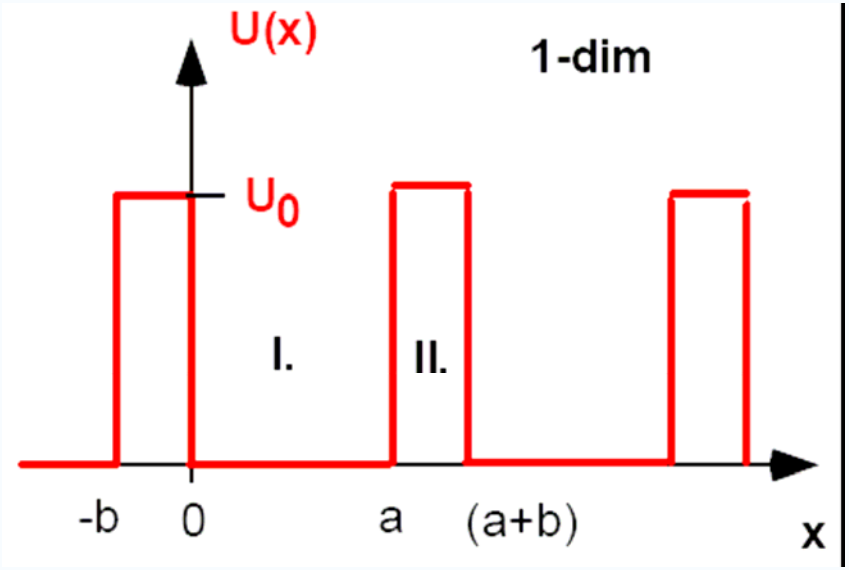
Electronic structure of solids (I)

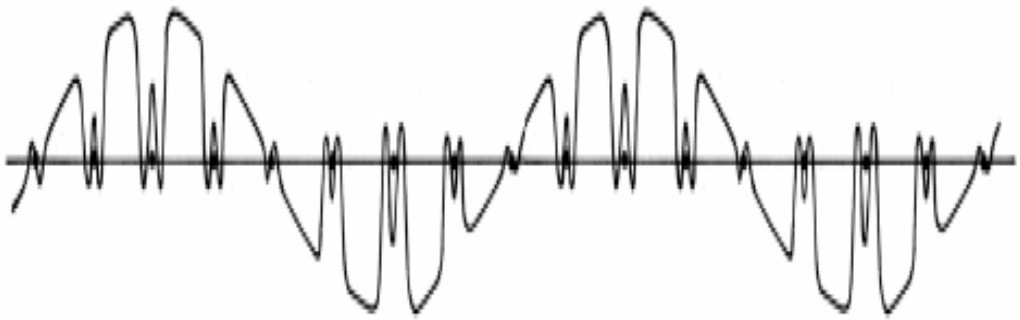
Kronig-Penney model

In order to simplify the problem the potential function is approximated by a rectangular potential:



Using Bloch's theorem,

$$\psi(x) = u_k(x)e^{ik_x x} \quad , \; u_k(x + na) = u_k(x)$$



we only need to find a solution for a single period, make sure it is continuous and smooth, and to make sure the function $u(x)$ is also continuous and smooth. Considering a single period of the potential. We have two regions here. We will solve for each independently:

$$0 < x < a - b : \frac{-\hbar^2}{2m}\psi_{xx} = E\psi$$
$$\Rightarrow \psi = Ae^{i\alpha x} + A'e^{-i\alpha x} \quad \left(\alpha^2 = \frac{2mE}{\hbar^2}\right)$$
$$-b < x < 0 : \frac{-\hbar^2}{2m}\psi_{xx} = (E + V_0)\psi$$
$$\Rightarrow \psi = Be^{i\beta x} + B'e^{-i\beta x} \quad \left(\beta^2 = \frac{2m(E + V_0)}{\hbar^2}\right)$$

In order to find $u(x)$ in each region we need to manipulate the probability function:

$$\psi(0 < x < a - b) = Ae^{i\alpha x} + A'e^{-i\alpha x} = e^{ikx} \cdot \left(Ae^{i(\alpha - k)x} + A'e^{-i(\alpha + k)x}\right)$$
$$\Rightarrow u(0 < x < a - b) = Ae^{i(\alpha - k)x} + A'e^{-i(\alpha + k)x}$$

And in the same manner:

$$u(-b < x < 0) = Be^{i(\beta - k)x} + B'e^{-i(\beta + k)x}$$

To complete the solution we need to make sure the probability function continuous and smooth, i.e:

$$\psi(0^-) = \psi(0^+) \quad \psi'(0^-) = \psi'(0^+)$$

And that $u(x)$ and $u'(x)$ are periodic

$$u(-b) = u(a - b) \quad u'(-b) = u'(a - b).$$

There conditions yield the following matrix:

$$\begin{pmatrix} 1 & 1 & -1 & -1 \\ \alpha & -\alpha & -\beta & \beta \\ e^{i(\alpha-k)(a-b)} & e^{-i(\alpha+k)(a-b)} & -e^{-i(\beta-k)b} & -e^{i(\beta+k)b} \\ (\alpha-k)e^{i(\alpha-k)(a-b)} & (\alpha+k)e^{-i(\alpha+k)(a-b)} & -(\beta-k)e^{-i(\beta-k)b} & (\beta+k)e^{i(\beta+k)b} \end{pmatrix} \begin{pmatrix} A \\ A' \\ B \\ B' \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

In order for us not to have the trivial solution, the determinant of the matrix must be 0. After playing a bit with the determinant we get the following expression:

$$\cos(ka) = \cos(\beta b)\cos[\alpha(a-b)] - \frac{\alpha^2+\beta^2}{2\alpha\beta}\sin(\beta b)\sin[\alpha(a-b)]$$

In order to further simplify the expression, we will perform the following approximations:

$$b \to 0 \ ; \ V_0 \to \infty \ ; \ V_0 b = \text{constant}$$

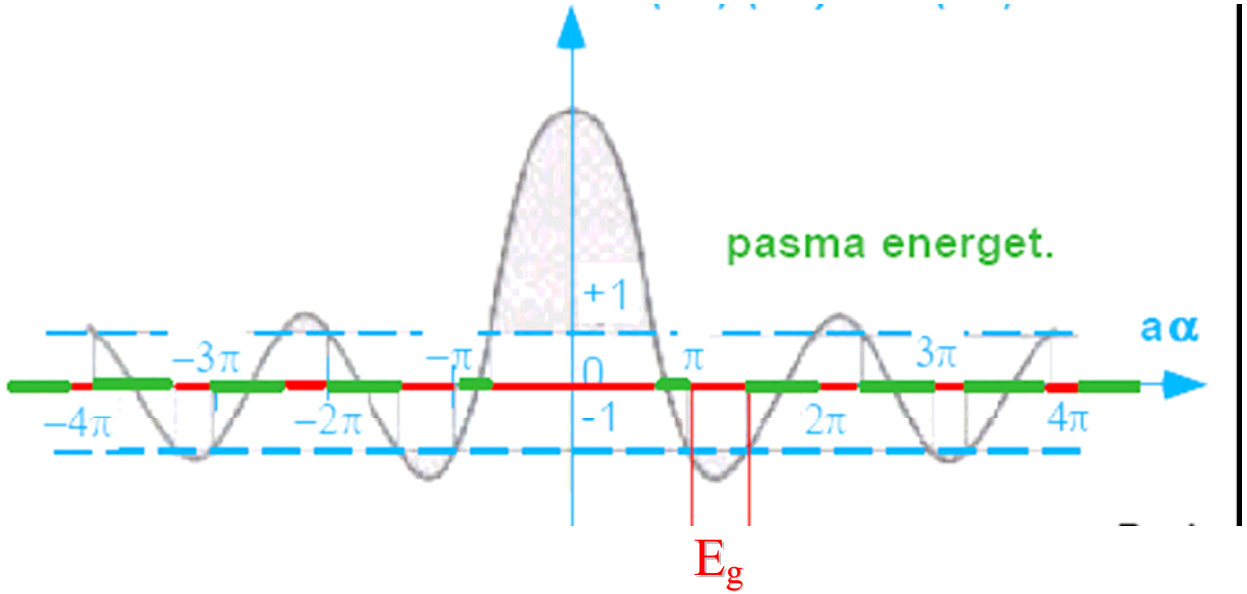
$$\Rightarrow \beta b \to 0 \ ; \ \beta^2 b = \text{constant} \ ; \ \alpha^2 b \to 0 \ ; \ \sin(\beta b) \to \beta b \ ; \ \cos(\beta b) \to 1$$

The expression will now be:

$$\cos(ka) = \cos(\alpha a) - P\frac{\sin(\alpha a)}{\alpha a} \qquad \left(P = \frac{\beta^2 ab}{2}\right)$$

$$\boxed{P\frac{\sin(\alpha a)}{\alpha a} + \cos(\alpha a) = \cos(ka)}$$

depending on energy $E > U_0$ or $E < U_0$



Origin of band gaps: **$-1 \le [\cos(\alpha a) - P \sin(\alpha a)/(\alpha a)] \le 1$**

Band gap width: E_g appears between angles ($n\pi$, $n\pi+2\phi$),

$$2\phi = 2arctg\left(\frac{mU_0}{\hbar^2} ab \frac{1}{a} \frac{\hbar}{\sqrt{2m}} E^{-1/2}\right) = 2arctg\left(\frac{const\sqrt{m}}{\sqrt{2}\hbar} E^{-1/2}\right)$$

$$\alpha = \frac{\sqrt{2m}}{\hbar} E^{1/2}$$

Conclusion: when electron energy increases energy gap (2ϕ) decreases, since electrons become to be more free.

Linear Combination of Atomic Orbitals (LCAO):

(2 atoms- e.g. hydrogen H_2)

$$H = T + V_1(\mathbf{r}) + V_2(\mathbf{r})$$

where T is the *kinetic energy* operator for the electron, $V_1(\mathbf{r})$ is the *Coulomb potential energy* operator describing the interaction of the electron with proton 1, and the last term, $V_2(\mathbf{r})$ is just the same thing but with proton 2. We will label our basis functions simply as |1> (1s function centred on proton 1) and |2> (1s function centred on proton 2). Then we have:

$$\langle 1|H|1\rangle = \langle 1|T + V_1(\mathbf{r})|1\rangle + \langle 1|V_2(\mathbf{r})|1\rangle = E_{1s} + V$$

Here, E_{1s} is the energy of the ground state of the isolated hydrogen atom, and V is the energy of interaction of the electron with the second proton.

The second matrix element, <1|H|2>, will look like this:

$$\langle 1|H|2\rangle = \langle 1|T + V_2(\mathbf{r})|2\rangle + \langle 1|V_1(\mathbf{r})|2\rangle.$$

But notice that the first term in the right hand side is zero, because we are assuming that <1| and |2> form an orthonormal set, and thus

$$\langle 1|T + V_2(\mathbf{r})|2\rangle = \langle 1|E_{1s}|2\rangle = E_{1s}\langle 1|2\rangle = 0.$$

Therefore we have

$$\langle 1|H|2\rangle = \langle 1|V_1(\mathbf{r})|2\rangle = W$$

Likewise, it is easy to see that the other remaining integrals are

$$\langle 2|H|1\rangle = \langle 1|H|2\rangle = W \quad \text{and} \quad \langle 2|H|2\rangle = \langle 1|H|1\rangle = E_{1s} + V$$

So, we now have the matrix form of the Hamiltonian for the H^+_2 molecule. Now, let's turn to the wave function; we still don't know what this is, but we do know that it will be expressed in terms of our basis set as

$$|\psi\rangle = C_1\,|1\rangle + C_2\,|2\rangle,$$

i.e. as a linear combination of our chosen basis set, the two 1s functions centred on either proton. And we also know that the wave function will be the solution of the Schrödinger equation. So let us write down the Schrödinger equation in matrix form:

$$\begin{bmatrix} \langle 1|H|1\rangle & \langle 1|H|2\rangle \\ \langle 2|H|1\rangle & \langle 2|H|2\rangle \end{bmatrix} \begin{bmatrix} C1 \\ C2 \end{bmatrix} = E \begin{bmatrix} C1 \\ C2 \end{bmatrix}$$

which, after some rearrangement is seen to be equivalent to

$$\begin{bmatrix} E1s + V - E & W \\ W & E1s + V - E \end{bmatrix} \begin{bmatrix} C1 \\ C2 \end{bmatrix} = 0$$

This system of equations can only have non-trivial solutions if the following condition holds

$$det \begin{bmatrix} E1s + V - E & W \\ W & E1s + V - E \end{bmatrix} = 0$$

which gives us a quadratic equation for the eigenvalue E, which once solved has two solutions:

$E_b = E_{1s} + V + W$ and $E_a = E_{1s} + V - W$

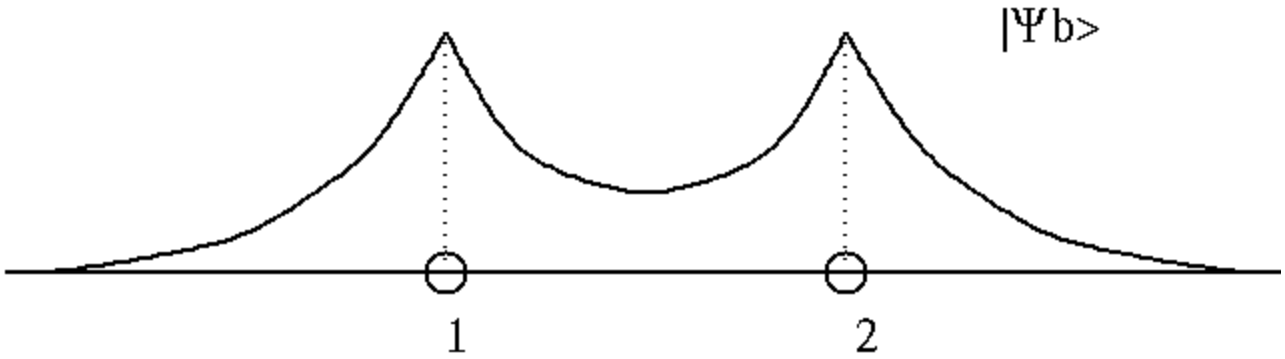
Thus we have obtained, in equations, the two eigenvalues of the system.

Wave functions and bond charge

To obtain the corresponding eigenstates, we take each of the found eigenvalues in turn and, substituting them in the Schrödinger equation, we solve for the values of C_1 and C_2. When we do this we find

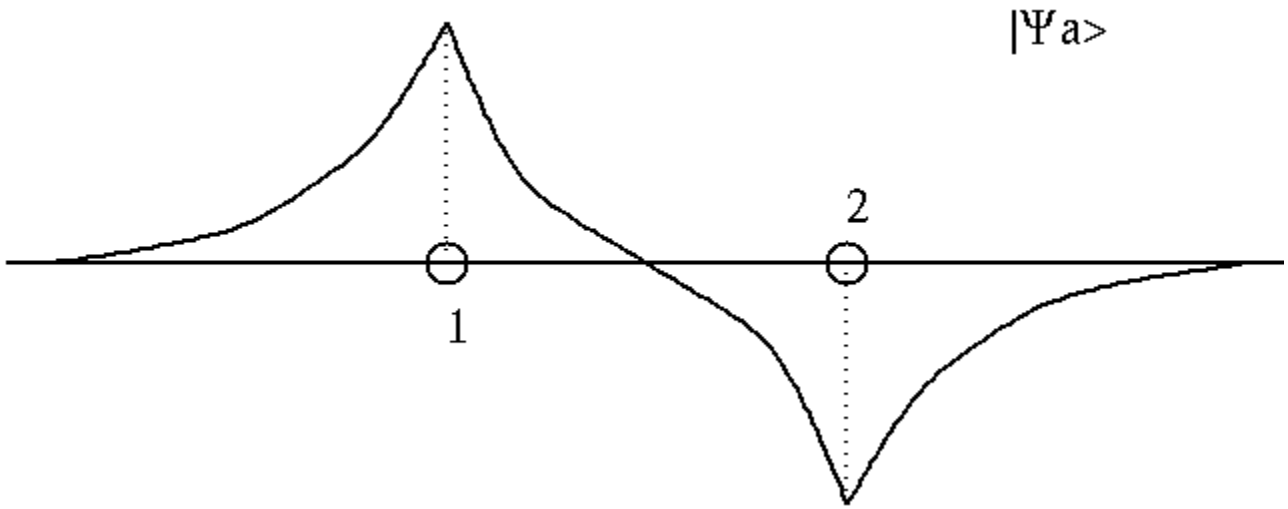
$$|\psi_b\rangle = N\,(\,|1\rangle + |2\rangle) \qquad \text{and} \qquad |\psi_a\rangle = N\,(\,|1\rangle - |2\rangle)$$

where N is a normalisation constant (equal to $2^{-½}$). Because W is negative, E_b is the lowest of the two eigenvalues, i.e. it is the energy of the ground state. $|\psi_b\rangle$, the ground state wave function, looks pictorially like this:

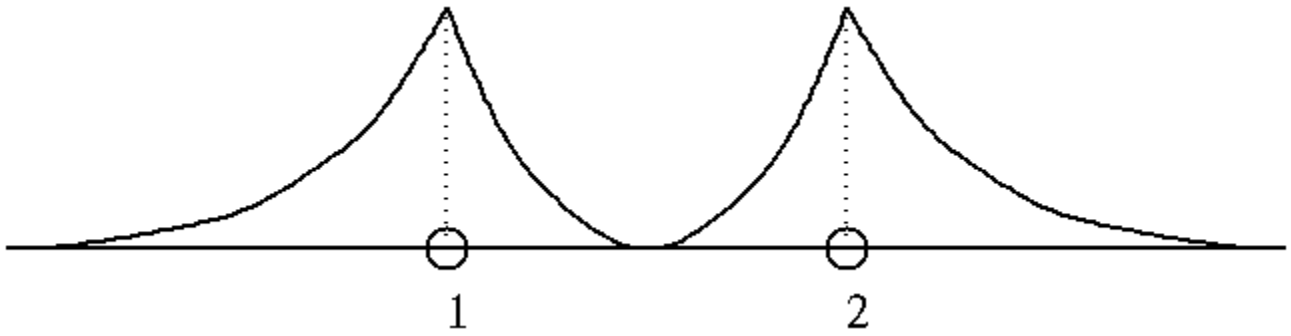


The charge density, $|\psi_b|^2$, looks more or less similar. As you can see, there is a build up of electronic charge in the region between the two protons, and this build up of charge helps to hold the molecule together, constituting a chemical bond. Because the molecule is actually held together by the sharing of an electron between two nuclei, this is an example of a *covalent* chemical bond.

