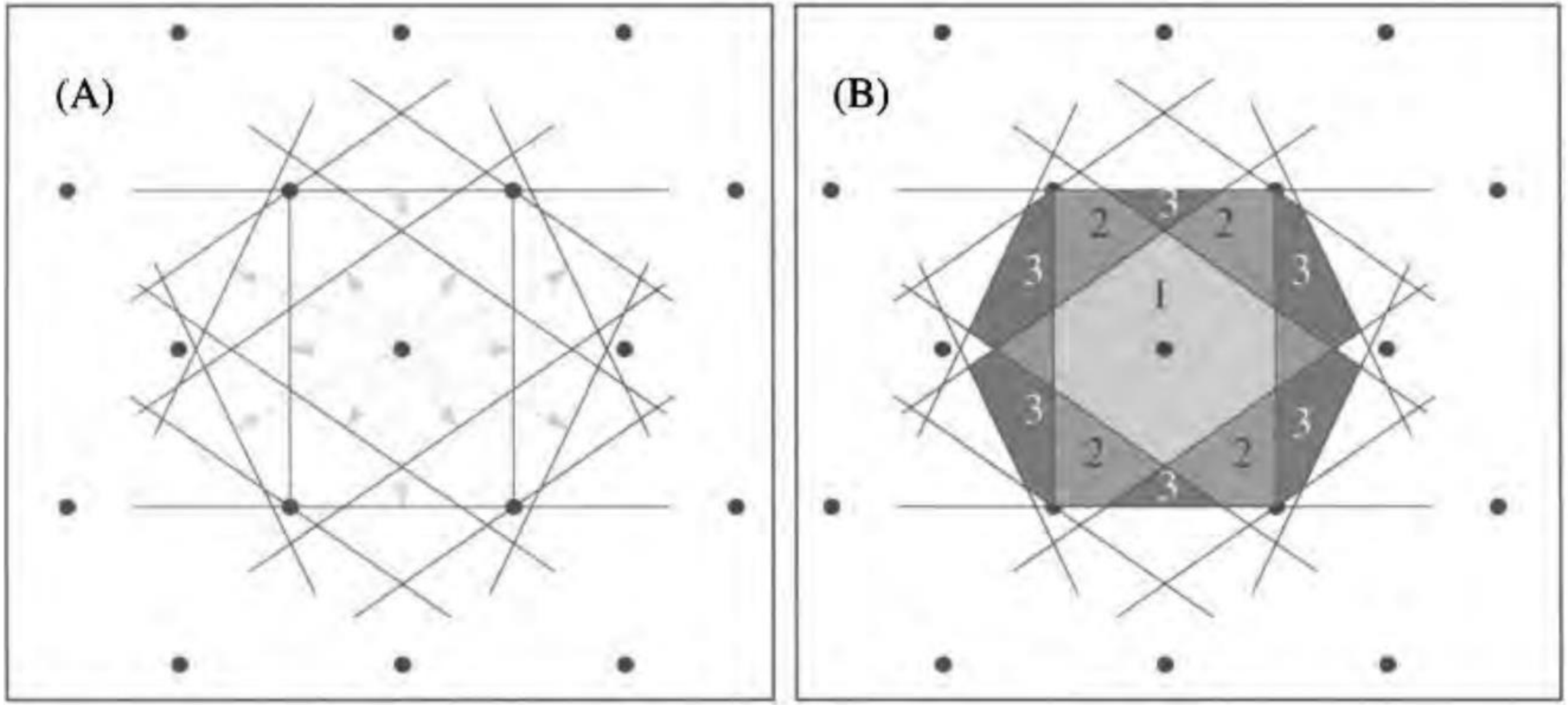


Figure 8.2. Construction of Brillouin zones. (A) Perpendicular bisectors are drawn between the origin and all nearby reciprocal lattice points. These are the zone boundaries. (B) The first, second, and third Brillouin zones are shaded in different colors. The first zone is the set of points closer to the origin than any other reciprocal lattice point, the second zone is the set of points that one reaches by passing a minimum of one zone boundary, and the third zone is the set of points that one reaches by crossing a minimum of two zone boundaries.

Brillouin Zones

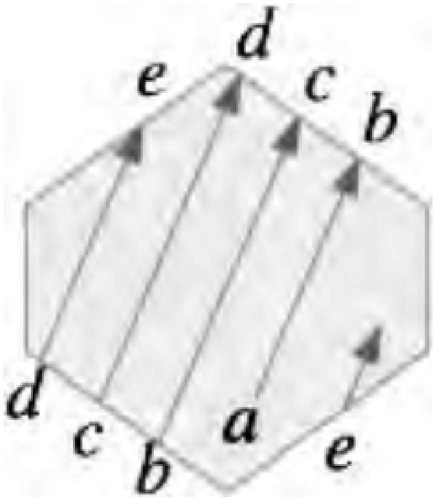
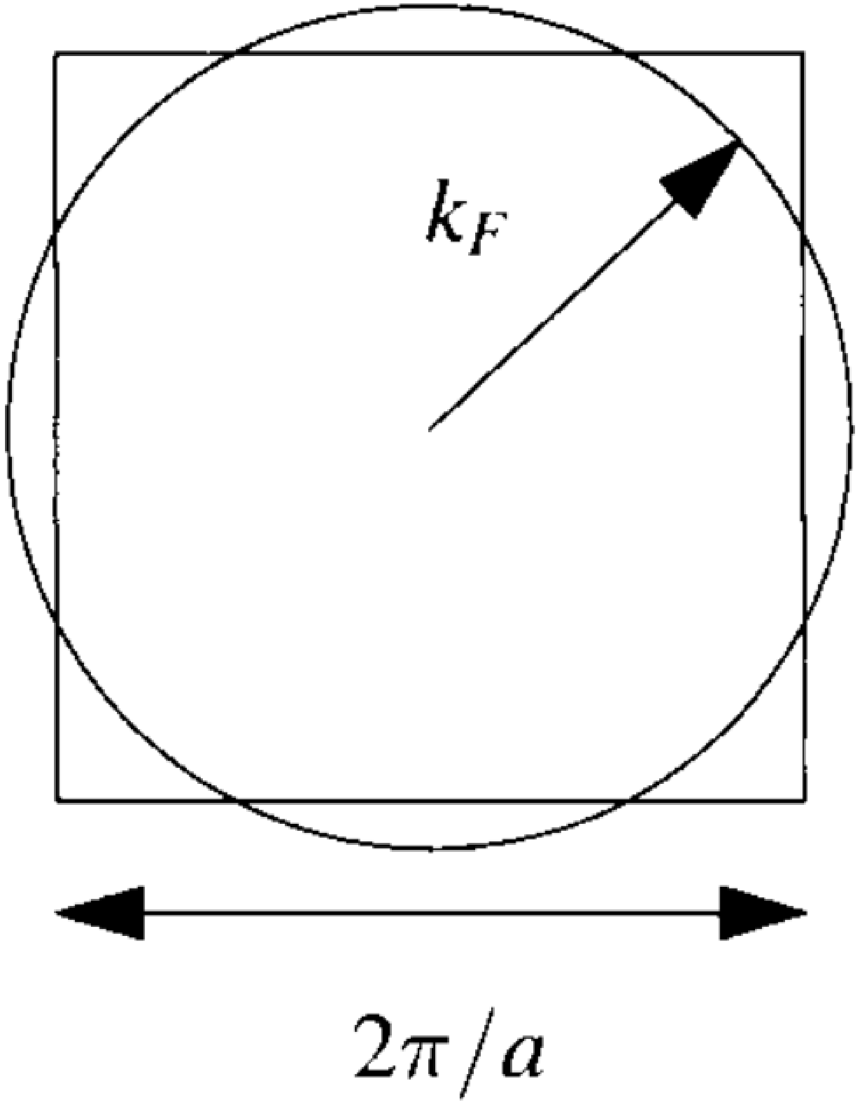
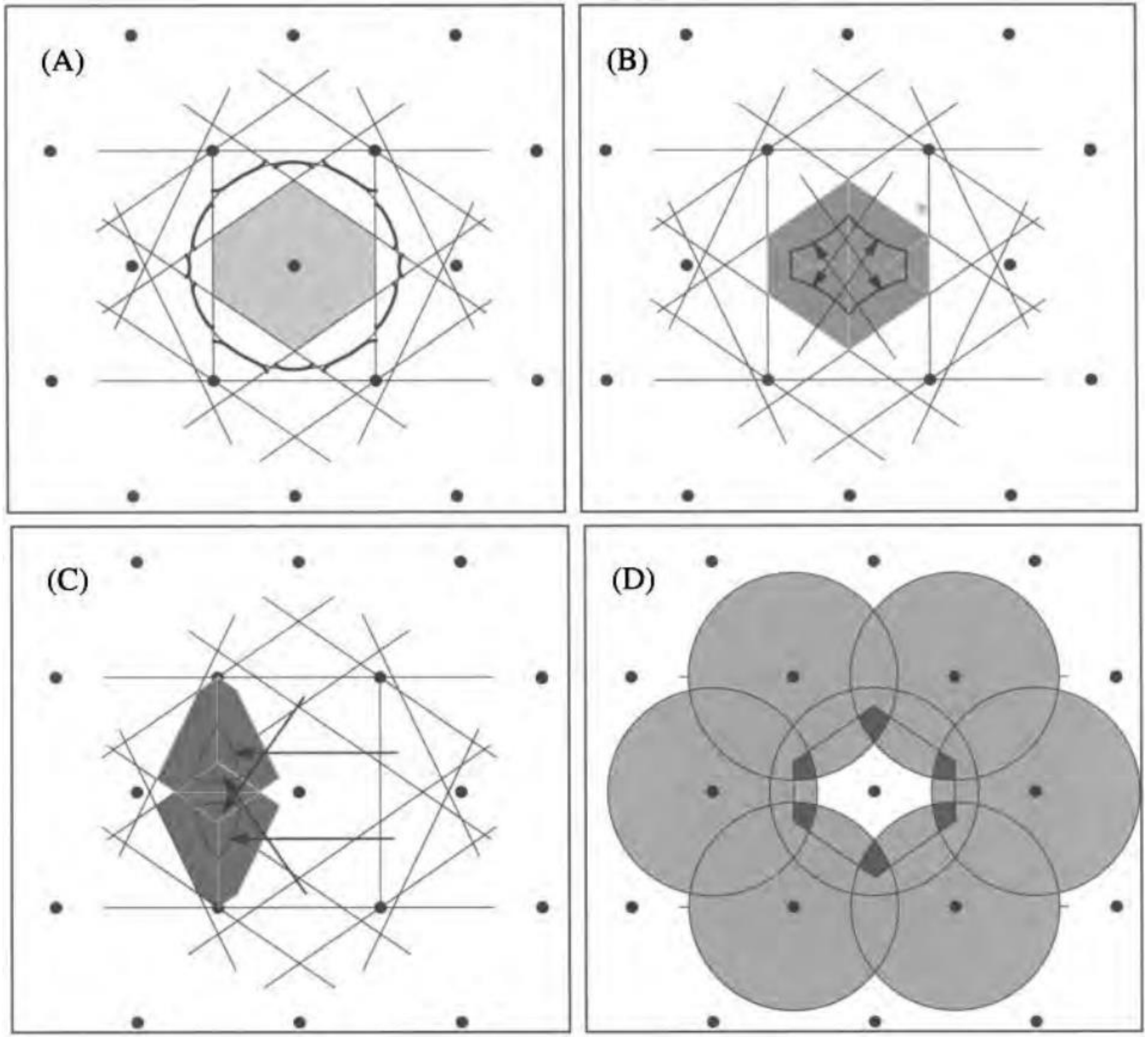


