# CALCULATION OF ENERGY BANDS

Wigner and Seitz, who in 1933 performed the first serious band calculations, refer to afternoons spent on the manual desk calculators of those days, using one afternoon for a trial wavefunction. Here we limit ourselves to three introductory methods: the tight-binding method, useful for interpolation; the Wigner-Seitz method, useful for the visualization and understanding of the alkali metals; and the pseudopotential method, utilizing the general theory of Chapter 7, which shows the simplicity of many problems.

# *Tight Binding Method for Energy Bands*

Let us start with neutral separated atoms and watch the changes in the atomic energy levels as the charge distributions of adjacent atoms overlap when the atoms are brought together to form a crystal. Consider two hydrogen atoms, each with an electron in the 1*s* ground state. The wavefunctions $\psi_A$, $\psi_B$ on the separated atoms are shown in Fig. 16a.

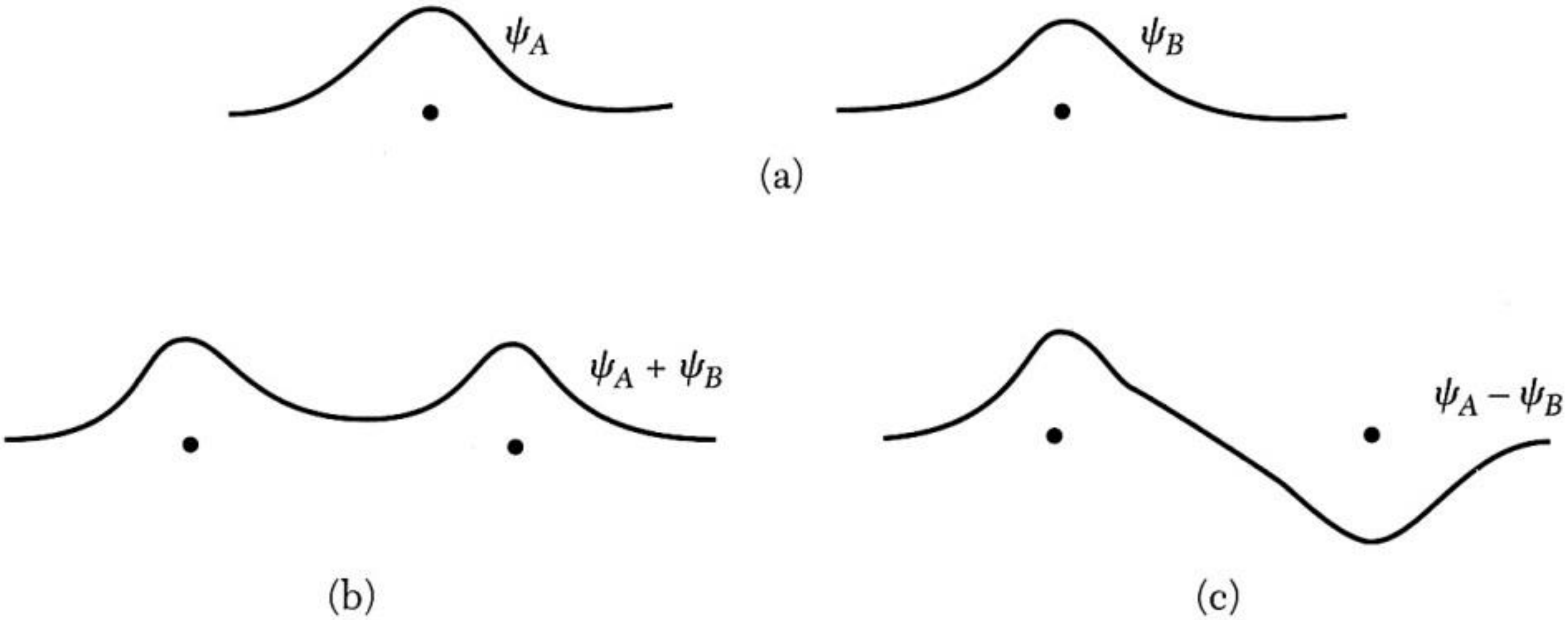

**Figure 16** (a) Schematic drawing of wavefunctions of electrons on two hydrogen atoms at large separation. (b) Ground state wavefunction at closer separation. (c) Excited state wavefunction.

As the atoms are brought together, their wavefunctions overlap. We consider the two combinations $\psi_A \pm \psi_B$. Each combination shares an electron with the two protons, but an electron in the state $\psi_A + \psi_B$ will have a somewhat lower energy than in the state $\psi_A - \psi_B$.

In $\psi_A + \psi_B$ the electron spends part of the time in the region midway between the two protons, and in this region it is in the attractive potential of both protons at once, thereby increasing the binding energy. In $\psi_A - \psi_B$ the probability density vanishes midway between the nuclei; an extra binding does not appear.