However, for the excited state, the wave function looks like this:



and the charge density (the squared norm of the wave function) looks like this:



Given a system characterised by the Hamiltonian H, and given an approximate wave function for the ground state of the system, ψ, then we can evaluate the following quantity

$$R_c = [\int \psi^* H \psi d\mathbf{r}] / [\int \psi^* \psi d\mathbf{r}]$$

which is known as the Rayleigh quotient. The Variational principle states simply that the Rayleigh quotient provides a value R_c which is *always larger* than the exact energy of the ground state, i.e.

$$R_c \geq E_{exact}$$

the equality occurring if and only if ψ is the exact wave function.

The variational principle is important not only because it tells us that an approximate wave function always gives an energy higher than the exact one, but it also tells us how to improve our approximate wave functions. Imagine that we have a basis set $\{\phi\}$ in which we wish to expand the wave function ψ, namely:

$$\psi = \sum_n c_n \phi_n.$$

Then the Rayleigh quotient would be written as

$$R_c = [\sum_m \sum_n c_m^* c_n H_{mn}] / [\sum_m \sum_n c_m^* c_n S_{mn}]$$

where

$$H_{nm} = \int \phi_m^* H \phi_n d\mathbf{r} \qquad \text{and} \qquad S_{nm} = \int \phi_m^* \phi_n d\mathbf{r}$$

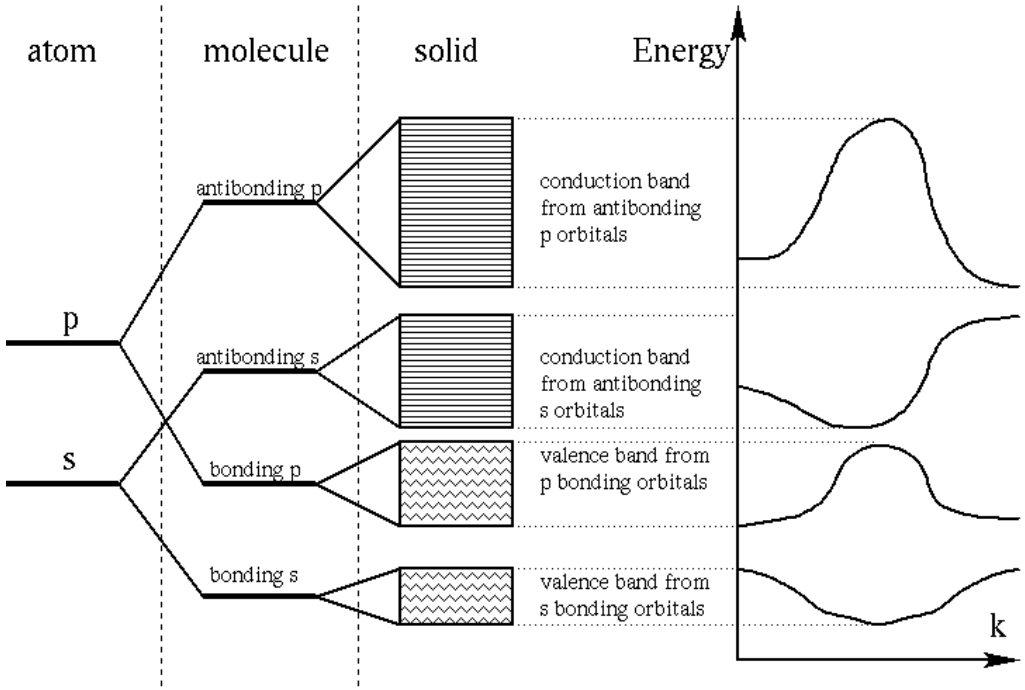
Coulomb integral **Overlap intergral**

are the Hamiltonian and overlap matrix elements respectively.

The condition that the Rayleigh quotient R_c be a minimum with respect to the values of the expansion coefficients is that the partial derivatives of the quotient with respect to each coefficient be all equal to zero. In other words:

$$\sum_n (H_{mn} - E S_{mn}) C_n = 0 \qquad \text{for all m.}$$

These constitute a set of N linear equations in the unknown coefficients C_n, where N is the size of the basis set. This type of set of linear equations constitutes an eigenvalue problem. The equations only have solution for certain allowed values of the energy E, the eigenvalues of the system. For each allowed value E_i, there is a non-trivial solution, i.e. a set of values of the coefficients $C_n^{(i)}$, which give the best approximation to the wave function of state i, within this basis set. This set of equations can be written in a more compact form using matrix notation as $HC = ESC$, where now C is a vector of length N, with each element being one of the C_n coefficients.



The general feature of the TB method is already clear from the 1D case of a line or ring of atoms. When overlaps are allowed only between nearest neighbours, the energy depends on k as cos(ka), i.e.

$$E = \alpha + \beta\cos(ka)$$

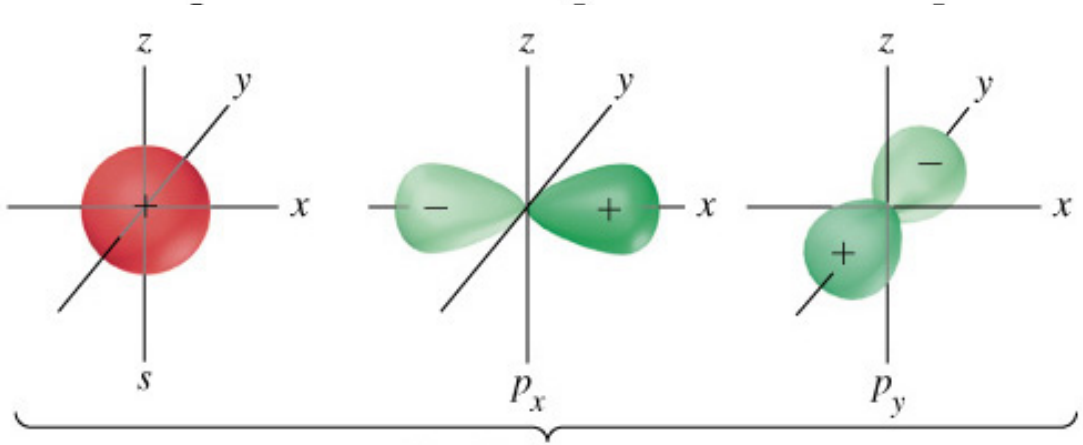
where $-\pi/a < k < \pi/a$ and a is the spacing along the chain. This says that k is confined to the first Brillouin zone. When more overlaps are allowed, e.g. with second nearest neighbours at distance $2a$, then the term in β becomes a sum of different βs, each with their own value, and correponding cosine terms with argument $(2ka)$, etc.

Generating corresponding series for 2D and 3D geometries of course involves the reciprocal lattice and the vector **k**, but is otherwise analogous. Thus the simplest 2D or 3D case, for centro-symmetric crystals, has an energy structure

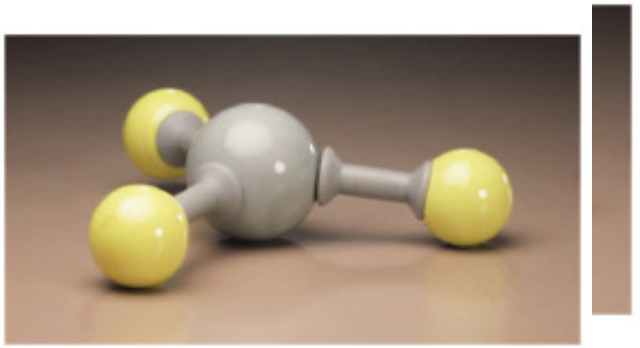
$$E = \alpha + 2\beta\{\sum_{\mathbf{R}}\cos(\mathbf{k}.\mathbf{R})\}$$

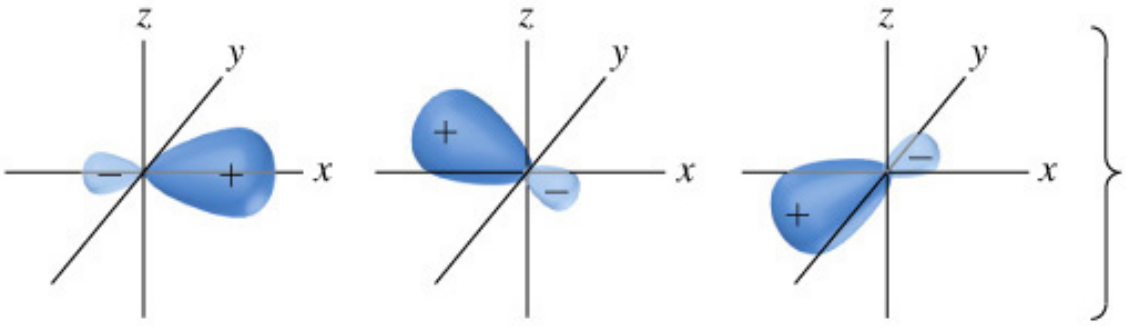
where the atom neighbours are found at positions + and - **R** with respect to the atom under consideration. Thus the band structure depends on the crystal structure via **R**, and the energy is a function of both the magnitude and the direction of **k**.