Figure 8.3. The first Brillouin zone can be viewed as a closed surface whose edges are connected to each other. Therefore a path that appears to be leaving from one edge is actually entering from another, as shown in this representation of straight line motion. This view of the first Brillouin zone is motivated by the fact that physical quantities such as $\mathcal{E}_{\vec{k}}$ are periodic functions over the first Brillouin zone.

Brillouin zone boundary intersection for square lattice in two dimensions

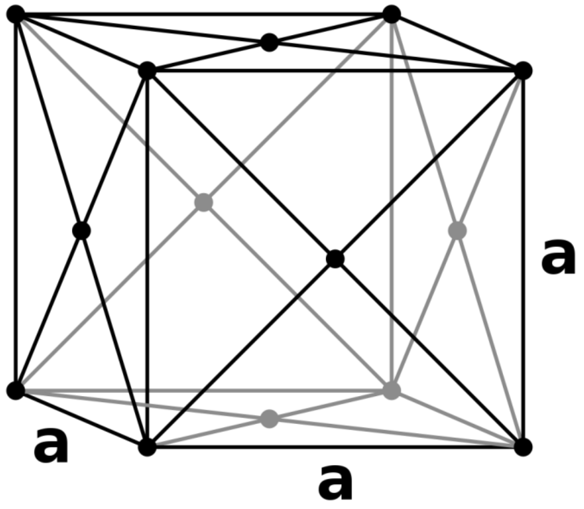


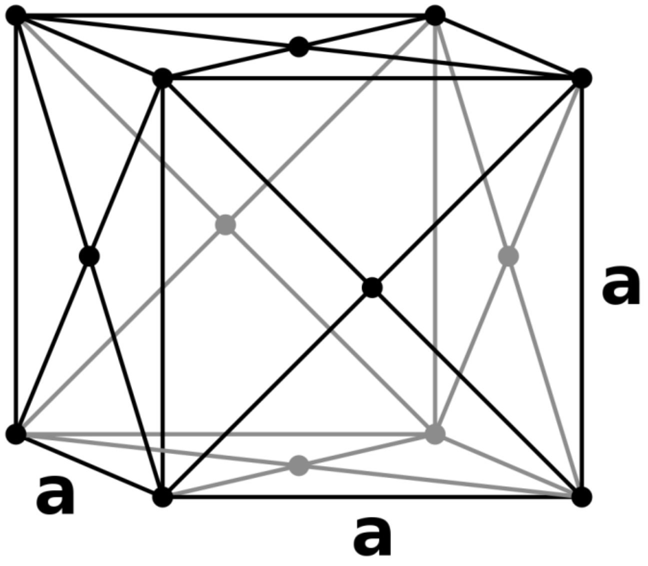
Nearly Free Electron Fermi Surfaces



Brillouin zone	Extended zone scheme	Reduced zone scheme
First	Empty	Empty
Second		
Third		

Figure 8.5. Fermi surface for three electrons per site in an fcc crystal. On the left the free-electron Fermi surface is shown in the extended zone scheme, while on the right the same surfaces are projected back into the first Brillouin zone in the reduced zone scheme.