As two atoms are brought together, two separated energy levels are formed for each level of the isolated atom. For $N$ atoms, $N$ orbitals are formed for each orbital of the isolated atom (Fig. 17).

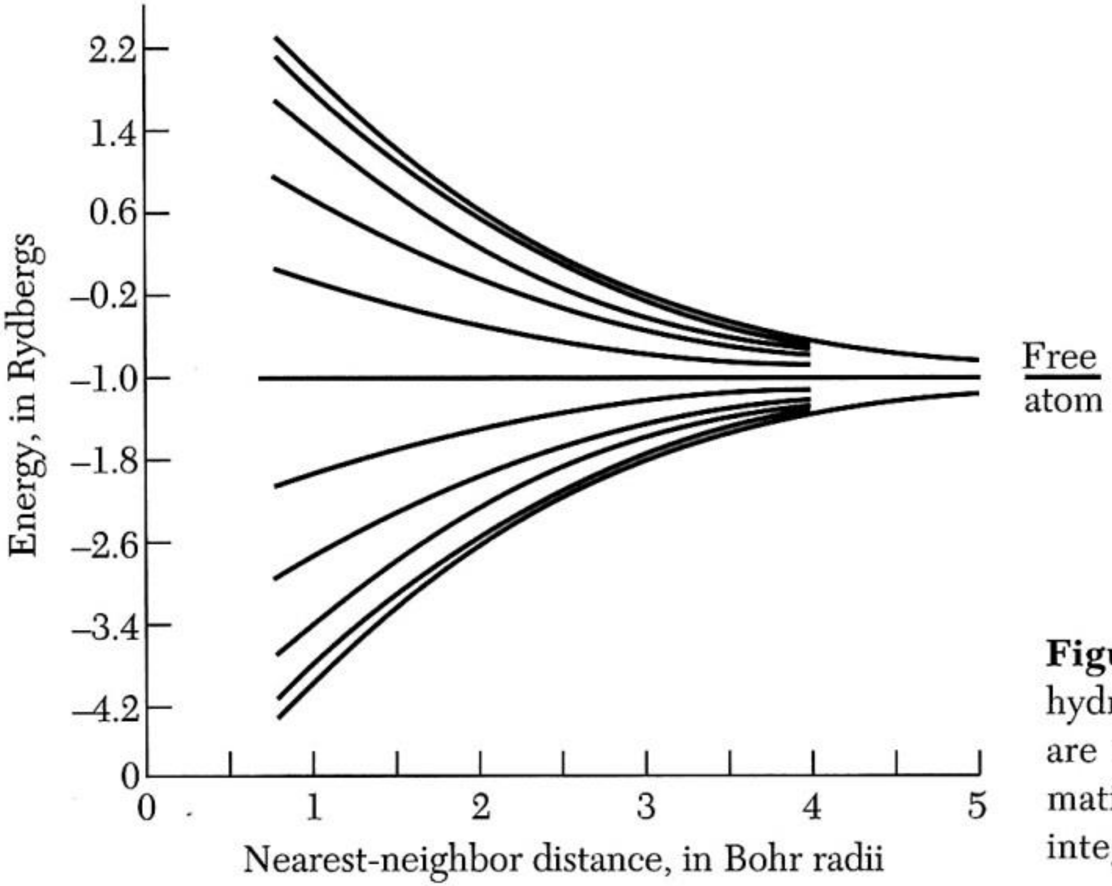

**Figure 17** The 1*s* band of a ring of 20 hydrogen atoms; the one-electron energies are calculated in the tight-binding approximation with the nearest-neighbor overlap integral of Eq. (9).

As free atoms are brought together, the coulomb interaction between the atom cores and the electron splits the energy levels, spreading them into bands. Each state of given quantum number of the free atom is spread in the crystal into a band of energies. The width of the band is proportional to the strength of the overlap interaction between neighboring atoms.

There will also be bands formed from $p$, $d$, . . . states ($l = 1, 2, \ldots$) of the free atoms. States degenerate in the free atom will form different bands. Each will not have the same energy as any other band over any substantial range of the wavevector. Bands may coincide in energy at certain values of $\mathbf{k}$ in the Brillouin zone.

The approximation that starts out from the wavefunctions of the free atoms is known as the tight-binding approximation or the LCAO (linear combination of atomic orbitals) approximation. The approximation is quite good for the inner electrons of atoms, but it is not often a good description of the conduction electrons themselves. It is used to describe approximately the $d$ bands of the transition metals and the valence bands of diamondlike and inert gas crystals.