sp^2 Hybrid atomic orbitals

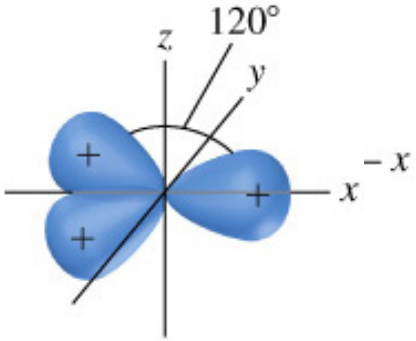


Combine to generate three sp^2 orbitals

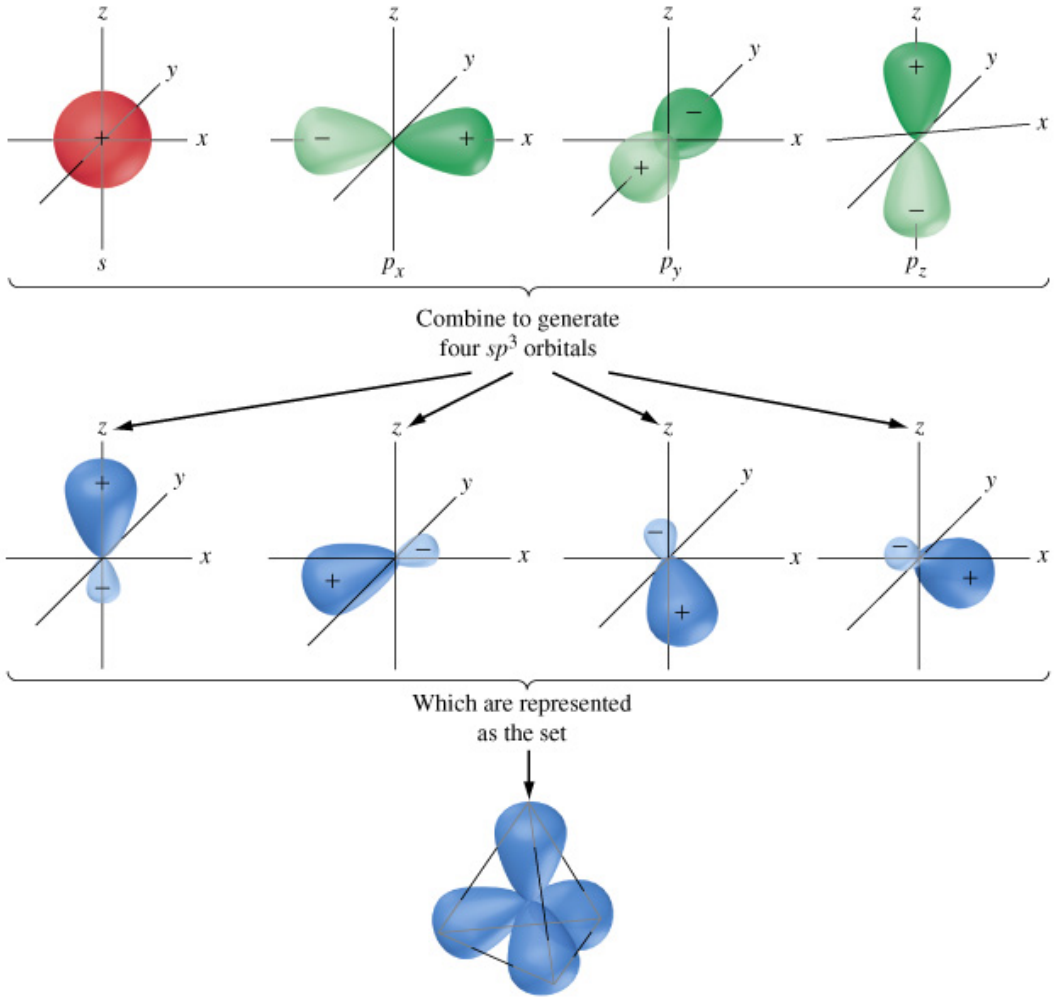


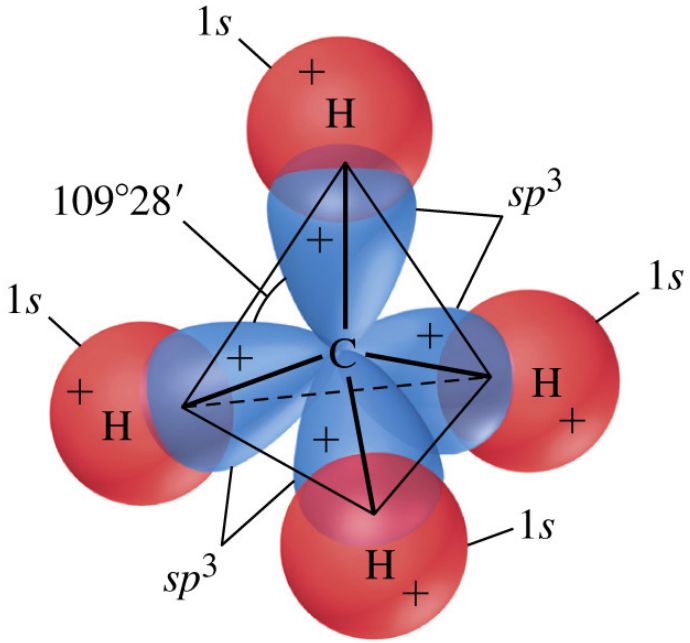


Which are represented as the set

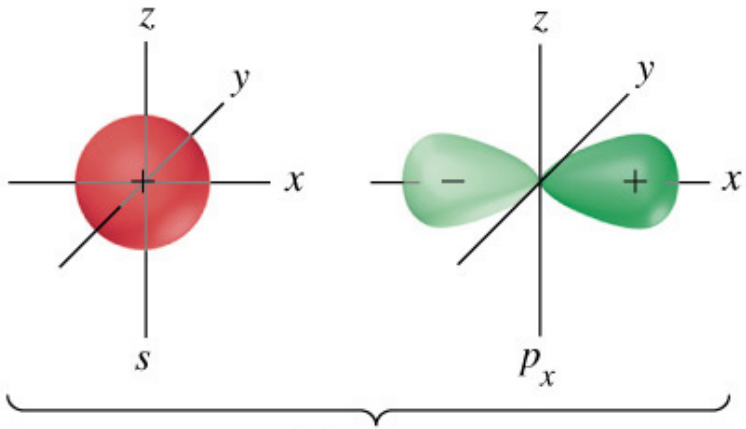


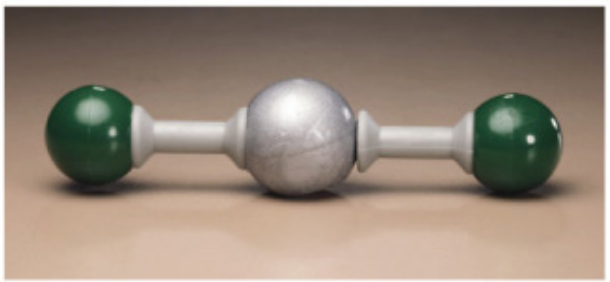
sp^3 Hybrid atomic orbitals

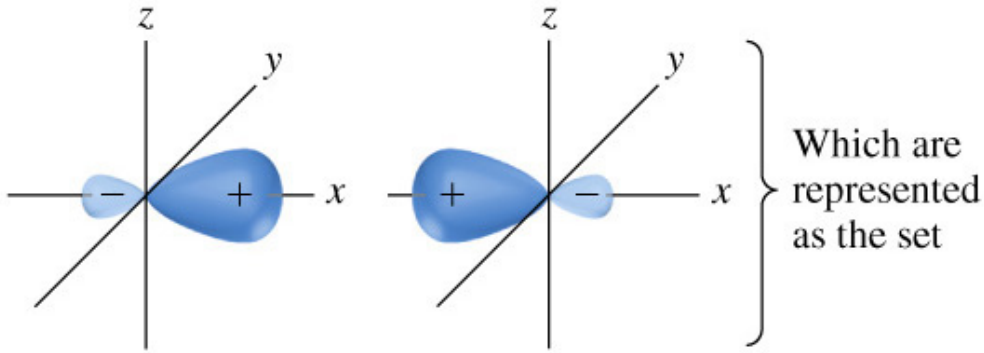


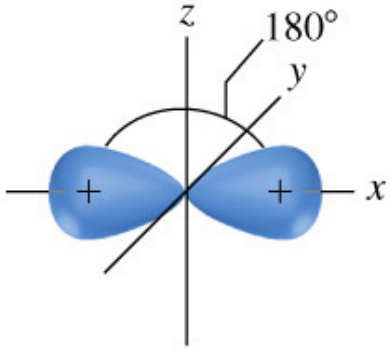


sp Hybrid atomic orbitals

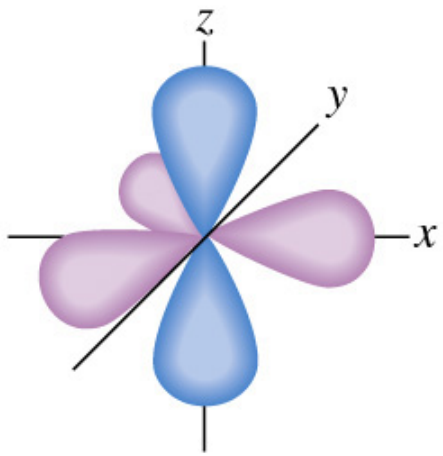




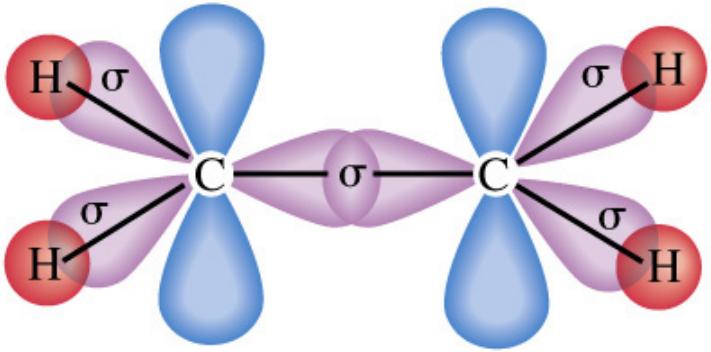




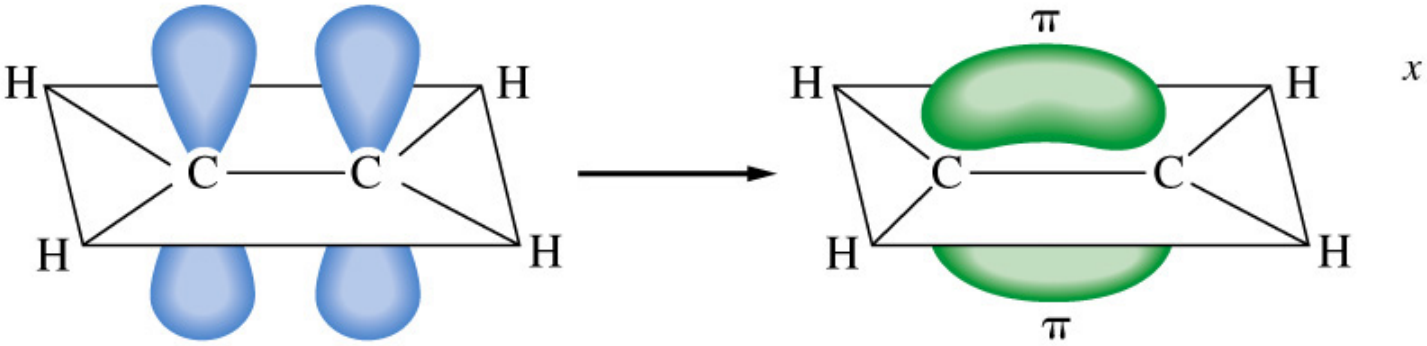
Multiple bonds with VB



The set of orbitals $sp^2 + p$

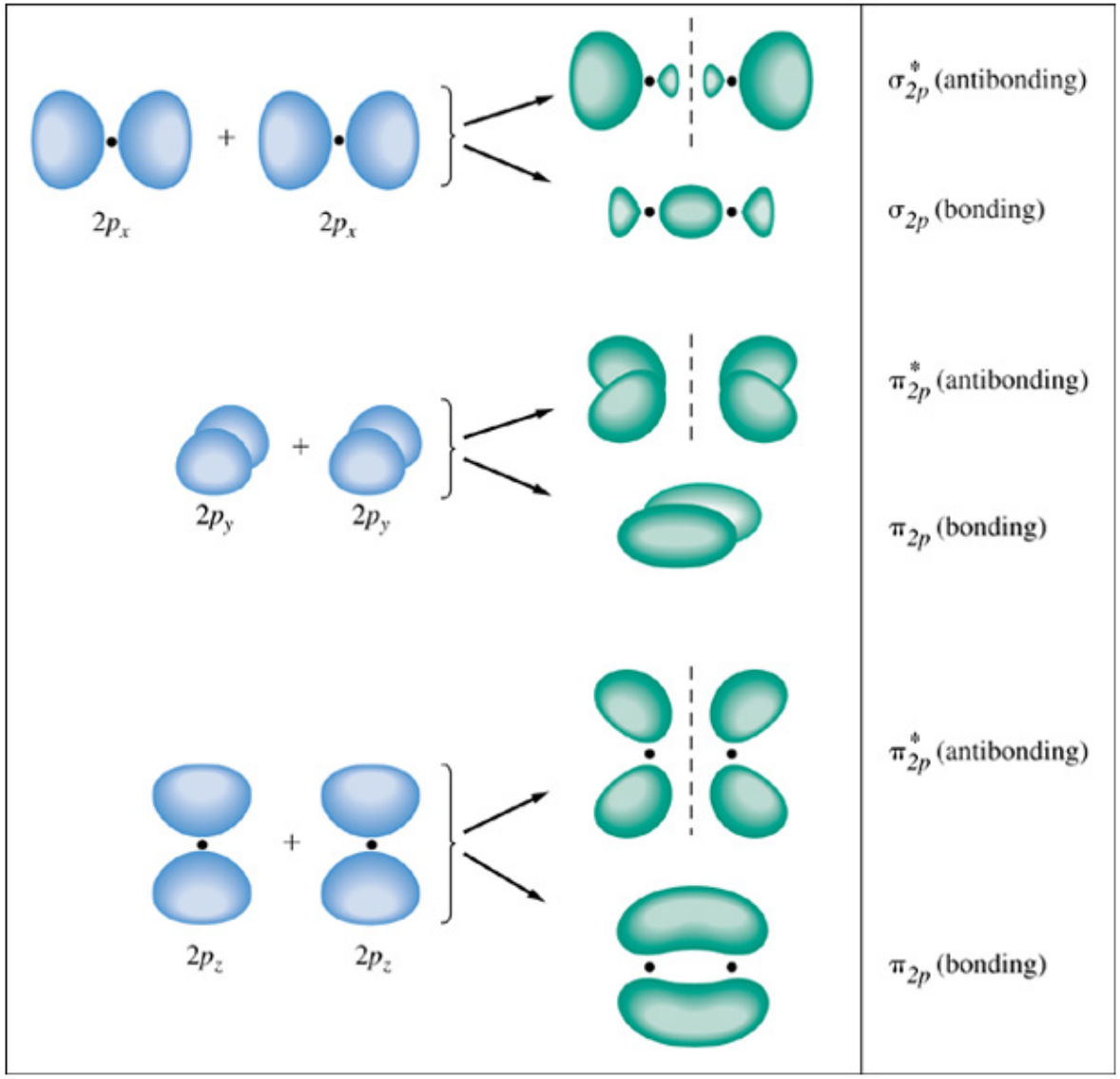


Sigma (σ) bonds

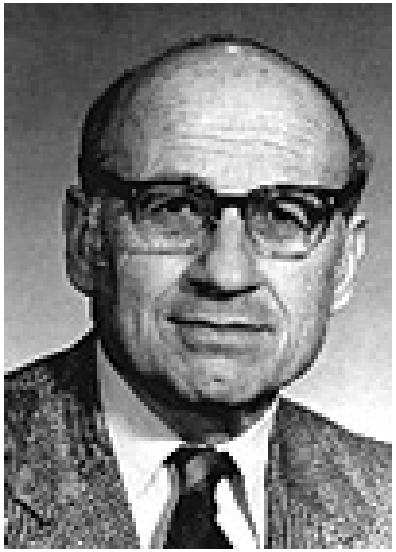


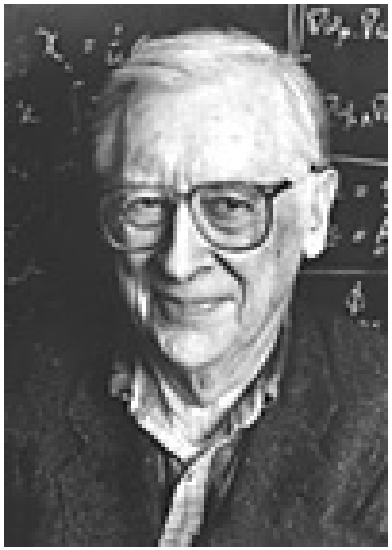
Overlap of p orbitals leading to pi (π) bond

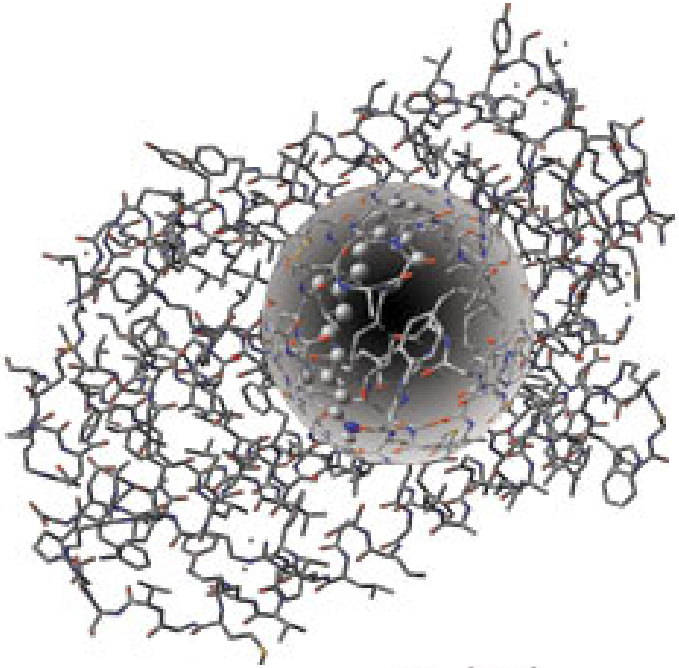
Molecular Orbitals from p A.O.

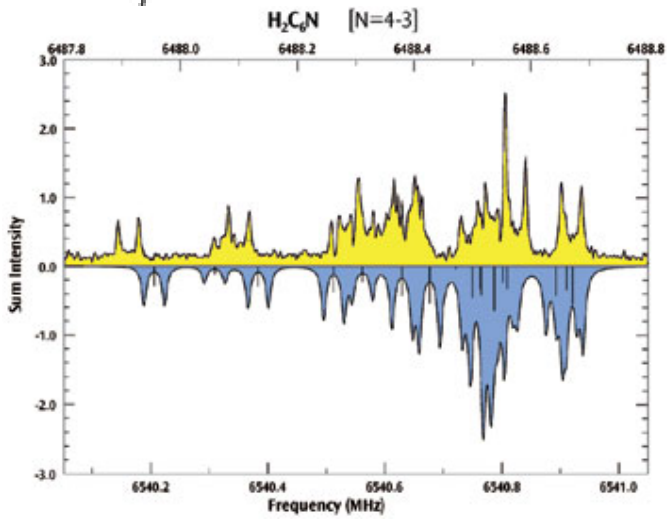


Modern MO calculations





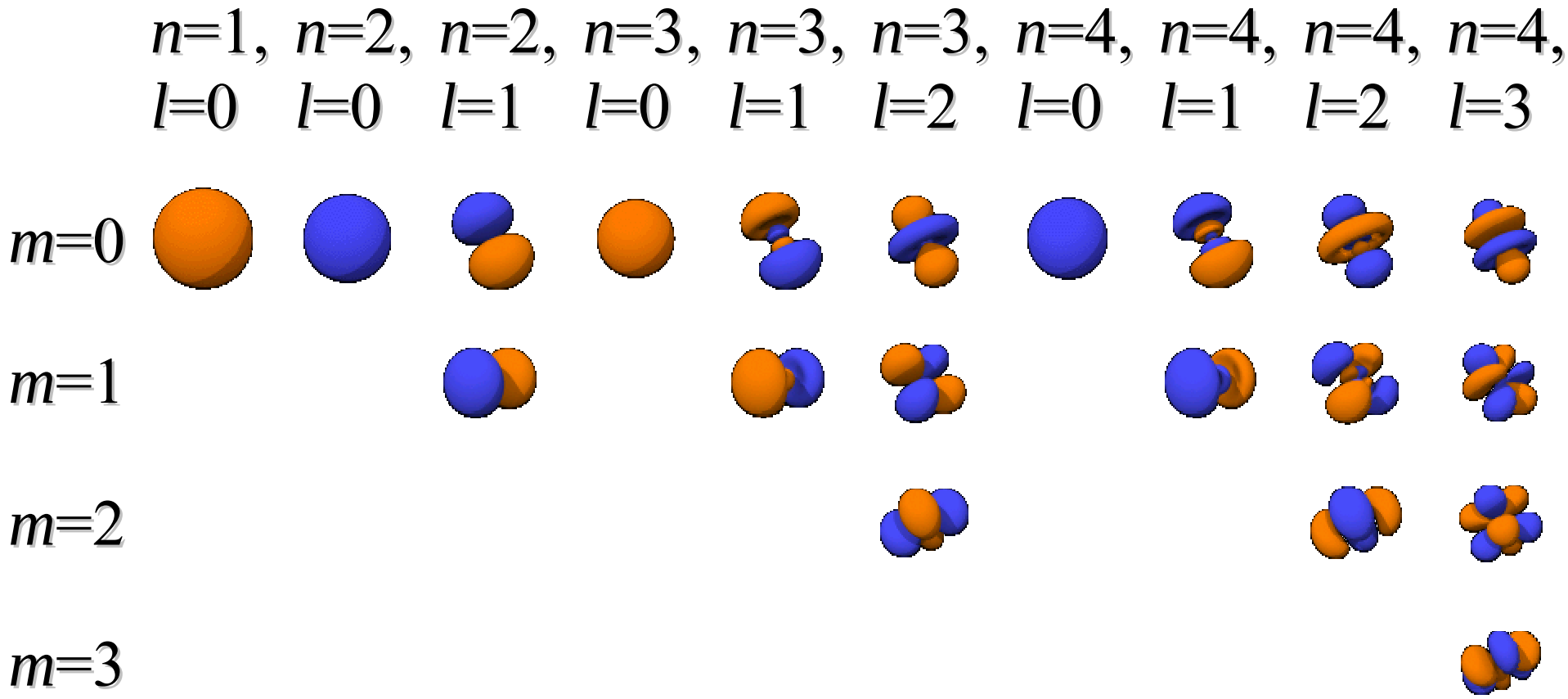




W. Kohn (1923-)

J. A. Pople (1925-2004)

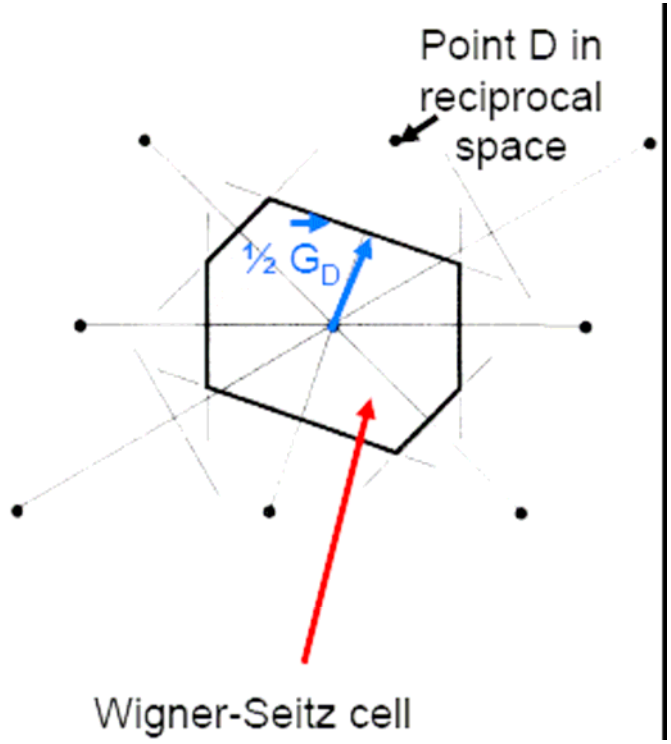
Nobel prize in Chemistry 1998


n=1, l=0
n=2, l=0
n=2, l=1
n=3, l=0
n=3, l=1
n=3, l=2
n=4, l=0
n=4, l=1
n=4, l=2
n=4, l=3
m=0
m=1
m=2
m=3

Theory of Brillouin zones and Fermi surface

A Brillouin Zone is defined as a Wigner-Seitz primitive cell in the reciprocal lattice.To find this, draw the reciprocal lattice. Then, use the same algorithm as for finding the Wigner-Seitz primitive cell in real space (draw vectors to all the nearest reciprocal lattice points, then bisect them. The resulting figure is your cell).The nice result of this is that it has a direct relation to the diffraction condition:

$$\mathbf{k} \cdot \tfrac{1}{2}\mathbf{G} = (G/2)^2$$



The zone we have drawn above using the Wigner-Seitz method is called the first Brillouin zone. The zone boundaries are k = +/-π/a (to make the total length to a side 2π/a in reciprocal space).The 1 st Brillouin zone is the smallest volume entirely enclosed by the planes that are perpendicular bisectors of the reciprocal lattice vectors drawn from the origin. Usually, we don't consider higher zones when we look at diffraction. However, they are of use in energy-band theory.