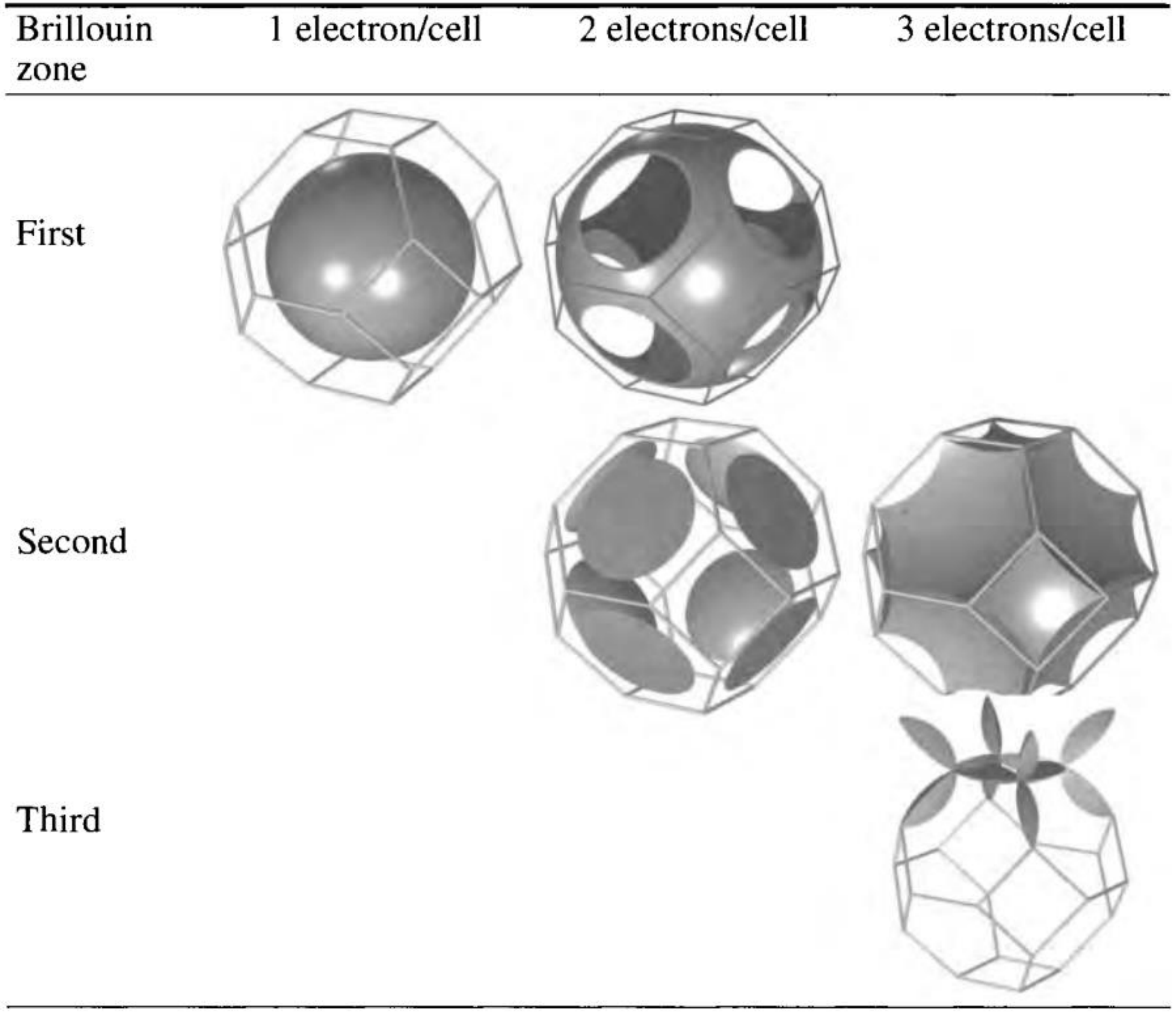
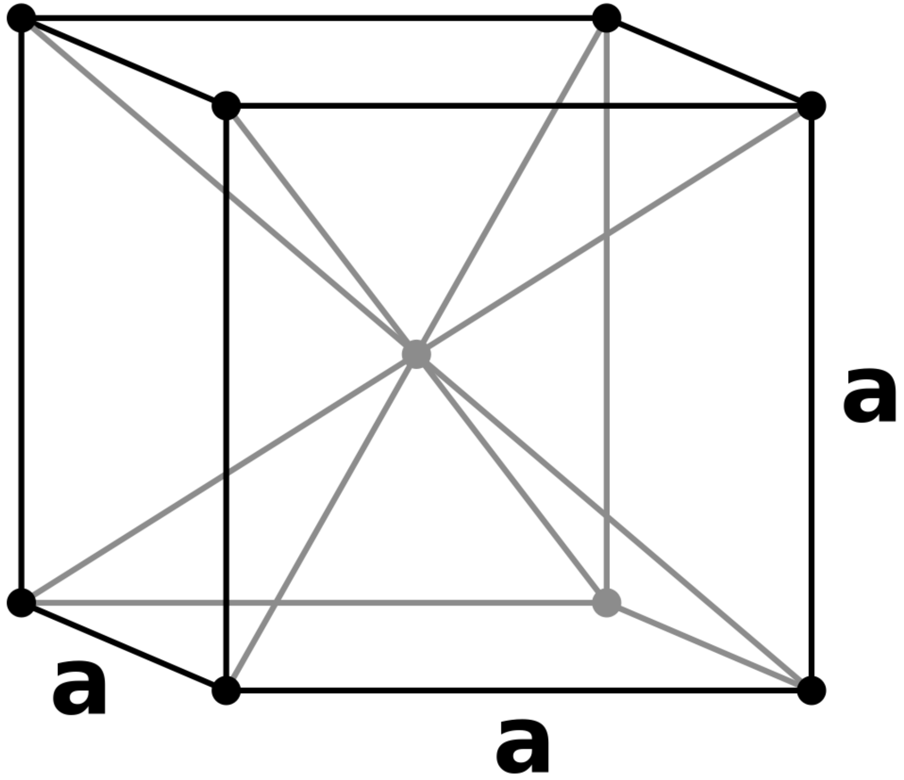


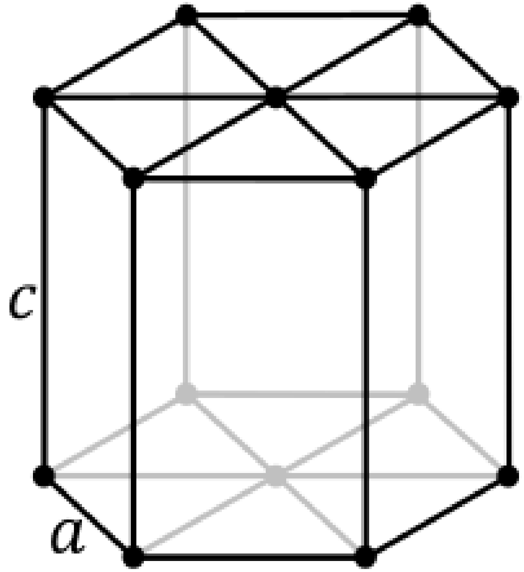
Figure 8.6. Nearly free electron Fermi surfaces for fcc crystals. With three electrons per unit cell the Fermi surface extends slightly into the fourth Brillouin zone, but the pocket is very small and is not shown.

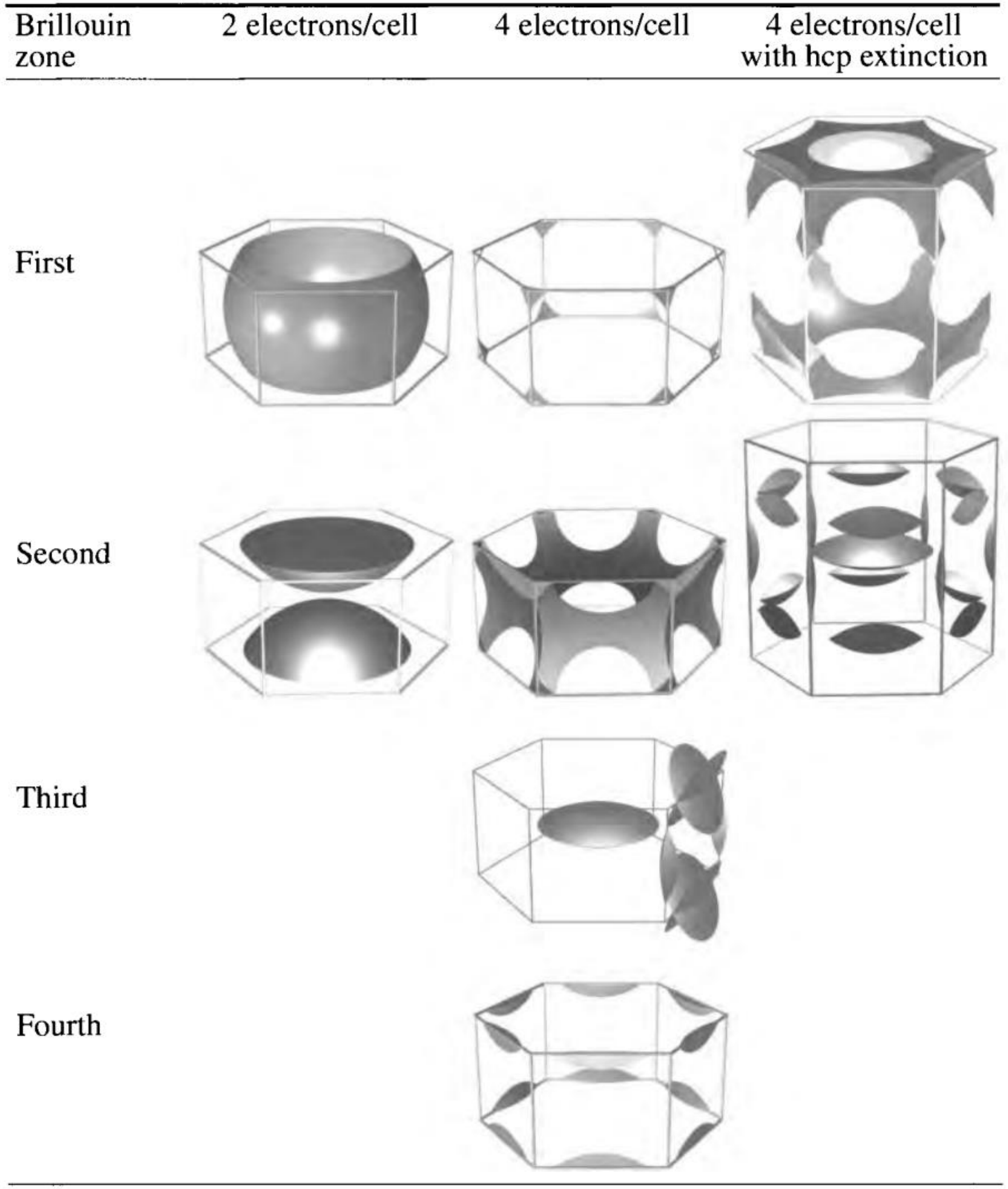
Nearly free electron Fermi surfaces for bcc crystals



Brillouin zone	1 electron/cell	2 electrons/cell	3 electrons/cell
First			
Second			
Third			
Fourth			