Suppose that the ground state of an electron moving in the potential $U(\mathbf{r})$ of an isolated atom is $\varphi(\mathbf{r})$, an $s$ state. The treatment of bands arising from degenerate ($p$, $d$, . . .) atomic levels is more complicated. If the influence of one atom on another is small, we obtain an approximate wavefunction for one electron in the whole crystal by taking

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_j C_{\mathbf{k}j}\varphi(\mathbf{r} - \mathbf{r}_j) \ , \tag{4}$$

where the sum is over all lattice points. We assume the primitive basis contains one atom. This function is of the Bloch form (7.7) if $C_{\mathbf{k}j} = N^{-1/2}\, e^{i\mathbf{k}\cdot\mathbf{r}}$, which gives, for a crystal of $N$ atoms,

$$\psi_{\mathbf{k}}(\mathbf{r}) = N^{-1/2} \sum_j \exp(i\mathbf{k}\cdot\mathbf{r}_j)\varphi(\mathbf{r} - \mathbf{r}_j) \ . \tag{5}$$

We prove (5) is of the Bloch form. Consider a translation $\mathbf{T}$ connecting two lattice points:

$$\begin{aligned}\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{T}) &= N^{-1/2}\sum_j \exp(i\mathbf{k}\cdot\mathbf{r}_j)\varphi(\mathbf{r}+\mathbf{T}-\mathbf{r}_j)\\ &= \exp(i\mathbf{k}\cdot\mathbf{T})\, N^{-1/2}\sum_j \exp[i\mathbf{k}\cdot(\mathbf{r}_j-\mathbf{T})]\varphi[\mathbf{r}-(\mathbf{r}_j-\mathbf{T})]\\ &= \exp(i\mathbf{k}\cdot\mathbf{T})\,\psi_{\mathbf{k}}(\mathbf{r})\ ,\end{aligned} \tag{6}$$

exactly the Bloch condition.

We find the first-order energy by calculating the diagonal matrix elements of the hamiltonian of the crystal:

$$\langle\mathbf{k}|H|\mathbf{k}\rangle = N^{-1}\sum_j\sum_m \exp[i\mathbf{k}\cdot(\mathbf{r}_j-\mathbf{r}_m)]\,\langle\varphi_m|H|\varphi_j\rangle\ , \tag{7}$$

where $\varphi_m \equiv \varphi(\mathbf{r}-\mathbf{r}_m)$. Writing $\boldsymbol{\rho}_m = \mathbf{r}_m - \mathbf{r}_j$,

$$\langle\mathbf{k}|H|\mathbf{k}\rangle = \sum_m \exp(-i\mathbf{k}\cdot\boldsymbol{\rho}_m)\int dV\,\varphi^*(\mathbf{r}-\boldsymbol{\rho}_m)H\varphi(\mathbf{r})\ . \tag{8}$$

We now neglect all integrals in (8) except those on the same atom and those between nearest neighbors connected by $\boldsymbol{\rho}$. We write

$$\int dV\, \varphi^*(\mathbf{r})H\varphi(\mathbf{r}) = -\alpha \;;\quad \int dV\, \varphi^*(\mathbf{r}-\boldsymbol{\rho})H\varphi(\mathbf{r}) = -\gamma \;; \tag{9}$$

and we have the first-order energy, provided $\langle \mathbf{k}|\mathbf{k}\rangle = 1$:

$$\boxed{\langle \mathbf{k}|H|\mathbf{k}\rangle = -\alpha - \gamma \sum_m \exp(-i\mathbf{k}\cdot\boldsymbol{\rho}_m) = \epsilon_{\mathbf{k}} \;.} \tag{10}$$

The dependence of the overlap energy $\gamma$ on the interatomic separation $\rho$ can be evaluated explicitly for two hydrogen atoms in $1s$ states. In rydberg energy units, $\mathrm{Ry} = me^4/2\hbar^2$, we have

$$\gamma(\mathrm{Ry}) = 2(1 + \rho/a_0)\exp(-\rho/a_0) \;, \tag{11}$$

where $a_0 = \hbar^2/me^2$. The overlap energy decreases exponentially with the separation.

For a simple cubic structure the nearest-neighbor atoms are at

$$\boldsymbol{\rho}_m = (\pm a,0,0) \ ; \quad (0,\pm a,0) \ ; \quad (0,0,\pm a) \ , \tag{12}$$

so that (10) becomes

$$\epsilon_{\mathbf{k}} = -\alpha - 2\gamma(\cos k_x a + \cos k_y a + \cos k_z a) \ . \tag{13}$$

Thus the energies are confined to a band of width $12\gamma$. The weaker the overlap, the narrower is the energy band. A constant energy surface is shown in Fig. 15. For $ka \ll 1$, $\epsilon_k \simeq -\alpha - 6\gamma + \gamma k^2 a^2$. The effective mass is $m^* = \hbar^2/2\gamma a^2$. When the overlap integral $\gamma$ is small, the band is narrow and the effective mass is high.