The set of all wave vectors **K** that yield plane waves with the periodicity of a given Bravais lattice is known as its reciprocal lattice. Analytically, **K** belongs to the reciprocal lattice of a Bravais lattice of points **R**, provided that the relation

$$e^{i\mathbf{K}\cdot(\mathbf{r}+\mathbf{R})} = e^{i\mathbf{K}\cdot\mathbf{r}}$$

holds for any **r**, and all **R** in Bravais lattice. Factoring out $e^{i\mathbf{K}\cdot\mathbf{r}}$

we can characterize the reciprocal lattice as the set of wave vectors **K** satisfying

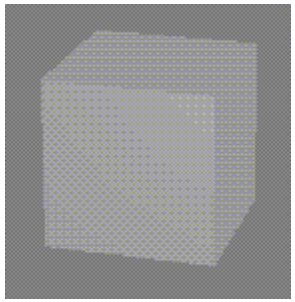
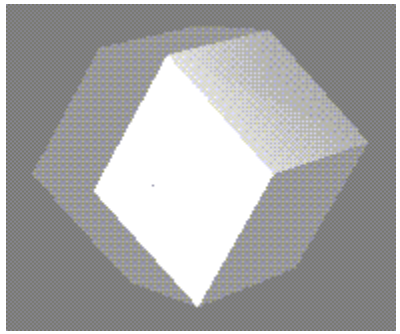
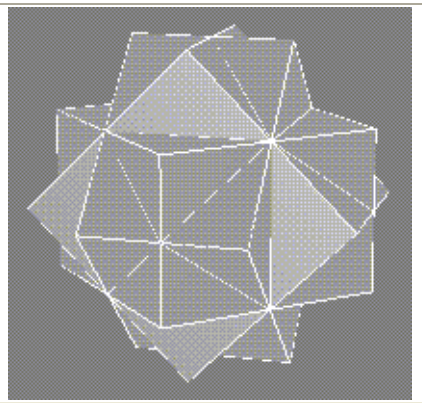
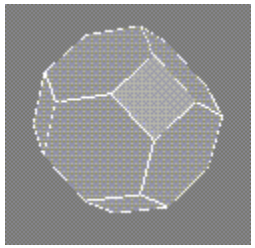
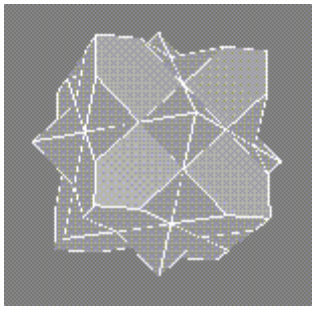
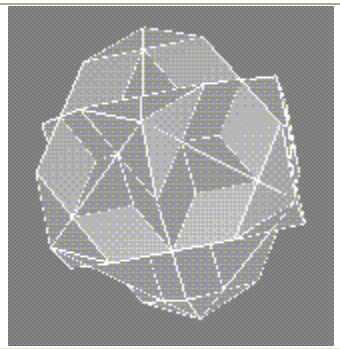
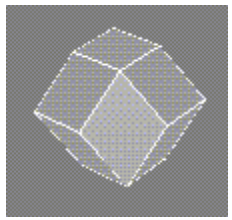
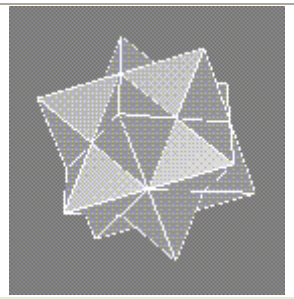
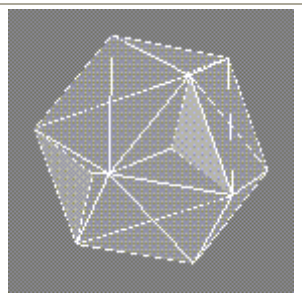
$$e^{i\mathbf{K}\cdot\mathbf{R}} = 1 \qquad \text{for all } \mathbf{R} \text{ in the Bravais lattice.}$$

The reciprocal lattice is itself a Bravais lattice and its primitive vectors can be generated from the vectors of the direct lattice. Let $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ be a set of primitive vectors, then the reciprocal lattice can be generated by the three primitive vectors:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \qquad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \qquad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

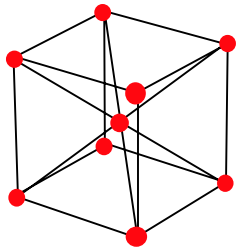
Using the relations between direct and reciprocal lattice it can be shown that the reciprocal lattice of *sc* is *sc* (at **k** space), the reciprocal of *bcc* is *fcc*, and reciprocal of *fcc* is *bcc*.

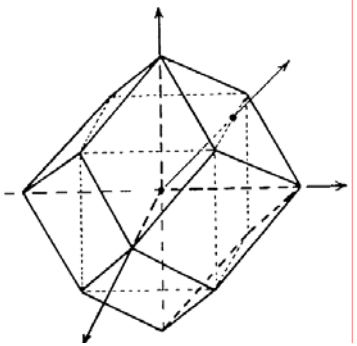
The first Brillouin zone could be defined as the set of points in **k** space that can be reached from the origin without crossing any Bragg plane; The second Brillouin zone is the set of points that can be reached from the first zone by crossing only one Bragg plane. The (*n* + 1)th Brillouin zone is the set of points not in the (*n* - 1)th zone that can be reached from the *n*th zone by crossing *n* - 1 Bragg planes.

	First zone	Second zone	Third zone
sc			
fcc			
bcc			

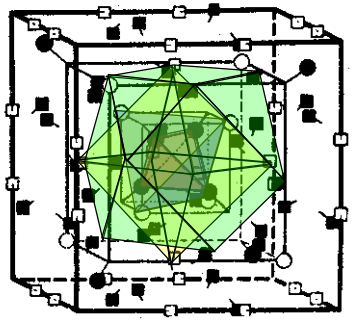
More complex cases: unit cell and corresponding Brillouin zone in different structures

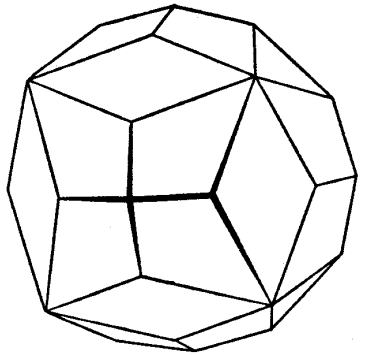
bcc, N=2, dodecahedron with 12 planes



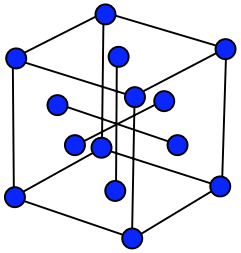


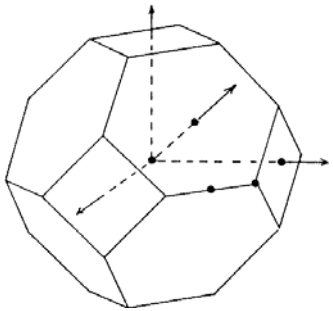
gamma-brass, N=52, polyhedron with 36 planes



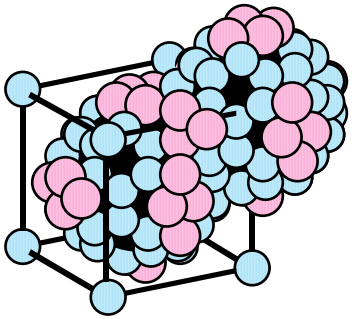


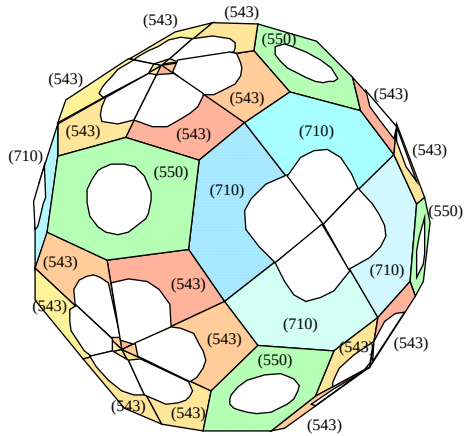
fcc, N=4, truncated octahedron with 14 planes



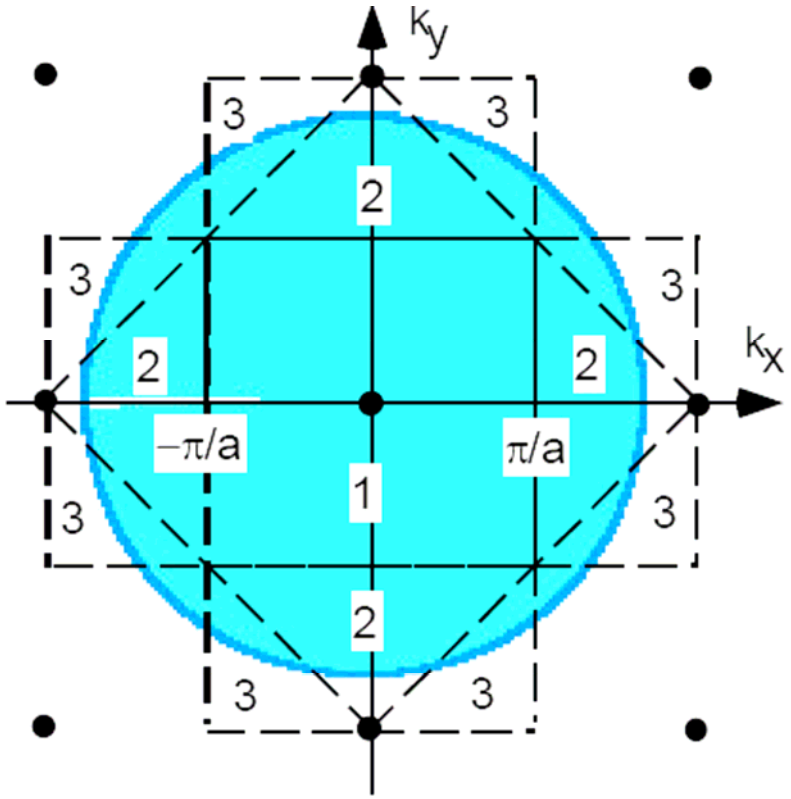


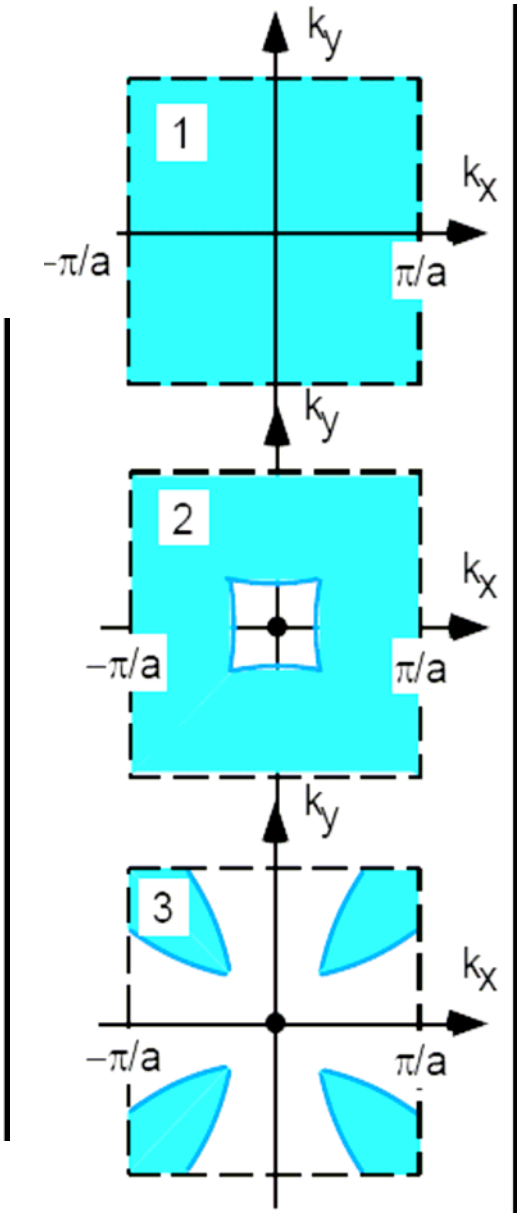
1/1-1/1-1/1 approximant, N=160, polyhedron with 84 planes

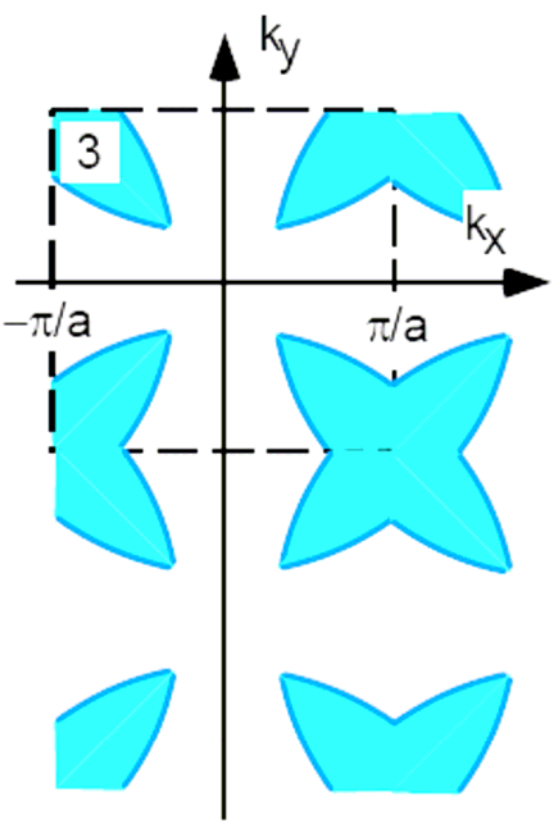




Harrison procedure for empty 2D lattice (Fermi surface sphere in 3 representations)







(extended zones)

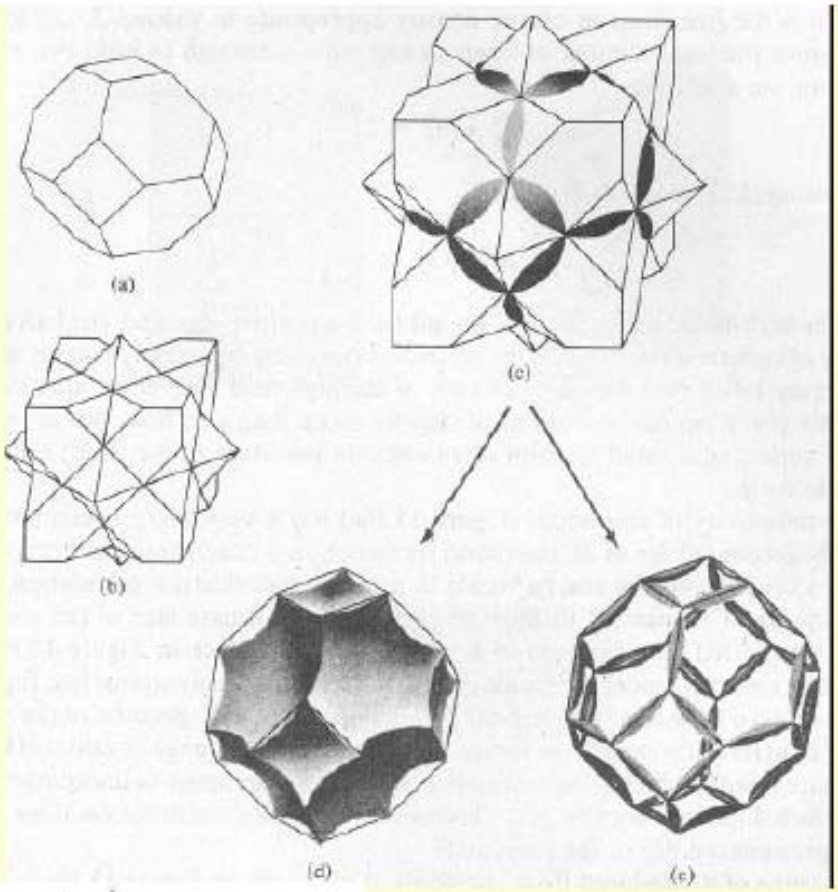
(periodic zone)

(reduced zone)

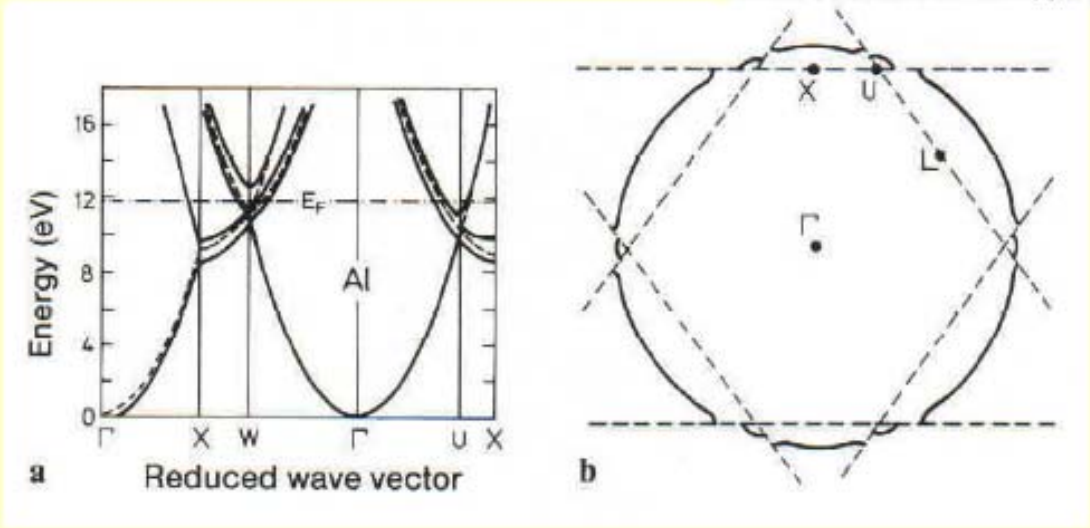
The Fermi surface of Al

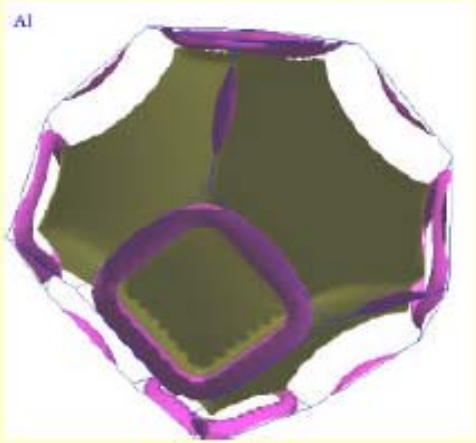
(Al is a trivalent metal with fcc lattice)