Nearly free electron Fermi surfaces for hexagonal crystals



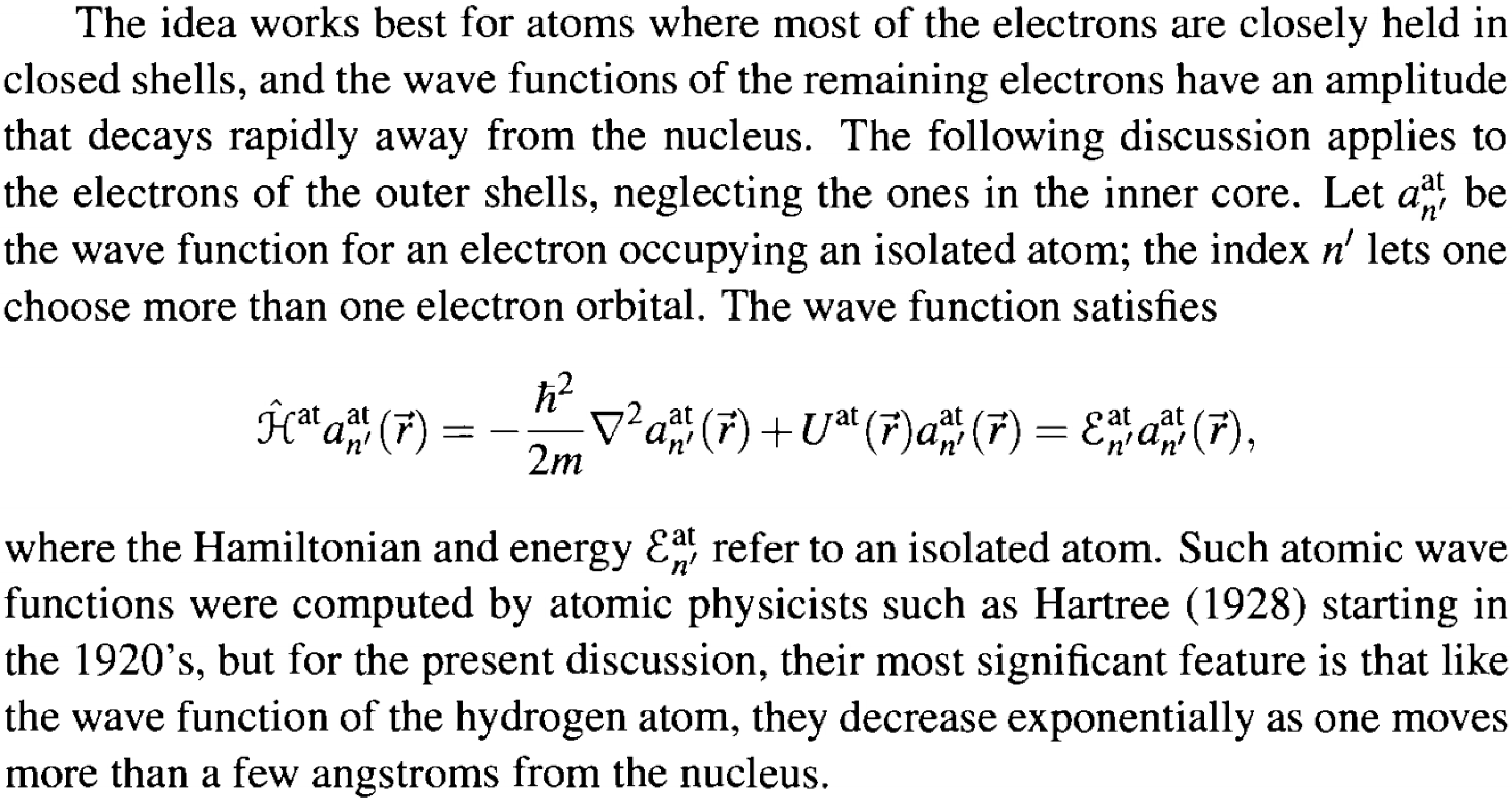


Tightly Bound Electrons

Solids are made from atoms, and viewed as a collection of atoms. Imagine a collection of isolated atoms and slowly bring them together to form a crystal. Surely in that case, the most appropriate approximation must begin with atomic wave functions.

- Linear Combinations of Atomic Orbitals (LCAO)
- Tight Binding Model

Linear Combinations of Atomic Orbitals (LCAO)



The idea works best for atoms where most of the electrons are closely held in closed shells, and the wave functions of the remaining electrons have an amplitude that decays rapidly away from the nucleus. The following discussion applies to the electrons of the outer shells, neglecting the ones in the inner core. Let $a^{\text{at}}_{n'}$ be the wave function for an electron occupying an isolated atom; the index n' lets one choose more than one electron orbital. The wave function satisfies

$$\hat{\mathcal{H}}^{\text{at}} a^{\text{at}}_{n'}(\vec{r}) = -\frac{\hbar^2}{2m}\nabla^2 a^{\text{at}}_{n'}(\vec{r}) + U^{\text{at}}(\vec{r}) a^{\text{at}}_{n'}(\vec{r}) = \mathcal{E}^{\text{at}}_{n'} a^{\text{at}}_{n'}(\vec{r}),$$

where the Hamiltonian and energy $\mathcal{E}^{\text{at}}_{n'}$ refer to an isolated atom. Such atomic wave functions were computed by atomic physicists such as Hartree (1928) starting in the 1920's, but for the present discussion, their most significant feature is that like the wave function of the hydrogen atom, they decrease exponentially as one moves more than a few angstroms from the nucleus.

Linear Combinations of Atomic Orbitals (LCAO)

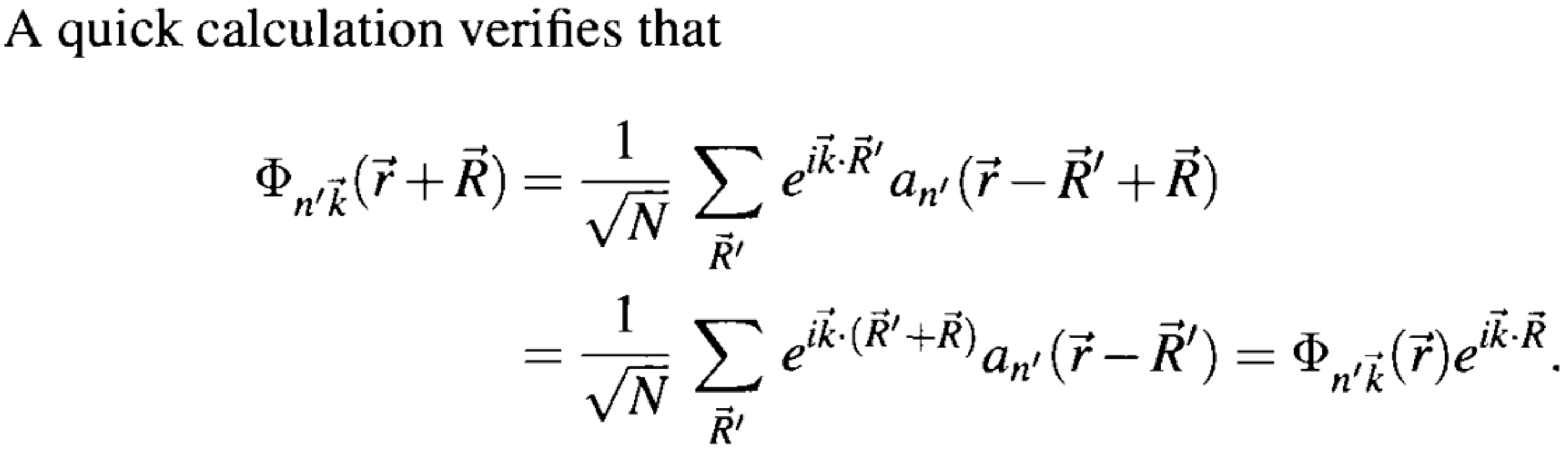
Now imagine bringing many such atoms together to form a crystal with lattice vectors $\vec{R}$, obtaining the Hamiltonian

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r}) = -\frac{\hbar^2}{2m}\nabla^2 + \sum_{\vec{R}} U^{\mathrm{at}}(\vec{r}-\vec{R}).$$

Using atomic waves functions to solve this Hamiltonian proceeds in two steps. The first is to build some wave functions that automatically satisfy Bloch's theorem, Eq. (7.36). They are

$$\Phi_{n'\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} a^{\mathrm{at}}_{n'}(\vec{r}-\vec{R}).$$

Linear Combinations of Atomic Orbitals (LCAO)



A quick calculation verifies that

$$\begin{aligned}\Phi_{n'\vec{k}}(\vec{r}+\vec{R}) &= \frac{1}{\sqrt{N}}\sum_{\vec{R}'} e^{i\vec{k}\cdot\vec{R}'} a_{n'}(\vec{r}-\vec{R}'+\vec{R}) \\ &= \frac{1}{\sqrt{N}}\sum_{\vec{R}'} e^{i\vec{k}\cdot(\vec{R}'+\vec{R})} a_{n'}(\vec{r}-\vec{R}') = \Phi_{n'\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{R}}.\end{aligned}$$

The wave functions Φ are neither normalized, nor eigenfunctions of the Hamiltonian. Just because solutions of Schrödinger's equation must have the form of Bloch wave function does not mean that all functions of this form solve Schrödinger's equation. They can however be used as *trial wave functions* and summed together so as to get the best solution of Schrödinger's equation possible.