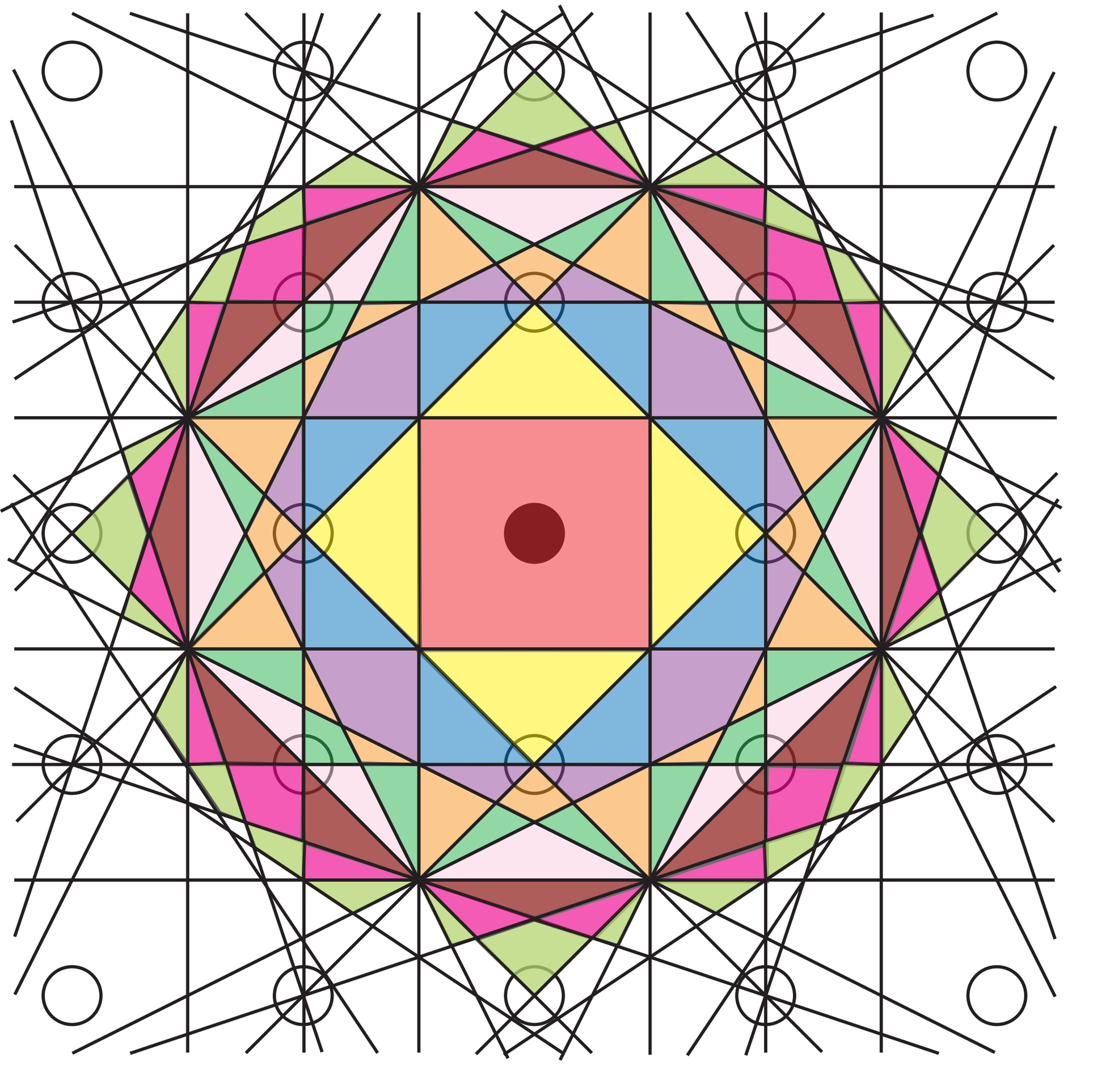
Empty lattice result

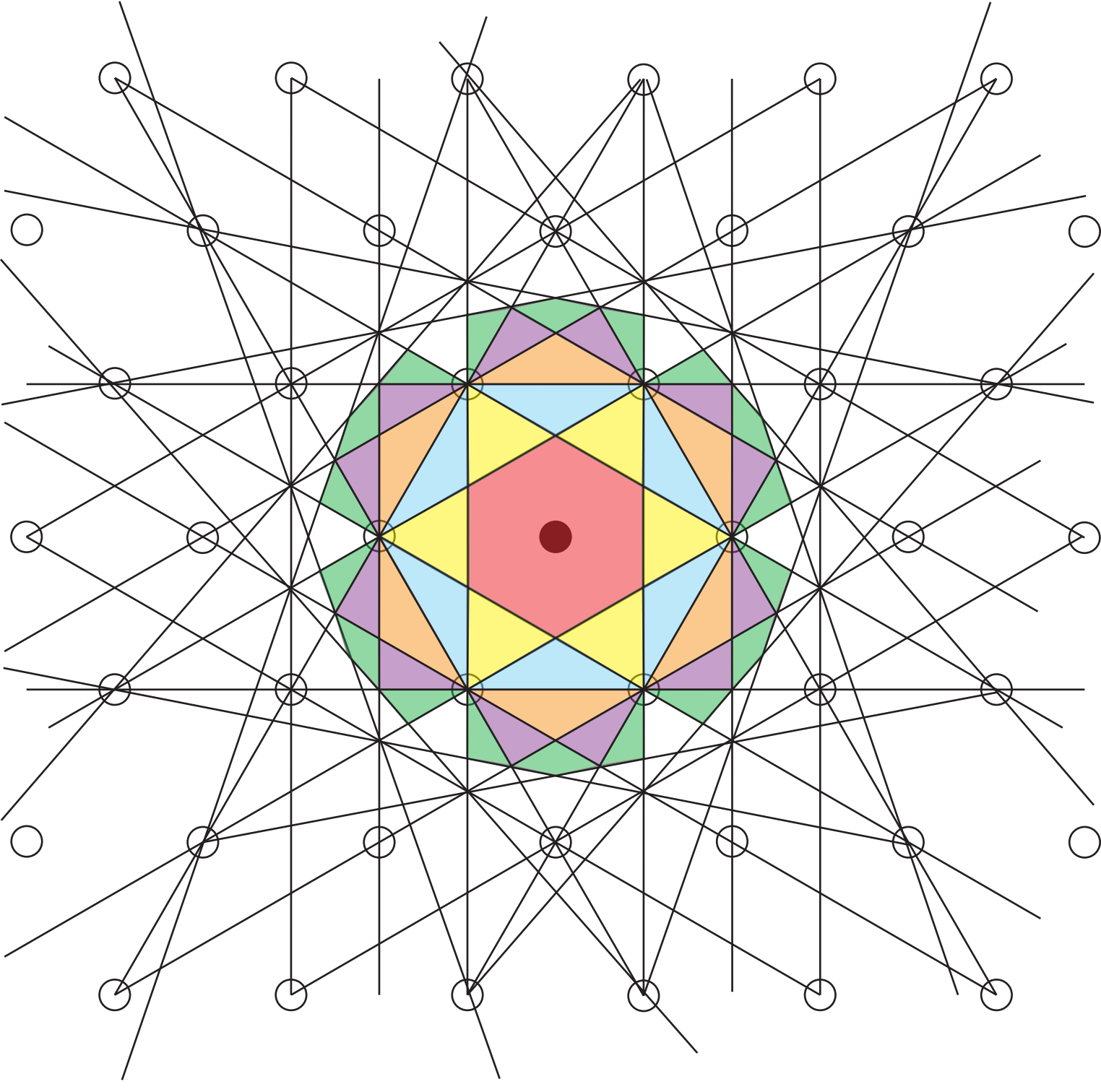


Actual Fermi surface









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Theory of Brillouin Zones and Symmetry Properties of Wave Functions in Crystals

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It is well known that if the interaction between electrons in a metal is neglected, the energy spectrum has a zonal structure. The problem of these "Brillouin zones" is treated here from the point of view of group theory. In this theory, a representation of the symmetry group of the underlying problem is associated with every energy value. The symmetry, in the present case, is the space group, and the main difference as compared with ordinary problems is that while in the latter the representations form a discrete manifold and can be characterized by integers (as e.g., the azimuthal quantum number), the representations of a space group form a continuous manifold, and must be characterized by continuously varying parameters. It can be shown that in the neighborhood of an energy value with a certain representation, there will be energy values with all the representations the parameters of which are close to the parameters of the original representation. This leads to the well-known result that the energy is a continuous function of the reduced wave vector (the components of which are parameters of the above-mentioned kind), but allows in addition to this a systematic treatment of the "sticking" together of Brillouin zones. The treatment is carried out for the simple cubic and the body-centered and face-centered cubic lattices, showing the different possible types of zones.

I.

INVESTIGATIONS of the electronic structure of crystal lattices in particular in metals, made on the basis of Bloch's theory, led to the conception of the so-called Brillouin zones.[1] In spite of these investigations, which cover a large part of the field, it seems desirable to develop the theory from a unique point of view. It appears that taking into account special symmetry properties of different lattices brings out interesting features of the constitution of the B-Z which are not evident from the existing general theory. These features can be dealt with

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[1] The existence of these zones was first noticed by M. J. O. Strutt, Ann. d. Physik **85**, 129 (1928); **86**, 319 (1929); and then, independently, by F. Bloch, Zeits. f. Physik **52**, 555 (1928); cf. also P. M. Morse, Phys. Rev. **35**, 1310 (1930). From another point of view, they were discussed by R. Peierls, Ann. d. Physik **4**, 121 (1930). Their connection with x-ray reflection was first pointed out by L. Brillouin (cf. e.g., *Die Quantenstatistik* (Berlin, 1931)). Important physical applications, were given by H. Jones, Proc. Roy. Soc. **A144**, 225 (1934); **147**, 396 (1934); H. Jones, N. F. Mott and H. W. B. Skinner, Phys. Rev. **45**, 379 (1934); J. C. Slater, Phys. Rev. **45**, 794 (1934); Rev. Mod. Phys. **6**, 209 (1934); F. Hund and B. Mrowka, Ber. Sachs. Akad. D. Wiss. **87**, 185, 325 (1935). Compare also F. Hund, Zeits. f. tech. Physik **16**, 331, 494 (1935); Zeits. f. Physik **99**, 119 (1936). Hund's work deals with those properties of the Brillouin zones which are common to all zones of the same lattice (as matter of fact he does not discriminate between different types of zones at all). We consider here the different types of zone separately. The differences between the different types are of the same kind as e.g. the difference between even and odd terms in atomic spectra. It is surprising that there are at all common properties of all zones but Hund has shown that this is the case for the more complicated crystal structures.

uniformly by the methods of group theory,[2] and we propose to take up the subject here from this point of view. The first start in this direction has been made by F. Seitz,[3] and we shall use his results extensively, though a knowledge of his work should not be necessary for the understanding of this paper.

In the theory of Bloch, every electron has a separate wave function. This assumption is identical with the Hartree-Fock approximation method and amounts to neglecting the statistical correlations between electrons. If we neglect these correlations, every electron obeys a separate Schrödinger equation of the type

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi+V\psi=E\psi \qquad (1)$$

in which V contains the ordinary and exchange potentials of the ions and electrons.[4] The potential V has the whole symmetry of the lattice, that is, the group of our Schrödinger equation (1) is the space group of the lattice.

It is clear from the ordinary group theory[2] that every characteristic value of (1) belongs to a certain representation of the space group and the dimension of the representation is equal to the number of characteristic functions belonging to this characteristic value.[5] Thus far the group theory of the B-Z is not different from the group theory of any other system. But while in atoms, molecules, etc., the characteristic values of (1) are well separated, the characteristic values of (1) for a crystal form a continuous manifold. There will be several characteristic values in the neighborhood of any one E and the representations of these characteristic values will be said to form the neighborhood of the representation of E for this B-Z. Thus a certain topology for the representations must exist and it will be shown that part of this topology is independent of the special B-Z. Even if E, E', $\cdots$ be in different B-Z but have the same representation, there will be energy values neighboring E (with a few exceptions) with the same representations as those of energy values neighboring E', etc. The investigation of the "topology" of representations will be essentially the subject of this paper, from the mathematical point of view.

II.

We must review next, the theory of representations of space groups. F. Seitz[3] has shown that all space groups are soluble groups and their representations can be obtained according to the general theory for these.[3, 6] Seitz first considers the invariant subgroup formed by the translations. Since these commute, the corresponding matrices in the representation can be assumed to have the diagonal form. This means that we shall consider such linear combinations ψ_μ ($\mu=1, 2, \cdots n$, where n is the dimension of the representation) of the wave functions, which are merely multiplied by constant factors ("multipliers") $\omega_{\mu 1}$, $\omega_{\mu 2}$, $\omega_{\mu 3}$ if a displacement by the three elementary identity periods is made. In other words, the matrix corresponding to the displacement by the first elementary identity period is a diagonal matrix with the diagonal elements ω_{11}, ω_{21}, $\cdots$, ω_{n1}, with similar matrices for the representatives of the other displacements. Since all matrices must be unitary, $|\omega_{\mu 1}|=|\omega_{\mu 2}|=|\omega_{\mu 3}|=1$; and if one writes

$$\begin{aligned}\omega_{\mu 1}&=e^{i(k_x x_1+k_y y_1+k_z z_1)}\\ \omega_{\mu 2}&=e^{i(k_x x_2+k_y y_2+k_z z_2)}\\ \omega_{\mu 3}&=e^{i(k_x x_3+k_y y_3+k_z z_3)}\end{aligned} \qquad (2)$$

with x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, z_3, the x, y, z components of the first, second and third identity periods, the vector $\mathbf{k}$ is called[7] "the reduced wave number vector." Of course, $\mathbf{k}$ will be, in general, different for the different wave functions ψ_1, ψ_2, $\cdots$, ψ_n. It must be remembered, how-

[2] Cf. e.g., E. Wigner, *Die Gruppentheorie und ihre Anwendungen* (Braunschweig, 1931). The first application of group theory to crystal lattices has been given by H. Bethe, Ann. d. Physik **3**, 133 (1929).

[3] F. Seitz, Ann. of Math. **37**, 17 (1936).

[4] L. Brillouin, *Actualités Scientifiques et Industrielles* (Paris, 1933).

[5] To the symmetry operations of the space group, the "reversal of time" (cf. E. Wigner, Gott. Nachr. 546 (1932)) should be added. It has been remarked by F. Hund (reference 1) that this will often be of great importance. It can be omitted, however, in the case of the cubic lattices investigated here.

[6] G. Frobenius, Berl. Ber. 337 (1893); I. Schur, Berl. Ber. 164 (1906).

[7] Cf. A. Sommerfeld and H. Bethe's article in *Handbuch der Physik*, Vol. 24 (Berlin, 1933), chapter 3. Also J. C. Slater, Rev. Mod. Phys. **6**, 209 (1934). For a simple cubic lattice $x_1=y_2=z_3=d$; $y_1=z_1=x_2=z_2=x_3=y_3=0$. For a face centered lattice $y_1=z_1=x_2=z_2=x_3=y_3=d/2$; $x_1=y_2=z_3=0$, etc.

ever, that the reduced wave vector **k** is defined by (2) only up to an integer multiple of a vector **r** of the reciprocal lattice, i.e., a vector **r**, for which

$$\begin{aligned} r_x x_1 + r_y y_1 + r_z z_1 &= 2\pi n_1 \\ r_x x_2 + r_y y_2 + r_z z_2 &= 2\pi n_2 \\ r_x x_3 + r_y y_3 + r_z z_3 &= 2\pi n_3 \end{aligned} \tag{2a}$$

always can be added to **k**, without changing its meaning. The space of **k** is periodic with all the periods **r**, satisfying (2a); two reduced wave vectors differing by such an **r** are considered identical. If there are no essential gliding planes and screw axes in the space group,[8] one needs to consider, in addition to the above translations, rotations and reflections only. If such a transformation is applied to ψ_μ, it will be transformed into a wave function, say ψ_λ, the reduced wave vector of which arises from that of ψ_μ by just the rotation or reflection considered. Thus the reduced wave vectors of the wave functions of one representation all arise from one another by the pure rotations and reflections of the group, i.e., the elements of the crystal class. If the reduced wave vector of one ψ_μ is transformed by every element of the crystal class into a different vector, this will be true for all of them, and we shall have as many wave functions $\psi_1, \cdots, \psi_n$ as the crystal class has elements. The matrices of the representation corresponding to rotations and reflections will merely interchange the different ψ_μ. If there are symmetry elements which leave a wave vector invariant, they form a group which we shall call *the group of the wave vector*. So, for example, if the wave vector lies in the x direction, its group will contain all rotations around x and all reflections in planes through x.

A wave function ψ_μ with a wave vector **k** either is left invariant under the transformations of the group of **k**, or else transformed into a new ψ_λ with the same wave vector, **k**, however. In the first case there will be only one wave function with the wave vector **k**. In the second case there will be several of them and they will transform under the transformations of the group of **k** by an irreducible representation of this group, which we shall call the *small representation*. These are the results of Seitz.

Hence the representations of the space group must be characterized by two symbols. The first gives the reduced wave vectors (or set of ω) which occur in the representation; the figure of all these wave vectors forms a "star" with all the rotational and reflection symmetries of the lattice. Three such stars are given in Fig. 1 for

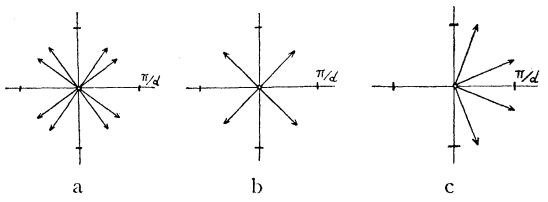


FIG. 1.

a two-dimensional quadratic lattice. The second symbol characterizes the small representation, which is an irreducible representation of the group of one wave vector (the groups of all wave vectors of a star are holomorphic). If the wave vectors lie in general positions (Fig. 1a) their group will contain the unit element only. In this case the second symbol may be omitted. It may be emphasized again that two wave vectors must be considered identical, if the corresponding set of ω's is the same. Thus for example, if the three $k_x x_i + k_y y_i + k_z z_i$ are all integer multiples of π (not necessarily of 2π) the wave vector k_x, k_y, k_z is identical with the wave vector $-k_x$, $-k_y$, $-k_z$ and the inversion ($x \to -x$, $y \to -y$, $z \to -z$) always belongs to the group of the wave vector.[9]

III.

We now consider an energy value E with a certain representation D and the wave functions $\psi_1, \cdots, \psi_n$. If we multiply one of these by $e^{i(\kappa_x x + \kappa_y y + \kappa_z z)}$ where κ_x, κ_y, κ_z, are the components

[8] We mean by this that all symmetry elements can be considered as products of two symmetry elements, the one of which is a pure translation, the other a pure rotation or reflection. This is the case in the most important space groups.

[9] It is in this connection that the time reversal is important (cf. F. Hund, reference 1). If the crystal class does not contain the inversion, k_x, k_y, k_z will still be carried over into $-k_x$, $-k_y$, $-k_z$ by the "time reversal." Since, as we shall see, the above consideration determines the surface of the *B-Z*, this will be fundamentally affected by the operation of time reversal.

of a very small vector, it will have the wave vector $\mathbf{k}+\boldsymbol{\kappa}$ and belong to a new representation D'. The set of new representations obtained in such a way will be called the neighborhood of D. It is clear that there will be near E, an E' with a representation D'. For if ψ_1 satisfies (1), $\psi_1 e^{i(\kappa_x x+\kappa_y y+\kappa_z z)}=\psi_1'$ satisfies

$$\left(-\frac{\hbar^2}{2m}\Delta+V\right)\psi_1'+\frac{\hbar^2 i}{m}\left(\kappa_x\frac{\partial}{\partial x}+\kappa_y\frac{\partial}{\partial y}+\kappa_z\frac{\partial}{\partial z}\right)\psi_1'$$
$$=\left(E+\frac{\hbar^2}{2m}(\kappa_x^2+\kappa_y^2+\kappa_z^2)\right)\psi_1'. \quad (3)$$

In this equation the second term is small, and its negative value may be treated as a perturbation. Performing the perturbation calculation, we shall obtain a characteristic value E' of (1) which is near E and the wave function of which will have the same translational symmetry as ψ_1', since both the original operator in (3), and the perturbation

$$-\frac{\hbar^2 i}{m}\left(\kappa_x\frac{\partial}{\partial x}+\kappa_y\frac{\partial}{\partial y}+\kappa_z\frac{\partial}{\partial z}\right) \quad (3a)$$

have the whole translational symmetry of the lattice.

This is all the general theory we need. If E had a star of the general type, the star of E' also will be of the general type and our result merely states the well-known fact, that the energy is a continuous (and even differentiable) function of the components of the wave vector. The set of all energies and wave functions which may be obtained from one single energy level continuously by this operation, never touching a point in which the star degenerates, is properly defined as one Brillouin zone. The restriction to such representations, the stars of which are of the general type, is necessary for the definition of a Brillouin zone, since, as we shall see, two or more Brillouin zones may stick together for degenerated stars (as those in Figs. 1b and 1c).

If we consider an energy value, the wave vectors of which are left invariant by some of the rotation or reflection operations, the situation still will be left essentially unchanged, if no two wave functions have the same reduced wave vector (the same multipliers). If, however, two or more (say s) wave functions have the same wave vector, and we choose κ_x, κ_y, κ_z in such a way that the new wave vector $(\mathbf{k}+\boldsymbol{\kappa})$ has the general position, there will be s orthogonal wave functions, with the wave vector $\mathbf{k}+\boldsymbol{\kappa}$ and with energies near E. Since for general wave vectors it never happens that two wave functions with the same wave vector belong to the same energy value, we must conclude that they all belong to different B-Z which are very close for small $\boldsymbol{\kappa}$ and that for the original energy value E these s B-Z "stick together." The sticking together will, therefore, always occur for such wave vectors which are left invariant by some symmetry operations.[10]

We must investigate two more cases. First let $\boldsymbol{\kappa}$ be such a vector that $\mathbf{k}+\boldsymbol{\kappa}$ still has the group of $\mathbf{k}$. In this case, the small representation of E is equivalent to the small representation of E'. Otherwise the wave functions would have to change abruptly even for a small change of $\mathbf{k}$. The sticking together will be the same along symmetry elements.

In the second case, the group of $\mathbf{k}+\boldsymbol{\kappa}$ is only a subgroup of $\mathbf{k}$, but still contains more than the identity. This case occurs, for instance, if we pass from a symmetry axis to a symmetry plane through this axis, or from the vector $\mathbf{k}=0$ to a symmetry axis. The small representations of E' will be irreducible representations of the subgroup, and if the small representation of E is not irreducible as representation of the group of $\mathbf{k}+\boldsymbol{\kappa}$, the B-Z which stuck together for $\mathbf{k}$ will be partly separated for $\mathbf{k}+\boldsymbol{\kappa}$. The small representations in these B-Z will be, for $\mathbf{k}+\boldsymbol{\kappa}$, the irreducible parts of the small representation of the group of $\mathbf{k}$.

The proposed characterization of a B-Z is given, hence, by the small representations of the groups of all wave vectors, which have a group greater than unity. For wave vectors lying in equivalent symmetry elements, the small representations are equivalent, and for a symmetry element which is a subgroup of another, the small representation must be contained in the small representation of the latter. Wherever the small representation is s dimensional, we have a sticking together of s B-Z, all of them having this same small representation for the

[10] Including the time reversal.

symmetry element under consideration. Again, it is important to remember that the group of the wave vector for which

$$k_x x_i + k_y y_i + k_z z_i = n_i \pi \quad (\text{for } i = i_1) \qquad (4)$$

holds for one i, say $i=i_1$, contains all elements which transform $\mathbf{k}$ in such a way, that $(k_x x_i + k_y y_i + k_z z_i)/\pi$ remains an integer for $i=i_1$ and is unchanged for the two other i, since the corresponding wave vectors are all the same.

The argument which shows that the small representation will be the same all along a symmetry element, breaks down for such points in which two B-Z touch each other, if no such touching is required by symmetry considerations. In the case that the energy for a certain value of $\mathbf{k}$ is the same in two B-Z, without this being the result of the symmetry, we speak of an accidental degeneracy.[10a] In points of accidental degeneracy, the small representations of the two B-Z may be interchanged, but the case of such an accidental degeneracy is explicitly excluded from the following considerations. One can see that it does not occur for very large lattice constants, though it may occur for the actual ones.

In the following sections, these results will be applied to the three most important cubic lattices, the simple, the face-centered, and the body-centered cubic lattices. Since, for instance all small representations of wave vectors in the fourfold axes are the same, this small representation will be called "the representation along the fourfold axis" and a similar notation will be used for the other symmetry elements.

It has been pointed out by J. C. Slater[1] that the energy as function of $\mathbf{k}$ should be considered as a periodic, multivalued function, the periods being the vectors of the reciprocal lattice. The "discontinuities" then arise from considering for some $\mathbf{k}$ one, for other $\mathbf{k}$ other branches of this multivalued function. In our way of talking, the periodicity is expressed by the fact that two wave vectors differing by a vector $\mathbf{r}$ of the reciprocal lattice, are considered identical. It is convenient to single out from all sets of "identical" vectors one (generally the shortest), and not to consider the rest at all. The manifold of these "reduced wave vectors" forms the inner of the B-Z, their boundary in the $k_x k_y k_z$ space (where the discontinuities are assumed ordinarily) forms the surface of the B-Z.

The energy as function of $\mathbf{k}$ has, furthermore, all the symmetry of the (reciprocal) lattice. This is clear, since wave functions with all the $\mathbf{k}$ of a star belong to the same representation, and have the same energy, hence.

IV.

We want to consider the effect of the time reversal, first. This transforms $\mathbf{k}$ into $-\mathbf{k}$. Thus $-\mathbf{k}$ is always in the star of $\mathbf{k}$, even if there is no inversion center present: the energy as function of $\mathbf{k}$ is always equal for $\mathbf{k}$ and $-\mathbf{k}$. Just as for x-ray reflection, the inversion is always added to the symmetry of the problem.[11]

For a triclinic lattice, for instance, this means that the derivative of energy with respect to $\mathbf{k}$ is zero in the middle of the faces, edges and at the corner points of the B-Z, i.e., for

$$k_x x_i + k_y y_i + k_z z_i = n_i \pi \quad (i=1, 2, 3). \qquad (5)$$

One can see directly also, that the group of these $\mathbf{k}$ contains the time reversal and the wave functions are real, hence. Thus the average value of the perturbation operator (3a) vanishes for these wave functions and the energy change goes with κ^2.

This cannot be claimed, however, for all the surface of the B-Z, i.e., for points for which only one of Eq. (5) is satisfied. The derivative of energy with respect to $\mathbf{k}$ will not vanish in these points and they will not really form the surface of the Brillouin zone.[12]

According to the program of section III, we shall determine now the small representations and their connections in the different types of B-Z for the simple cubic, body-centered, and face-centered cubic lattice. We shall begin with the simple cubic lattice, although no metal with this structure is known.

[10a] The case of an accidental degeneracy will be treated in a paper by C. Herring, to appear shortly. We wish to thank Mr. Herring for interesting discussions on this subject.

[11] Cf. G. Friedel, Comptes rendus **157**, 1533 (1913). For a more critical discussion of Friedel's rule, cf., however, e.g., P. P. Ewald's article in *Handbuch der Physik*, Vol. 23/2 (Berlin, 1933).

[12] It is not always true, thus, that the k for which $\partial E/\partial k = 0$, are those for which the Bragg conditions are satisfied.

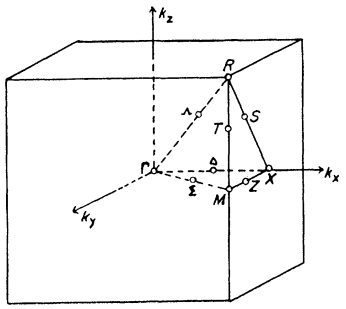


FIG. 2.

V.

Simple cubic lattice. Here the surface of the B-Z is a cube as represented in Fig. 2, with the cube edge $2\pi/d$. The inner symmetry elements are: the center Γ, the threefold axis Λ, the fourfold axis Δ, the twofold axis Σ, the symmetry planes $\Delta\Sigma$, $\Sigma\Lambda$ and $\Lambda\Delta$. The simplest way to obtain the group of a wave vector ending on the surface is to draw in all equally long wave vectors which are "identical" with it. The group of the figure constructed in this way is the group of the wave vector. For the arbitrary vector of the surface π/d, k_y, k_z, for instance, the figure contains the vector $-\pi/d$, k_y, k_z, and the group of the wave vector is, hence, the symmetry plane k_yk_z. Similarly, for the point T, there are four vectors $\pm\pi/d$, $\pm\pi/d$, k_z, and the group contains the fourfold axis k_z and all the symmetry planes through it. It is holomorphic with the group of the wave vector ending at Δ which contains the fourfold axis k_x and the symmetry planes through this. The group of S is holomorphic with that of Σ; that of Z contains the symmetry planes k_xk_y and k_yk_z and the rotation by π about k_y. R has the full cubic group like Γ; M has the group of T and, in addition, the symmetry plane k_xk_y. X has the same symmetry.

The tables[13] give the characters of the irreducible representations for the groups of the wave vectors designated in the upper left corner. The corresponding representations will be the "small representations" characterizing the B-Z. The upper right corner contains the group elements. E is the identity, its character will be the dimension of the representation. C_3 is the threefold axis; C_4, the rotation by $\pm\pi/2$ about the fourfold axis; C_4^2, the rotation by π about the same axis; and C_2 is the rotation about the twofold axis; J is the inversion. JC_4 is the product of J and C_4, etc. JC_2 and JC_4^2 are the reflections in the symmetry planes perpendicular to the twofold and fourfold axes, respectively. The figures before the symbols of group elements denote how many group elements of that kind are present in the group. The lower left corner gives the notation to be used to designate the small representation in question; it is always given for one of the wave vectors only, as, for instance, for Γ in Table I. The small representation of the wave vector R which has the same character as Γ_{12}' will be designated by R_{12}', etc. The lower right corner contains the character of the group element above it, for the representation to the left.

In order to save space we have included in the

[13] The representations of most crystallographic groups were given already by H. Bethe, loc. cit., reference 2. All of them are given in E. Wigner, Gött. Nachr. (1930), p. 133.

TABLE I. *Characters of small representations of* Γ, R, H.

Γ, R, H	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	J	$3JC_4^2$	$6JC_4$	$6JC_2$	$8JC_3$
Γ_1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	−1	−1	1	1	1	−1	−1	1
Γ_{12}	2	2	0	0	−1	2	2	0	0	−1
Γ_{15}'	3	−1	1	−1	0	3	−1	1	−1	0
Γ_{25}'	3	−1	−1	1	0	3	−1	−1	1	0
Γ_1'	1	1	1	1	1	−1	−1	−1	−1	−1
Γ_2'	1	1	−1	−1	1	−1	−1	1	1	−1
Γ_{12}'	2	2	0	0	−1	−2	−2	0	0	1
Γ_{15}	3	−1	1	−1	0	−3	1	−1	1	0
Γ_{25}	3	−1	−1	1	0	−3	1	1	−1	0

TABLE II. *Characters for the small representations of* Δ, T.

Δ, T	E	C_4^2	$2C_4$	$2JC_4^2$	$2JC_2$
Δ_1	1	1	1	1	1
Δ_2	1	1	−1	1	−1
Δ_2'	1	1	−1	−1	1
Δ_1'	1	1	1	−1	−1
Δ_5	2	−2	0	0	0

TABLE III. *Characters for the small representations of* Λ, F.

Λ, F	E	$2C_3$	$3JC_2$
Λ_1	1	1	1
Λ_2	1	1	−1
Λ_3	2	−1	0

TABLE IV. *Characters for the small representations of Σ, S.*

Σ, S	E	C_2	JC_4^2	JC_2
Σ_1	1	1	1	1
Σ_2	1	1	−1	−1
Σ_3	1	−1	−1	1
Σ_4	1	−1	1	−1

tables some wave vectors (H and F) important for the body-centered lattice only.

For the points dealt with so far, it was sufficient to denote the group elements by the symbols C_2, C_3, etc., all the rotations about twofold axes being in the same class and having the same character in all representations. But for the point M, the rotation by π about the fourfold axes k_x, k_y is not equivalent to the rotation about the fourfold axis, k_z, which is perpendicular to the wave vector. The latter will be denoted by $C_4^2\perp$. Although the groups of the wave vectors ending at M and at X are holomorphic, the element in the second group which corresponds to $C_4^2\perp$ of the first is the rotation by π about k_x, which is the axis parallel to the wave vector ΓX. It will be denoted by $C_4^2\parallel$.

TABLE V. *Characters of small representations of M, X.*

M / X	E / E	$2C_4^2$ / $2C_4^2\perp$	$C_4^2\perp$ / $C_4^2\parallel$	$2C_4\perp$ / $2C_4\parallel$	$2C_2$ / $2C_2$	J / J	$2JC_4^2$ / $2JC_4^2\perp$	$JC_4^2\perp$ / $JC_4^2\parallel$	$2JC_4\perp$ / $2JC_4\parallel$	$2JC_2$ / $2JC_2$
M_1	1	1	1	1	1	1	1	1	1	1
M_2	1	1	1	−1	−1	1	1	1	−1	−1
M_3	1	−1	1	−1	1	1	−1	1	−1	1
M_4	1	−1	1	1	−1	1	−1	1	1	−1
M_1'	1	1	1	1	1	−1	−1	−1	−1	−1
M_2'	1	1	1	−1	−1	−1	−1	−1	1	1
M_3'	1	−1	1	−1	1	−1	1	−1	1	−1
M_4'	1	−1	1	1	−1	−1	1	−1	−1	1
M_5	2	0	−2	0	0	2	0	−2	0	0
M_5'	2	0	−2	0	0	−2	0	2	0	0

TABLE VI. *Characters of small representations of Z, G, K, U, D.*

Z / G, K, U / D	E / E / E	C_4^2 / C_2 / C_2	JC_4^2 / JC_4^2 / JC_2	$JC_4^2\perp$ / JC_2 / $JC_2\perp$
Z_1	1	1	1	1
Z_2	1	1	−1	−1
Z_3	1	−1	−1	1
Z_4	1	−1	1	−1

This finishes the investigation of the symmetry axes in Fig. 2, and there remain only the symmetry planes. A somewhat closer inspection will show, however, that the small representations

TABLE VII. *Compatibility relations between Γ and Δ, Λ, Σ.*

Γ_1	Γ_2	Γ_{12}	Γ_{15}'	Γ_{25}'
Δ_1	Δ_2	$\Delta_1\Delta_2$	$\Delta_1'\Delta_5$	$\Delta_2'\Delta_5$
Λ_1	Λ_2	Λ_3	$\Lambda_2\Lambda_3$	$\Lambda_1\Lambda_3$
Σ_1	Σ_4	$\Sigma_1\Sigma_4$	$\Sigma_2\Sigma_3\Sigma_4$	$\Sigma_1\Sigma_2\Sigma_3$
Γ_1'	Γ_2'	Γ_{12}'	Γ_{15}	Γ_{25}
Δ_1'	Δ_2'	$\Delta_1'\Delta_2'$	$\Delta_1\Delta_5$	$\Delta_2\Delta_5$
Λ_2	Λ_1	Λ_3	$\Lambda_1\Lambda_3$	$\Lambda_2\Lambda_3$
Σ_2	Σ_3	$\Sigma_2\Sigma_3$	$\Sigma_1\Sigma_3\Sigma_4$	$\Sigma_1\Sigma_2\Sigma_4$

TABLE VIII. *Compatibility relations between M and Σ, Z, T.*

M_1	M_2	M_3	M_4	M_1'	M_2'	M_3'	M_4'	M_5	M_5'
Σ_1	Σ_4	Σ_1	Σ_4	Σ_2	Σ_3	Σ_2	Σ_3	$\Sigma_2\Sigma_3$	$\Sigma_1\Sigma_4$
Z_1	Z_1	Z_3	Z_3	Z_2	Z_2	Z_4	Z_4	Z_2Z_4	Z_1Z_3
T_1	T_2	T_2'	T_1'	T_1'	T_2'	T_2	T_1	T_5	T_5

TABLE IX. *Compatibility relations between X and Δ, Z, S.*

X_1	X_2	X_3	X_4	X_1'	X_2'	X_3'	X_4'	X_5	X_5'
Δ_1	Δ_2	Δ_2'	Δ_1'	Δ_1'	Δ_2'	Δ_2	Δ_1	Δ_5	Δ_5
Z_1	Z_1	Z_4	Z_4	Z_2	Z_2	Z_3	Z_3	Z_3Z_2	Z_1Z_4
S_1	S_4	S_1	S_4	S_2	S_3	S_2	S_3	S_2S_3	S_1S_4

prevailing on the symmetry axes already determine the representations for the symmetry planes, i.e., they determine whether the wave function will remain unchanged or assume the negative value, if reflected in one of the symmetry planes.