Linear Combinations of Atomic Orbitals (LCAO)

$$\boxed{\psi_{n\vec{k}}(\vec{r}) = \sum_{n'} C_{nn'} \Phi_{n'\vec{k}}(\vec{r})}$$

To choose the constants $C_{nn'}$, use the variational principle. Forming $\langle \psi_{n\vec{k}} | \hat{\mathcal{H}} - \mathcal{E} | \psi_{n\vec{k}} \rangle$ and varying with respect to $C^*_{nn'}$ gives

$$0 = \sum_{n'} C_{nn'} \langle \Phi_{n''\vec{k}} | \hat{\mathcal{H}} - \mathcal{E} | \Phi_{n'\vec{k}} \rangle$$

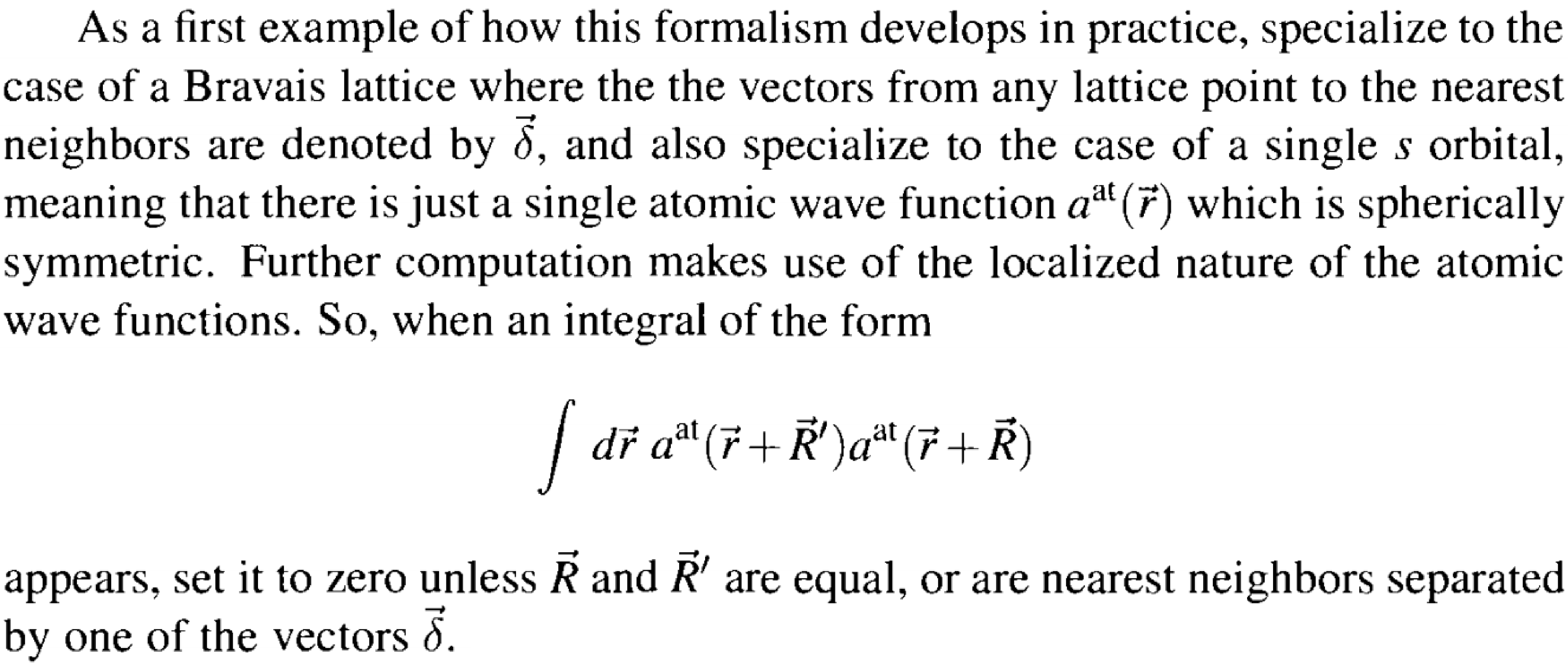
$$\Rightarrow 0 = \sum_{n'} C_{nn'} \left(\mathcal{H}_{n''n'} - \mathcal{E}_n \mathcal{S}_{n''n'} \right)$$

This is an eigenvalue equation for $\mathcal{E}$ and $\vec{C}_n$. Adding a subscript on $\mathcal{E}$ acknowledges that the eigenvector $\vec{C}_n$ and eigenvalue $\mathcal{E}_n$ are linked. The equation can be put in more familiar form by multiplying from the left by $\mathcal{S}^{-1}$.

where

$$\mathcal{H}_{nn'} \equiv \langle \Phi_{n\vec{k}} | \hat{\mathcal{H}} | \Phi_{n'\vec{k}} \rangle \quad \text{and the overlap matrix} \quad \mathcal{S}_{nn'} \equiv \langle \Phi_{n\vec{k}} | \Phi_{n'\vec{k}} \rangle .$$

Linear Combinations of Atomic Orbitals (LCAO)



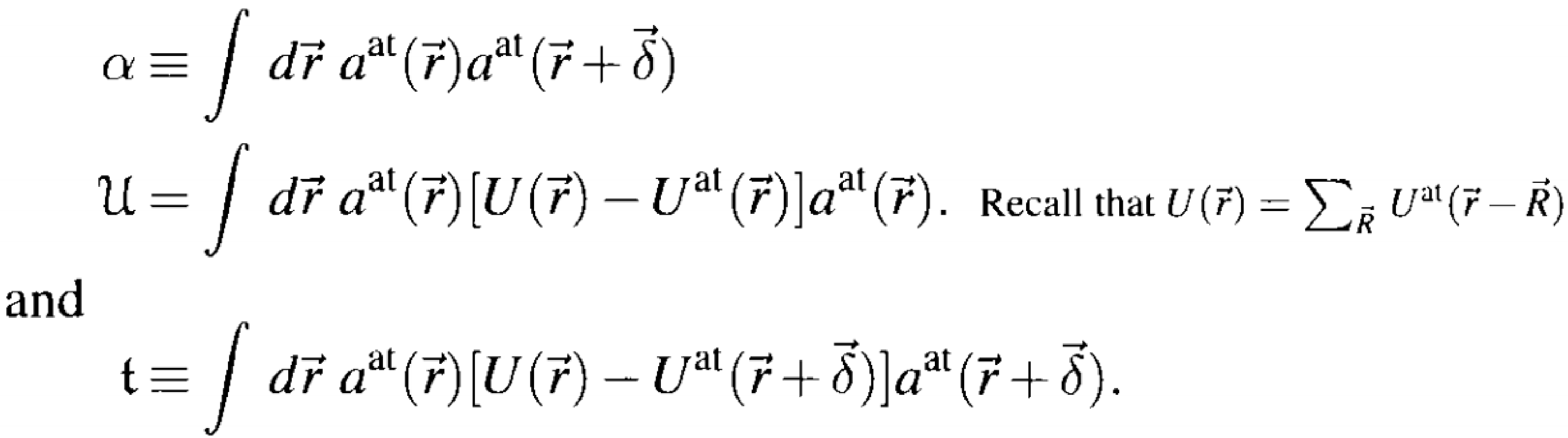
As a first example of how this formalism develops in practice, specialize to the case of a Bravais lattice where the the vectors from any lattice point to the nearest neighbors are denoted by $\vec{\delta}$, and also specialize to the case of a single s orbital, meaning that there is just a single atomic wave function $a^{\mathrm{at}}(\vec{r})$ which is spherically symmetric. Further computation makes use of the localized nature of the atomic wave functions. So, when an integral of the form

$$\int d\vec{r}\; a^{\mathrm{at}}(\vec{r}+\vec{R}')a^{\mathrm{at}}(\vec{r}+\vec{R})$$

appears, set it to zero unless $\vec{R}$ and $\vec{R}'$ are equal, or are nearest neighbors separated by one of the vectors $\vec{\delta}$.

Linear Combinations of Atomic Orbitals (LCAO)

There are only three *overlap integrals* that appear in the computation, namely



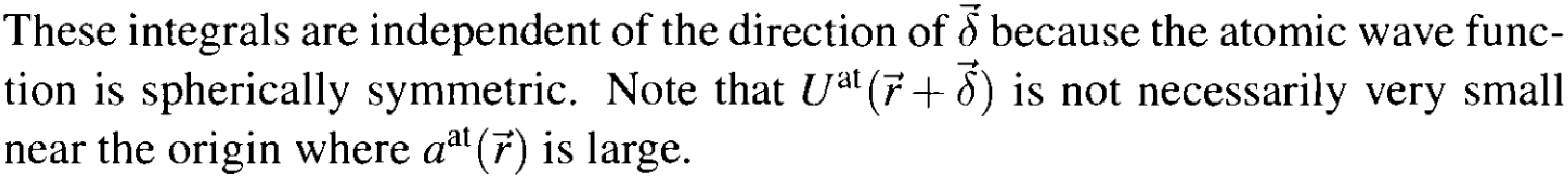
$$\alpha \equiv \int d\vec{r}\; a^{\mathrm{at}}(\vec{r})a^{\mathrm{at}}(\vec{r}+\vec{\delta})$$

$$\mathfrak{U} = \int d\vec{r}\; a^{\mathrm{at}}(\vec{r})[U(\vec{r}) - U^{\mathrm{at}}(\vec{r})]a^{\mathrm{at}}(\vec{r}).$$

Recall that $U(\vec{r}) = \sum_{\vec{R}} U^{\mathrm{at}}(\vec{r}-\vec{R})$

and

$$\mathfrak{t} \equiv \int d\vec{r}\; a^{\mathrm{at}}(\vec{r})[U(\vec{r}) - U^{\mathrm{at}}(\vec{r}+\vec{\delta})]a^{\mathrm{at}}(\vec{r}+\vec{\delta}).$$



These integrals are independent of the direction of $\vec{\delta}$ because the atomic wave function is spherically symmetric. Note that $U^{\mathrm{at}}(\vec{r}+\vec{\delta})$ is not necessarily very small near the origin where $a^{\mathrm{at}}(\vec{r})$ is large.

Linear Combinations of Atomic Orbitals (LCAO)

$$\sum_{n'} C_{nn'} \left(\mathcal{H}_{n''n'} - \mathcal{E}_n \mathcal{S}_{n''n'}\right) = 0$$

Since there is only one orbital, the indices n and n' range over only one value one can call s, and the single constant C_{ss} simply drops out. Thus one can write in the case of a single s orbital that

$$\boxed{\mathcal{E} = \mathcal{H}_{ss}/\mathcal{S}_{ss}.}$$

Linear Combinations of Atomic Orbitals (LCAO)

To evaluate $\mathcal{S}_{ss}$ write

$$\mathcal{S}_{ss} = \sum_{\vec{R}\vec{R}'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} \frac{1}{N} \int d\vec{r}\; a^{\mathrm{at}}(\vec{r}-\vec{R}) a^{\mathrm{at}}(\vec{r}-\vec{R}')$$

The atomic wave functions are real.

$$= 1 + \sum_{\vec{\delta}} e^{i\vec{k}\cdot\vec{\delta}} \int d\vec{r}\; a^{\mathrm{at}}(\vec{r}) a^{\mathrm{at}}(\vec{r}+\vec{\delta})$$

Whenever $\vec{R} = \vec{R}'$ the integral gives 1, and there are N such terms.

$$= 1 + \sum_{\vec{\delta}} e^{i\vec{k}\cdot\vec{\delta}} \alpha$$

Linear Combinations of Atomic Orbitals (LCAO)

$$\langle \Phi_s | \hat{\mathcal{H}} | \Phi_s \rangle = \sum_{\vec{R}\vec{R}'} \int d\vec{r} a^{\mathrm{at}}(\vec{r}-\vec{R})[-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})] a^{\mathrm{at}}(\vec{r}-\vec{R}') \frac{e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}}{N}$$

$$= \sum_{\vec{R}\vec{R}'} \int d\vec{r} a^{\mathrm{at}}(\vec{r}-\vec{R}) \left\{ \begin{array}{l} [-\frac{\hbar^2}{2m}\nabla^2 + U^{\mathrm{at}}(\vec{r}-\vec{R}')] a^{\mathrm{at}}(\vec{r}-\vec{R}') \\ + [U(\vec{r}) - U^{\mathrm{at}}(\vec{r}-\vec{R}')] a^{\mathrm{at}}(\vec{r}-\vec{R}') \end{array} \right\} \frac{e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}}{N}$$

$$= \int d\vec{r} \sum_{\vec{R}\vec{R}'} \mathcal{E}^{\mathrm{at}} \frac{a^{\mathrm{at}}(\vec{r}-\vec{R}) a^{\mathrm{at}}(\vec{r}-\vec{R}')}{N} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}$$

Because a^{at} solves the atomic Hamiltonian with eigenvalue $\mathcal{E}^{\mathrm{at}}$.

$$+ \int d\vec{r} \sum_{\vec{R}\vec{R}'} a^{\mathrm{at}}(\vec{r}-\vec{R})[U(\vec{r}) - U^{\mathrm{at}}(\vec{r}-\vec{R}')] a^{\mathrm{at}}(\vec{r}-\vec{R}') \frac{e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}}{N}$$

$$= \mathcal{E}^{\mathrm{at}}(1 + \alpha \sum_{\vec{\delta}} e^{i\vec{k}\cdot\vec{\delta}}) + \mathcal{U} + \mathfrak{t} \sum_{\vec{\delta}} e^{i\vec{k}\cdot\vec{\delta}}.$$

Linear Combinations of Atomic Orbitals (LCAO)

$$\boxed{\mathcal{E} = \mathcal{H}_{ss}/\mathcal{S}_{ss}.}$$

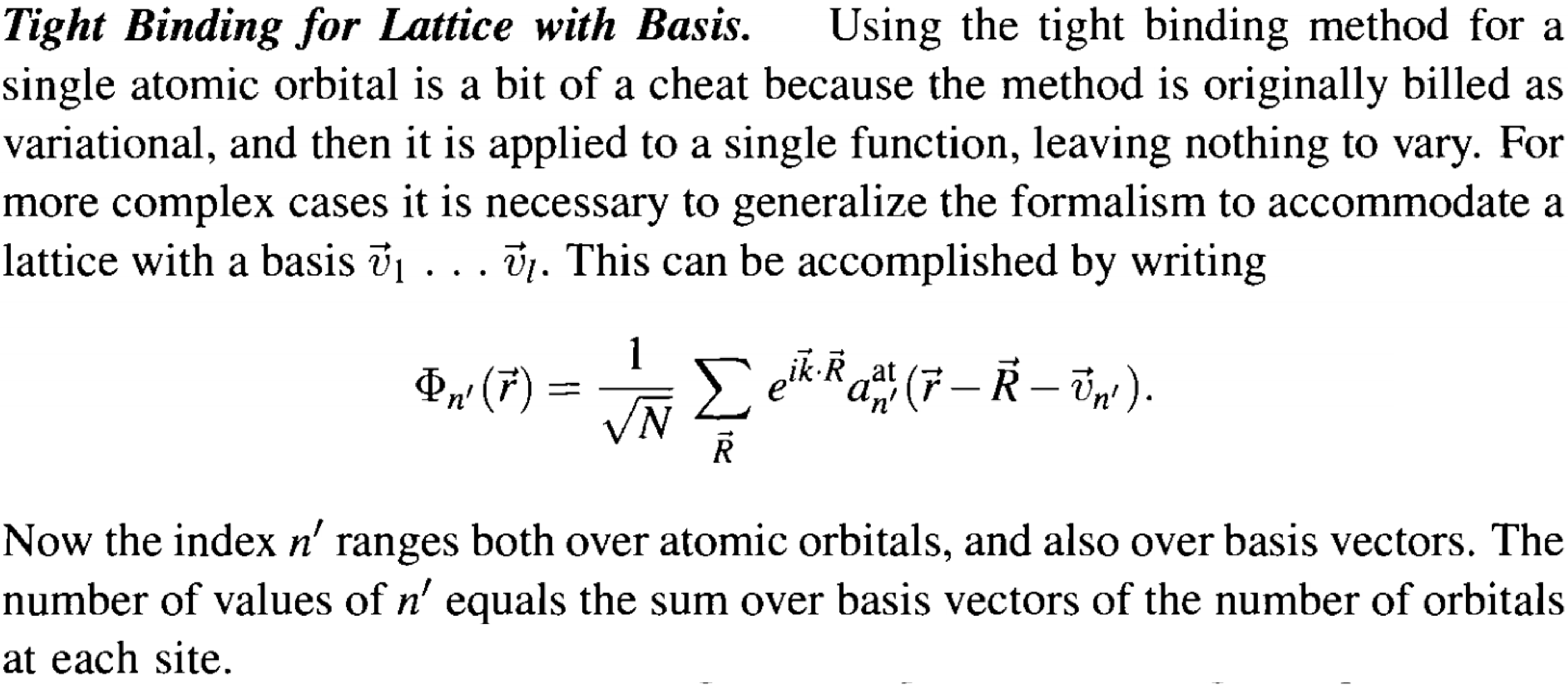
$$\mathcal{E}_{\vec{k}} \approx \mathcal{E}^{\text{at}} + \frac{\mathcal{U} + \mathrm{t}\sum_{\vec{\delta}} e^{i\vec{k}\cdot\vec{\delta}}}{(1 + \alpha\sum_{\vec{\delta}} e^{i\vec{k}\cdot\vec{\delta}})}.$$