A B-Z must be characterized by one each of the following 10 symbols: Γ, Δ, Λ, Σ, R, T, M, S, X and Z. If there is an accidental degeneracy, however, the representation may change on an axis, etc. Not all the combinations of symbols correspond to possible B-Z. The small representation Δ on the fourfold axis must be contained in the representation Γ of the center, if this is considered as a representation of the group of Δ, and similar conditions exist between all pairs of adjoining symmetry elements. Table VII shows with which Δ, Λ, Σ, a certain Γ can be combined in the symbol of a possible B-Z. The compatibility relations between R and T, Λ, S, are the same as those between Γ and Δ, Λ, Σ. (Table VII.) These compatibility relations reduce considerably the number of possible types of B-Z. In addition to these compatibility relations, there are others originating from the four sets of wave vectors characterized by $k_z=0$; $k_x=k_y$; $k_y=k_z$; $k_x=\pi/d$. Every wave

vector satisfying one of these equations, has a group consisting of a symmetry plane, and the corresponding wave function will belong either to the symmetric, or to the antisymmetric representation of this group. This representation must be contained in the small representations of the axes lying in this plane. Table X gives, under +,

TABLE X. *Compatibility relations on symmetry planes.*

SYMMETRY PLANE	+	−
$k_z=0$	$\Sigma_1\Sigma_4$ $\Delta_1\Delta_2\Delta_5$ Z_1Z_3	$\Sigma_2\Sigma_3$ $\Delta_1'\Delta_2'\Delta_5$ Z_2Z_4
$k_x=k_y>k_z$	$\Sigma_1\Sigma_3$ $\Lambda_1\Lambda_3$ $T_1T_2'T_5$	$\Sigma_2\Sigma_4$ $\Lambda_2\Lambda_3$ $T_2T_1'T_5$
$k_y=k_z<k_x$	$\Lambda_1\Lambda_3$ S_1S_3 $\Delta_1\Delta_2'\Delta_5$	$\Lambda_2\Lambda_3$ S_2S_4 $\Delta_2\Delta_1'\Delta_5$
$k_x=\pi/d$	S_1S_4 $T_1T_2T_5$ Z_1Z_4	S_2S_3 $T_1'T_2'T_5$ Z_2Z_3

those representations along the axes, which are compatible with the symmetric representation in the plane, and under − those which are compatible with the antisymmetric representation. It shows that, for instance, Σ_1 is incompatible with Δ_1', Δ_2', Z_2, Z_4, Λ_2, T_2, T_1'.

As an example, we may consider the three B-Z which stick together at $k_x=k_y=k_z=0$ having for this wave vector the representation Γ_{25}. These three B-Z will be separated along the twofold axis, having there the small representations Σ_1, Σ_2, Σ_4, respectively (Table VII). We may consider the one with Σ_2. This necessarily goes with Δ_5 along the fourfold axis (Tables VII and X), and sticks together with one of the other zones there. Along the threefold axis it may have one of the two representations Λ_2 or Λ_3. We shall assume that it has Λ_2. For R, we still have the choice of R_2, R_{15}', R_1' or R_{25}. We shall choose R_2. This requires, then, S_4 and T_2, and hence Z_4. According to Table VIII, it will have M_3' and according to Table IX, X_5'. Its whole symbol will be $\Gamma_{25}\Sigma_2\Delta_5\Lambda_2R_{15}T_2S_4Z_4M_3'X_5'$ and we see that most small representations were uniquely given by the compatibility tables and the previous choices.

We believe that the above description of B-Z for the simple cubic lattice is complete from the point of view of symmetry. We are well aware, of course, that many of the types which are possible geometrically will not be important physically, since they have, for example, too high energies. It appeared to us, however, that for the sake of clarity a complete geometric discussion should be given once for a simple case.

The construction of the compatibility tables is very easy. If one is interested, e.g., in the compatibilities between Σ and M, one considers for M the characters corresponding to elements which are contained in Σ. These elements are E, C_2, $JC_4^2\perp$, JC_2 (one must take $JC_4^2\perp$, not JC_4^2, since the latter are the symmetry planes k_xk_z, k_yk_z which do not occur in the group of Σ). The corresponding characters in M_5, for instance, are 2, 0, −2, 0. One sees that this is the sum of the characters of Σ_2 and Σ_3 and these are, consequently, compatible with M_5. Thus it will not be necessary to give the compatibility relations for the other lattices explicitly.

VI. BODY-CENTERED CUBIC LATTICE

The shape of the surface of the B-Z is self-evident in the simple cubic lattice but not in the body-centered lattice. The identity periods can be taken as three space diagonals, with coordinates $1/2d$, $\pm1/2d$, $\pm1/2d$. The shortest vectors of the reciprocal lattice are the face diagonals, with coordinates 0, $\pm2\pi/d$, $\pm2\pi/d$; $\pm2\pi/d$, 0, $\pm2\pi/d$; $\pm2\pi/d$, $\pm2\pi/d$, 0. Since the inner of the B-Z should contain only different vectors $\mathbf{k}$, the addition of a vector of the reciprocal lattice to a $\mathbf{k}$ lying inside the B-Z must lead to a vector in the outside. This is most simply accomplished by choosing the rhombododecahedron of Fig. 3 as the surface, in which

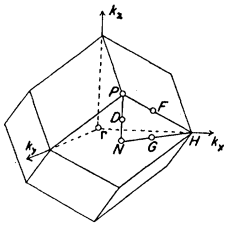


FIG. 3.

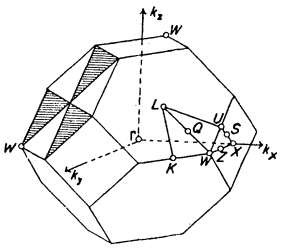


FIG. 4.

opposite faces just differ by a vector of the reciprocal lattice. The distance ΓH is $2\pi/d$.[14]

The symmetry elements in the inside of the B-Z are the same as in the simple cubic lattice, Γ, Δ, Λ, Σ, and the compatibility relations between these are also maintained. The point H has, however, the full cubic symmetry, since the vectors of the reciprocal lattice transfer it to all the end points of the coordinate axes. The point P is identical with three similar vertices, forming a tetrahedron.

TABLE XI. *Characters for the small representations of P.*

P	E	$3C_4^2$	$8C_3$	$6JC_4$	$6JC_2$
P_1	1	1	1	1	1
P_2	1	1	1	−1	−1
P_3	2	2	−1	0	0
P_4	3	−1	0	−1	1
P_5	3	−1	0	1	−1

TABLE XII. *Characters for the small representations of N.*

N	E	C_4^2	$C_2\parallel$	$C_2\perp$	J	JC_4^2	$JC_2\perp$	$JC_2\parallel$
N_1	1	1	1	1	1	1	1	1
N_2	1	−1	1	−1	1	−1	−1	1
N_3	1	−1	−1	1	1	−1	1	−1
N_4	1	1	−1	−1	1	1	−1	−1
N_1'	1	−1	1	−1	−1	1	1	−1
N_2'	1	1	1	1	−1	−1	−1	−1
N_3'	1	1	−1	−1	−1	−1	1	1
N_4'	1	−1	−1	1	−1	1	−1	1

The small representations for the other points were already given in the previous tables. We shall not give the compatibility relations between axes and points, since they are easily obtained by the method outlined in the previous section. It may be mentioned that the group of the vectors ending in a general point of the surface is the symmetry plane JC_2. The following relations are analogous to those of Table X.

TABLE XIII. *Compatibility relations for symmetry planes.*

SYMMETRY PLANE	+	−
$k_z=0$	$\Sigma_1\Sigma_4$, $\Delta_1\Delta_2\Delta_5$, G_1G_4	$\Sigma_1\Sigma_2$, $\Delta_1'\Delta_2'\Delta_5$, G_2G_3
$k_x=k_y>k_z$	$\Sigma_1\Sigma_3$, $\Delta_1\Lambda_3$, D_1D_3	$\Sigma_2\Sigma_4$, $\Lambda_2\Lambda_3$, D_2D_4
$k_y=k_z<k_x$	$\Lambda_1\Lambda_3$, $\Delta_1\Delta_2'\Delta_5$, F_1F_3	$\Lambda_2\Lambda_3$, $\Delta_2\Delta_1'\Delta_5$, F_2F_3
$k_x+k_y=2\pi$	D_1D_4, F_1F_3, G_1G_3	D_2D_3, F_2F_3, G_2G_4

[14] The vectors $\mathbf{k}$ in the inside of the *B-Z* are transformed under this choice again into vectors in the inside by every symmetry element.

Since the surface of the B-Z is a symmetry plane, the derivative of the energy perpendicular to this plane is zero on the surface.

VII. FACE-CENTERED CUBIC LATTICE

The B-Z of the face-centered cubic lattice have a rather complicated structure. The reciprocal lattice is the body-centered lattice, the shortest vectors of which are the space diagonals with components $\pm 2\pi/d$, $\pm 2\pi/d$, $\pm 2\pi/d$. If we assume the inner of the B-Z to be bounded by the octahedron with the 8 planes $\pm x \pm y \pm z = 3\pi/d$, then no wave vectors of the inside will differ by one such vector. Nevertheless, some of them will be equivalent, differing by the sum of two shortest vectors of the reciprocal lattice, $\pm 4\pi/d, 0, 0\,;\, 0, \pm 4\pi/d, 0\,;\, 0, 0, \pm 4\pi/d$. In order to exclude these, one must cut off the corners of the octahedron by planes parallel to the coordinate planes at the distance $\pm 2\pi/d$ from these. The resulting figure is the well-known truncated octahedron of Fig. 4. With this choice of the surface of the B-Z, every wave vector of the inside will go over into a wave vector of the inside by all the symmetry operations. This requirement, however, which determines the whole shape of the surface for the simple cubic and body centered cases, fixes the surface here only at the truncating planes, but not at the octahedral planes. One could, for instance, bulge out in all octahedral planes the part which is shaded on one of the planes in Fig. 4 and bulge in by an equal amount the unshaded regions. The resulting surface would still satisfy all requirements. The truncating planes, on the other hand, cannot be deformed. If we pushed out a point on the $k_x=2\pi/d$ plane, we would have to push in the corresponding point on the $k_x=-2\pi/d$ plane. After this, however, the reflection on the k_yk_z plane would carry over wave vectors of the inside to the outside of the surface of the B-Z.

The B-Z is always uniquely determined if there is a symmetry plane perpendicular to the vector $\mathbf{r}$ of the reciprocal lattice,[15] which generates that part of the surface. In this case the surface lies at the distance $r/2$ on both sides of the symmetry plane. This was true for the vectors parallel to the coordinate axes which generated the surface

[15] Cf. Eq. (2a).

for the simple cubic lattice, it was true for the vectors parallel to the face diagonals in the body-centered structure and it is true for the vectors generating the truncating planes in Fig. 4. The situation for the octahedral plane of Fig. 4, however, is similar to that for the triclinic lattice and will be shown to have similar consequences.

Although the surface of the B-Z is thus left undetermined by general requirements, it is certainly allowable to assume it to have the shape of Fig. 4.

In the inside of the B-Z we have again the same situation as for the simple cubic lattice with the same compatibility relations holding between the small representations of Γ and the two-, three- and fourfold axes. This also applies to the points X, S and Z on the cubic plane. The point W is identical with three other points of the surface, two of which are shown on the figure, while one at the bottom is hidden. The small

TABLE XIV. *Characters of small representations of W.*

W	E	C_4^2	$2C_2$	$2JC_4$	$2JC_4^2$
W_1	1	1	1	1	1
W_1'	1	1	1	−1	−1
W_2	1	1	−1	1	−1
W_2'	1	1	−1	−1	1
W_3	2	−2	0	0	0

TABLE XV. *Characters of small representations of L.*

L	E	$2C_3$	$3C_2$	J	$2JC_3$	$3JC_2$
L_1	1	1	1	1	1	1
L_2	1	1	−1	1	1	−1
L_3	2	−1	0	2	−1	0
L_1'	1	1	1	−1	−1	−1
L_2'	1	1	−1	−1	−1	1
L_3'	2	−1	0	−2	1	0

representations for the points K and U were given in Table VI. L is identical with its antipode. The points Q on the line LW cannot be moved in or out. They belong to the surface, since they are carried over into themselves (i.e., into the "identical" point on the opposite face) by the twofold axis bisecting the Z and $-X$ axes. The wave function of the wave vector ending at Q will be either symmetric or antisymmetric with respect to this rotation. In the former case it is compatible with L_1, L_1', L_3, L_3' on one side and with $W_1W_1'W_3$ on the other. If it is antisymmetric, it is compatible with L_2, L_2', L_3, L_3' and W_2, W_2' and W_3.

The group of the points on the lines LK, KW, LU, UW contains only the symmetry plane on which they lie, they have no additional symmetry owing to their position on the surface. This is natural, since the surface can be shifted away from them. The Compatibility Table X holds for $k_x=k_y>k_z$ between Σ and Λ, but there is nothing to replace T, and T must be omitted also from the last section of $(k_x=\pi/d)$ of this table. The rest of the table remains valid, however, and should be supplemented by the compatibilities just given, owing to the symmetry of the point Q.

The surface of the B-Z at the octahedral planes cannot be chosen in such a way that the "identical" point $k_x-2\pi/d$, $k_y-2\pi/d$, $k_z-2\pi/d$ to every point of the surface could be reached by a symmetry operation also. This has the consequence that the derivative of the energy perpendicular to the somewhat arbitrarily chosen plane octahedral face will only vanish on the diagonals (LW) corresponding to the separating lines between shaded and unshaded regions. On the other hand, it will have the consequence also that the energy for $k_x=\pi/d+\mu$, $k_y=\pi/d-\mu-v$, $k_z=\pi/d+v$ will be equal to the energy for $-\pi/d+\mu$, $-\pi/d-\mu-v$, $-\pi/d+v$ and, because of the twofold axis, also equal to the energy for $\pi/d-v$, $\pi/d+\mu+v$, $\pi/d-\mu$. The energy as function of $\mathbf{k}$ will be symmetric with respect to the line LW on the surface and, hence, will have on the octahedral *surface*, a sixfold rotational symmetry.

Points inside the Brillouin zone

Notes by Andrea Dal Corso (SISSA - Trieste)

1 Brillouin zone

QUANTUM ESPRESSO (QE) support for the definition of high symmetry lines inside the Brillouin zone (BZ) is still rather limited. However QE can calculate the coordinates of the vertexes of the BZ and of particular points inside the BZ. These notes show the shape and orientation of the BZ used by QE. The principal direct and reciprocal lattice vectors, as implemented in the routine `latgen`, are illustrated here together with the labels of each point. These labels can be given as input in a band or phonon calculation to define paths in the BZ. This feature is available with the option `tpiba_b` or `crystal_b` in a `'bands'` calculation or with the option `q_in_band_form` in the input of the `matdyn.x` code. Lines in reciprocal space are defined by giving the coordinates of the starting and ending points and the number of points of each line. The coordinates of the starting and ending points can be given explicitly with three real numbers or by giving the label of a point known to QE. For example:

```
X  10
gG 25
0.5 0.5 0.5 1
```

indicate a path composed by two lines. The first line starts at point X, ends at point Γ, and has 10 $\mathbf{k}$ points. The second line starts at Γ, ends at the point of coordinates `(0.5,0.5,0.5)` and has 25 $\mathbf{k}$ points. Greek labels are prefixed by the letter `g`: `gG` indicates the Γ point, `gS` the Σ point etc. Subscripts are written after the label: the point P_1 is indicated as `P1`. In the following section you can find the labels of the points defined in each BZ. There are many conventions to label high symmetry points inside the BZ. The variable `point_label_type` selects the set of labels used by QE. The default is `point_label_type='SC'` and the labels have been taken from W. Setyawan and S. Curtarolo, Comp. Mat. Sci. **49**, 299 (2010). Other choices can be more convenient in other situations. The names reported in the web pages `http://www.cryst.ehu.es/cryst/get_kvec.html` are available for some BZ. You can use them by setting (`point_label_type='BI'`), others can be added in the future. This option is available only with `ibrav`$\neq$`0` and for all positive `ibrav` with the exception of the base centered monoclinic (`ibrav=13`), and triclinic (`ibrav=14`) lattices. In these cases you have to give all the coordinates of the $\mathbf{k}$-points.