Discarding terms of order $\alpha\mathcal{U}$ and $\alpha\mathrm{t}$ on the grounds that α, t, and $\mathcal{U}$ are already small, one obtains

$$\mathcal{E}_{\vec{k}} \approx \mathcal{E}^{\text{at}} + \mathcal{U} + \mathrm{t}\sum_{\vec{\delta}} e^{i\vec{k}\cdot\vec{\delta}}.$$

Energy of tightly bound electrons

Tight Binding for Lattice with Basis



Tight Binding for Lattice with Basis. Using the tight binding method for a single atomic orbital is a bit of a cheat because the method is originally billed as variational, and then it is applied to a single function, leaving nothing to vary. For more complex cases it is necessary to generalize the formalism to accommodate a lattice with a basis $\vec{v}_1 \ldots \vec{v}_l$. This can be accomplished by writing

$$\Phi_{n'}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} a_{n'}^{\text{at}}(\vec{r} - \vec{R} - \vec{v}_{n'}).$$

Now the index n' ranges both over atomic orbitals, and also over basis vectors. The number of values of n' equals the sum over basis vectors of the number of orbitals at each site.

Wannier Functions

Calculations employing atomic orbitals can be put on a much more general footing by constructing *Wannier functions*. These are a set of orthonormal wave functions that one can always construct from Bloch functions and which are plausibly localized on atomic sites.

Suppose that one has found all the eigenfunctions of the Hamiltonian and has arranged them as allowed by Bloch's theorem. Then the Wannier function for electrons from band *n* centered at lattice site ***R*** is defined to be

$$\boxed{\langle \vec{r} | \vec{R} \rangle \equiv w_n(\vec{R}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}} \psi_{n\vec{k}}(\vec{r}).}$$

The Wannier functions form an orthonormal set, as may be seen by computing

$$\int d\vec{r}\, w_n(\vec{R},\vec{r}) w_m^*(\vec{R}',\vec{r}) = \int d\vec{r} \sum_{\vec{k}} \sum_{\vec{k}'} \frac{1}{N} e^{-i\vec{k}\cdot\vec{R}+i\vec{R}'\cdot\vec{k}'} \psi^*_{n\vec{k}}(\vec{r}) \psi_{m,\vec{k}'}(\vec{r})$$

$$= \frac{1}{N} \sum_{\vec{k}\vec{k}'} e^{-i\vec{k}\cdot\vec{R}+\vec{R}'\cdot\vec{k}'} \delta_{m,n} \delta_{\vec{k},\vec{k}'}$$

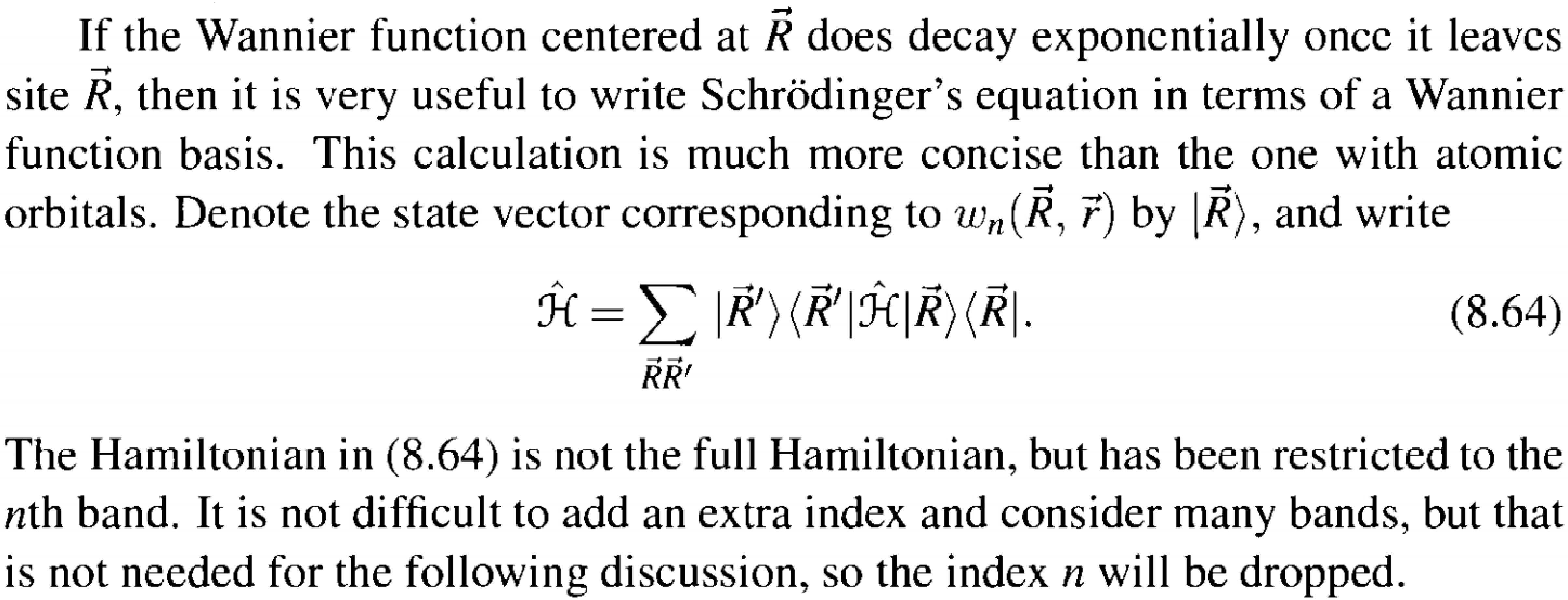
$$= \delta_{\vec{R},\vec{R}'} \delta_{n,m}.$$

The sum is normalized because as shown in Section 7.2.4, the number of $\vec{k}$ in the first Brillouin zone equals N.

If one should happen to know the Wannier functions, the Bloch functions can be recovered from them by computing

$$\frac{1}{\sqrt{N}} \sum_{\vec{R}} w_n(\vec{R},\vec{r}) e^{i\vec{k}\cdot\vec{R}} = \psi_{n\vec{k}}(\vec{r}).$$

Tight Binding Model

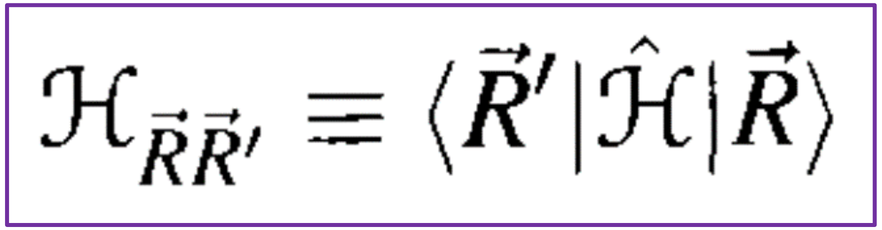


If the Wannier function centered at $\vec{R}$ does decay exponentially once it leaves site $\vec{R}$, then it is very useful to write Schrödinger's equation in terms of a Wannier function basis. This calculation is much more concise than the one with atomic orbitals. Denote the state vector corresponding to $w_n(\vec{R}, \vec{r})$ by $|\vec{R}\rangle$, and write

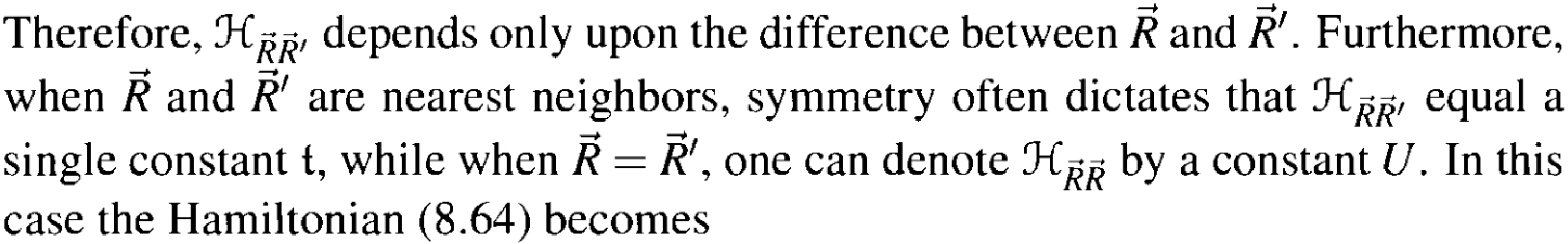
$$\hat{\mathcal{H}} = \sum_{\vec{R}\vec{R}'} |\vec{R}'\rangle\langle\vec{R}'|\hat{\mathcal{H}}|\vec{R}\rangle\langle\vec{R}|. \tag{8.64}$$

The Hamiltonian in (8.64) is not the full Hamiltonian, but has been restricted to the *n*th band. It is not difficult to add an extra index and consider many bands, but that is not needed for the following discussion, so the index *n* will be dropped.

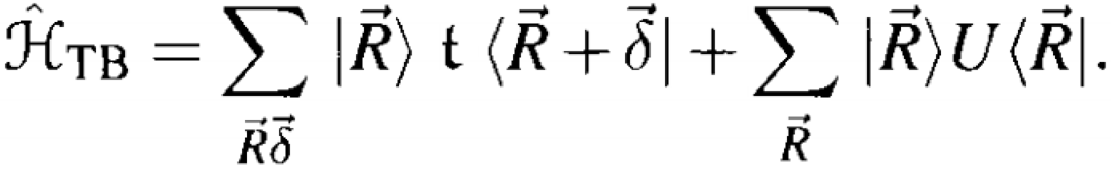
Tight Binding Model



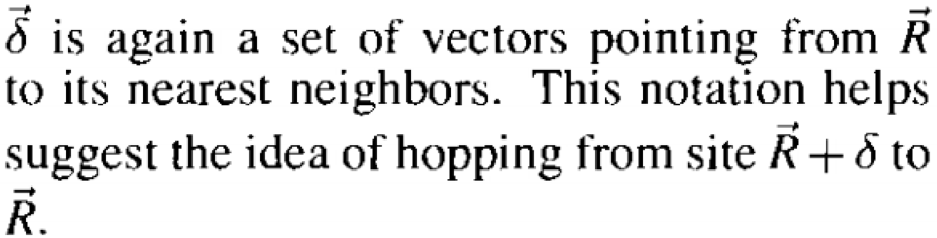
$$\mathcal{H}_{\vec{R}\vec{R}'} \equiv \langle \vec{R}' | \hat{\mathcal{H}} | \vec{R} \rangle$$



Therefore, $\mathcal{H}_{\vec{R}\vec{R}'}$ depends only upon the difference between $\vec{R}$ and $\vec{R}'$. Furthermore, when $\vec{R}$ and $\vec{R}'$ are nearest neighbors, symmetry often dictates that $\mathcal{H}_{\vec{R}\vec{R}'}$ equal a single constant t, while when $\vec{R} = \vec{R}'$, one can denote $\mathcal{H}_{\vec{R}\vec{R}}$ by a constant U. In this case the Hamiltonian (8.64) becomes



$$\hat{\mathcal{H}}_{\mathrm{TB}} = \sum_{\vec{R}\vec{\delta}} |\vec{R}\rangle \, \mathrm{t} \, \langle \vec{R} + \vec{\delta}| + \sum_{\vec{R}} |\vec{R}\rangle U \langle \vec{R}|.$$



$\vec{\delta}$ is again a set of vectors pointing from $\vec{R}$ to its nearest neighbors. This notation helps suggest the idea of hopping from site $\vec{R} + \delta$ to $\vec{R}$.

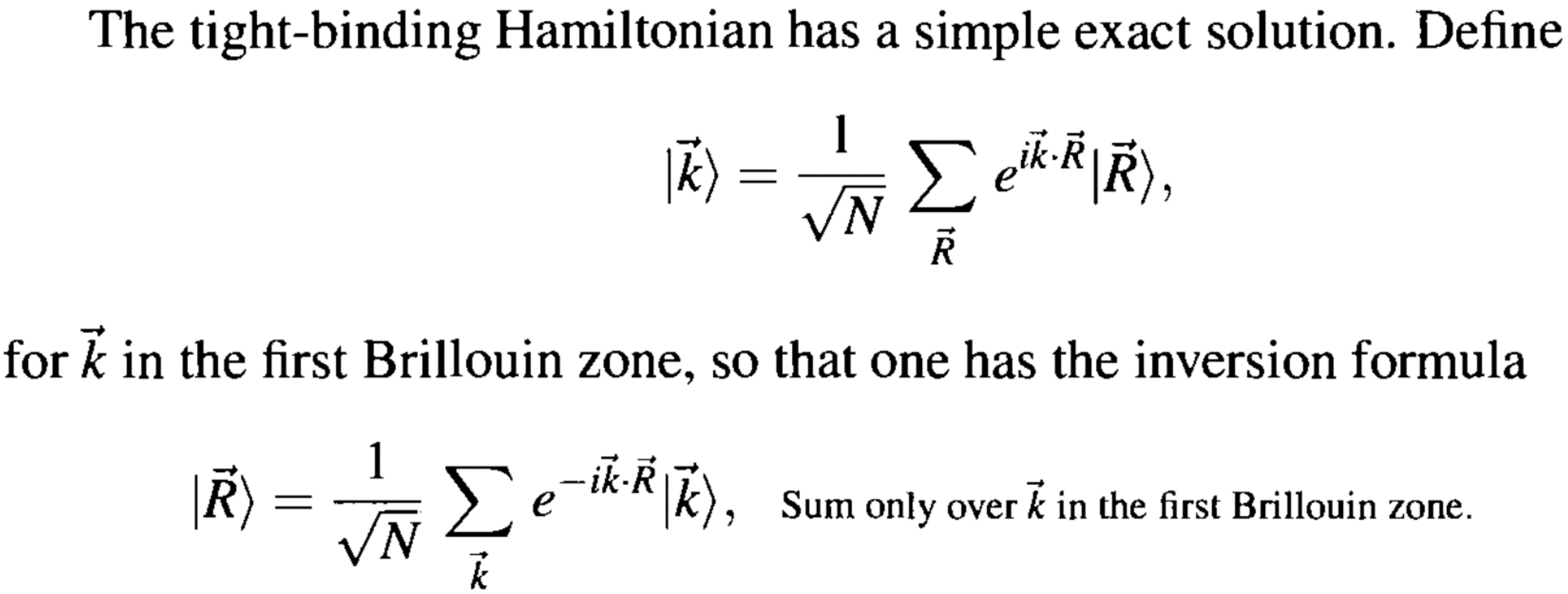
Tight-binding Hamiltonian

Tight Binding Hamiltonian

$$\hat{\mathcal{H}}_{\mathrm{TB}} = \sum_{\vec{R}\vec{\delta}} |\vec{R}\rangle\ t\ \langle\vec{R}+\vec{\delta}| + \sum_{\vec{R}} |\vec{R}\rangle U \langle\vec{R}|.$$

The first term on the right hand side is the hopping term that allows electrons to move from one site to another. The second term is an *on-site term* that describes the energy of placing an electron at a lattice site.

Tight Binding Model



The tight-binding Hamiltonian has a simple exact solution. Define

$$|\vec{k}\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} |\vec{R}\rangle,$$

for $\vec{k}$ in the first Brillouin zone, so that one has the inversion formula

$$|\vec{R}\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}} |\vec{k}\rangle,$$

Sum only over $\vec{k}$ in the first Brillouin zone.

Tight Binding Model

$$\hat{\mathcal{H}}_{\mathrm{TB}} = \sum_{\vec{R}\vec{\delta}} \frac{1}{N} \sum_{\vec{k}\vec{k}'} |\vec{k}\rangle \mathrm{t} e^{-i\vec{k}\cdot\vec{R}+i\vec{k}'\cdot(\vec{R}+\vec{\delta})} \langle\vec{k}'| + \sum_{\vec{R}} \frac{1}{N} \sum_{\vec{k}\vec{k}'} |\vec{k}\rangle U e^{-i\vec{k}\cdot\vec{R}+i\vec{k}'\cdot\vec{R}} \langle\vec{k}'|$$

$$= \sum_{\vec{k}} \mathcal{E}_{\vec{k}} |\vec{k}\rangle \langle\vec{k}|$$

with

$$\mathcal{E}_{\vec{k}} = U + \mathrm{t} \sum_{\vec{\delta}} e^{i\vec{k}\cdot\vec{\delta}}.$$

Tight Binding Model

$$\mathcal{E}_{\vec{k}} \approx \mathcal{E}^{\mathrm{at}} + \mathcal{U} + \mathrm{t} \sum_{\vec{\delta}} e^{i\vec{k}\cdot\vec{\delta}}.$$

$$\mathcal{E}_{\vec{k}} = U + \mathrm{t} \sum_{\vec{\delta}} e^{i\vec{k}\cdot\vec{\delta}}.$$