1.1 `ibrav=1`, simple cubic lattice

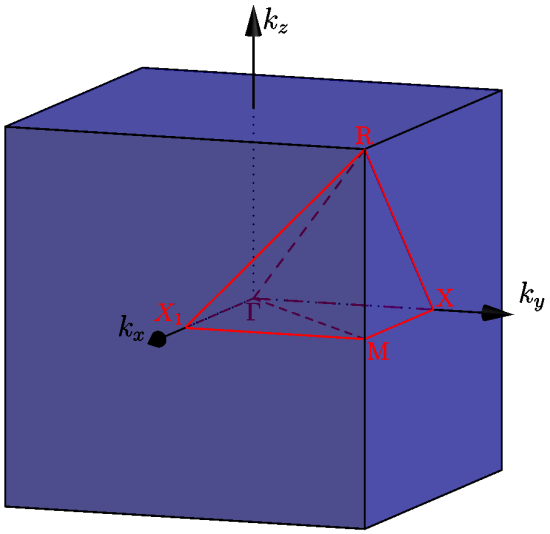
The primitive vectors of the direct lattice are:

$$\begin{aligned} \mathbf{a}_1 &= a(1,0,0), \\ \mathbf{a}_2 &= a(0,1,0), \\ \mathbf{a}_3 &= a(0,0,1), \end{aligned}$$

while the reciprocal lattice vectors are:

$$\begin{aligned} \mathbf{b}_1 &= \frac{2\pi}{a}(1,0,0), \\ \mathbf{b}_2 &= \frac{2\pi}{a}(0,1,0), \\ \mathbf{b}_3 &= \frac{2\pi}{a}(0,0,1). \end{aligned}$$

The Brilloin zone is:



X_1 is available only with `point_label_type='BI'`.

1.2 `ibrav=2`, face centered cubic lattice

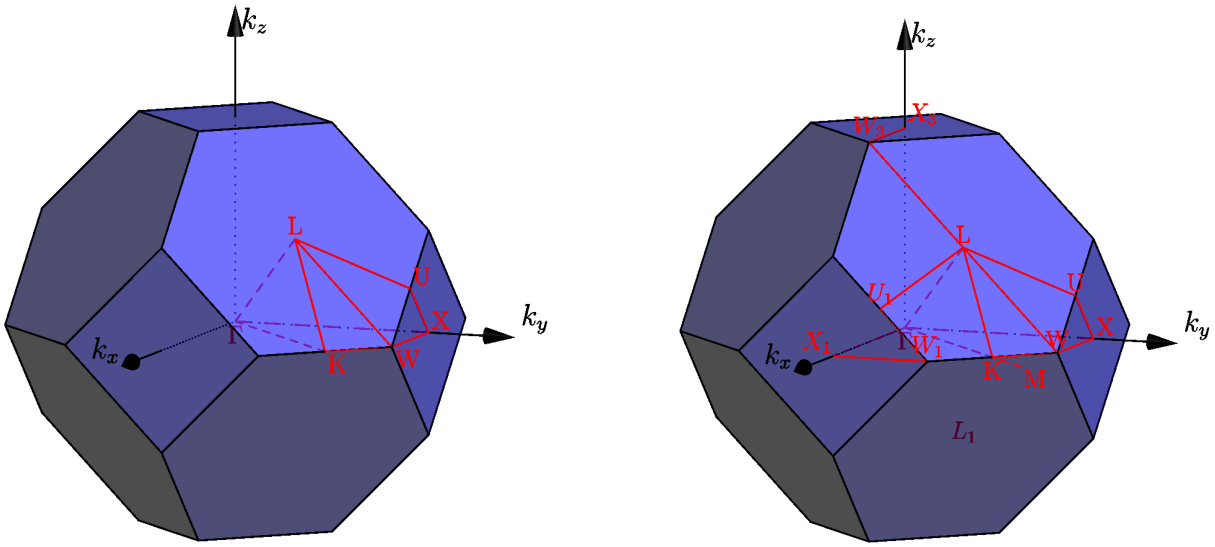
The primitive vectors of the direct lattice are:

$$\begin{aligned}
\mathbf{a}_1 &= \frac{a}{2}(-1,0,1), \\
\mathbf{a}_2 &= \frac{a}{2}(0,1,1), \\
\mathbf{a}_3 &= \frac{a}{2}(-1,1,0),
\end{aligned}$$

while the reciprocal lattice vectors are:

$$\begin{aligned}
\mathbf{b}_1 &= \frac{2\pi}{a}(-1,-1,1), \\
\mathbf{b}_2 &= \frac{2\pi}{a}(1,1,1), \\
\mathbf{b}_3 &= \frac{2\pi}{a}(-1,1,-1).
\end{aligned}$$

The Brillouin zone is:



Labels corresponding to `point_label_type='SC'` and to `point_label_type='BI'` are shown on the left and on the right, respectively.

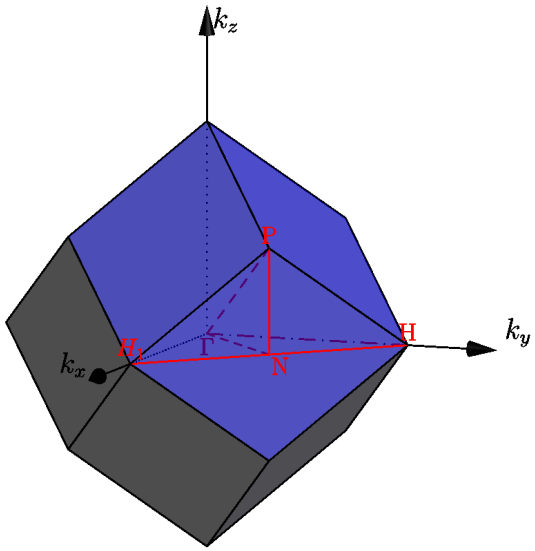
1.3 `ibrav=3`, body centered cubic lattice

The primitive vectors of the direct lattice are:

$$\begin{aligned} \mathbf{a}_1 &= \frac{a}{2}(1,1,1), \\ \mathbf{a}_2 &= \frac{a}{2}(-1,1,1), \\ \mathbf{a}_3 &= \frac{a}{2}(-1,-1,1), \end{aligned}$$

while the reciprocal lattice vectors are:

$$\begin{aligned} \mathbf{b}_1 &= \frac{2\pi}{a}(1,0,1), \\ \mathbf{b}_2 &= \frac{2\pi}{a}(-1,1,0), \\ \mathbf{b}_3 &= \frac{2\pi}{a}(0,-1,1). \end{aligned}$$



H_1 is available only with `point_label_type='BI'`.

1.4 `ibrav=4`, hexagonal lattice

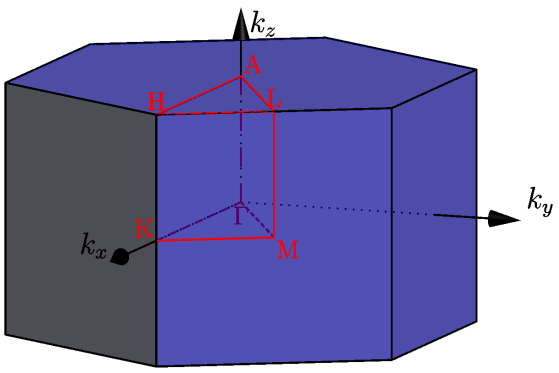
The primitive vectors of the direct lattice are:

$$\begin{aligned}
\mathbf{a}_1 &= a(1,0,0), \\
\mathbf{a}_2 &= a(-\frac{1}{2}, \frac{\sqrt{3}}{2}, 0), \\
\mathbf{a}_3 &= a(0,0,\frac{c}{a}),
\end{aligned}$$

while the reciprocal lattice vectors are:

$$\begin{aligned}
\mathbf{b}_1 &= \frac{2\pi}{a}(1, \frac{1}{\sqrt{3}}, 0), \\
\mathbf{b}_2 &= \frac{2\pi}{a}(0, \frac{2}{\sqrt{3}}, 0), \\
\mathbf{b}_3 &= \frac{2\pi}{a}(0,0,\frac{a}{c}).
\end{aligned}$$

The BZ is:



The figure has been obtained with $c/a = 1.4$.

1.5 `ibrav=5`, trigonal lattice

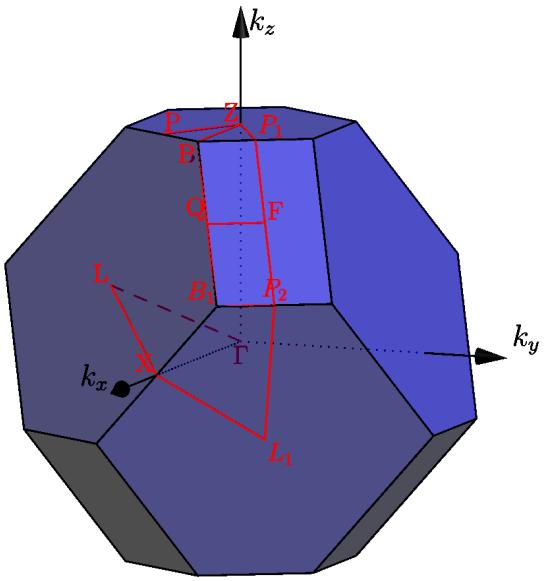
The primitive vectors of the direct lattice are:

$$\begin{aligned}
\mathbf{a}_1 &= a(\frac{\sqrt{3}}{2}\sin\theta, -\frac{1}{2}\sin\theta, \cos\theta), \\
\mathbf{a}_2 &= a(0, \sin\theta, \cos\theta), \\
\mathbf{a}_3 &= a(-\frac{\sqrt{3}}{2}\sin\theta, -\frac{1}{2}\sin\theta, \cos\theta),
\end{aligned}$$

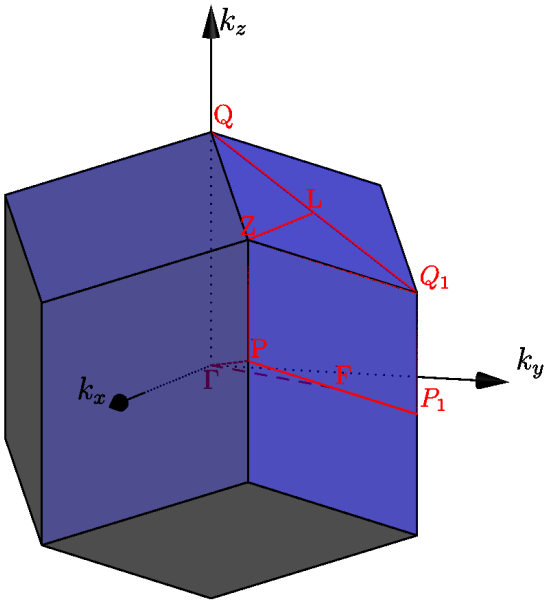
while the reciprocal lattice vectors are:

$$\begin{aligned}
\mathbf{b}_1 &= \frac{2\pi}{a}(\frac{\sqrt{3}}{2}\sin\theta, -\frac{1}{2}\sin\theta, \cos\theta), \\
\mathbf{b}_2 &= \frac{2\pi}{a}(0, \sin\theta, \cos\theta), \\
\mathbf{b}_3 &= \frac{2\pi}{a}(-\frac{\sqrt{3}}{2}\sin\theta, -\frac{1}{2}\sin\theta, \cos\theta),
\end{aligned}$$

where $\sin\theta = \sqrt{\frac{2}{3}}\sqrt{1-\cos\alpha}$ and $\cos\theta = \sqrt{\frac{1}{3}}\sqrt{1+2\cos\alpha}$ and α is the angle between any two primitive direct lattice vectors. There are two possible shapes of the BZ, depending on the value of the angle α. For $\alpha < 90°$ we have:



The figure has been obtained with $\alpha = 70°$. For $90° < \alpha < 120°$ we have:



The figure has been obtained with $\alpha = 110°$.

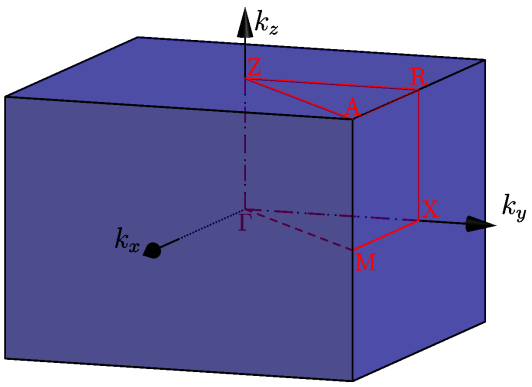
1.6 `ibrav=6`, simple tetragonal lattice

The primitive vectors of the direct lattice are:

$$\begin{aligned} \mathbf{a}_1 &= a(1,0,0), \\ \mathbf{a}_2 &= a(0,1,0), \\ \mathbf{a}_3 &= a(0,0,\frac{c}{a}), \end{aligned}$$

while the reciprocal lattice vectors are:

$$\begin{aligned} \mathbf{b}_1 &= \frac{2\pi}{a}(1,0,0), \\ \mathbf{b}_2 &= \frac{2\pi}{a}(0,1,0), \\ \mathbf{b}_3 &= \frac{2\pi}{a}(0,0,\frac{a}{c}). \end{aligned}$$



The figure has been obtained with $c/a = 1.4$.

1.7 `ibrav=7`, centered tetragonal lattice

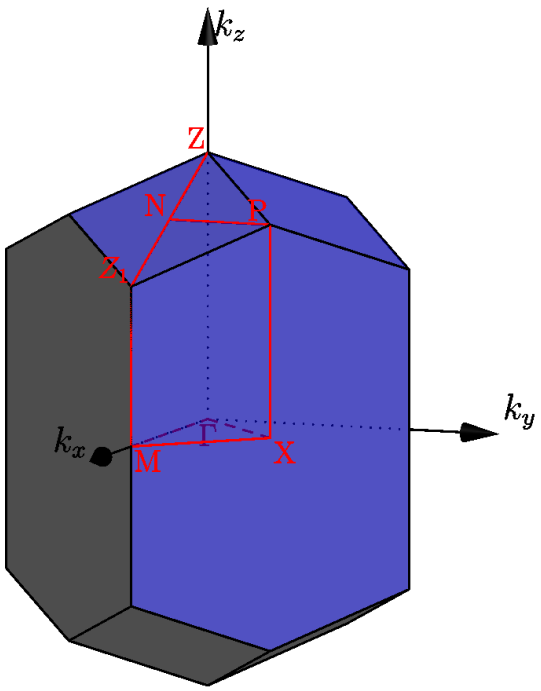
The primitive vectors of the direct lattice are:

$$\begin{aligned}
\mathbf{a}_1 &= \frac{a}{2}(1,1,\frac{c}{a}),\\
\mathbf{a}_2 &= \frac{a}{2}(1,-1,\frac{c}{a}),\\
\mathbf{a}_3 &= \frac{a}{2}(-1,-1,\frac{c}{a}),
\end{aligned}$$

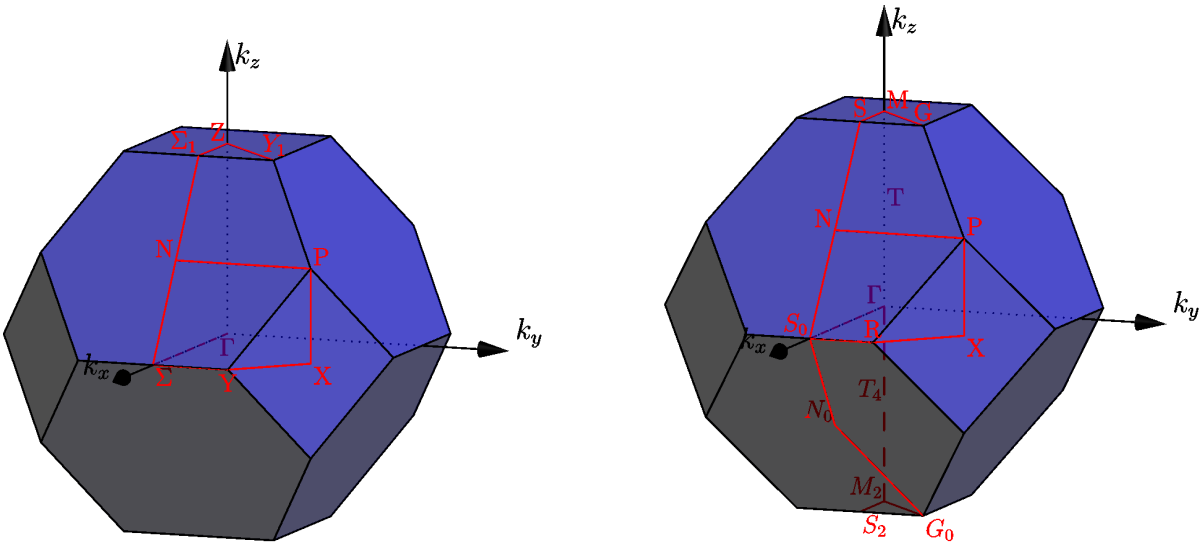
while the reciprocal lattice vectors are:

$$\begin{aligned}
\mathbf{b}_1 &= \frac{2\pi}{a}(1,-1,0),\\
\mathbf{b}_2 &= \frac{2\pi}{a}(0,1,\frac{a}{c}),\\
\mathbf{b}_3 &= \frac{2\pi}{a}(-1,0,\frac{a}{c}).
\end{aligned}$$

In this case there are two different shapes of the BZ depending on the c/a ratio. For $c/a < 1$ we have:



The figure has been obtained with $c/a = 0.5$ ($a > c$). For $c/a > 1$ we have:



The figure has been obtained with $c/a = 1.4$ ($a < c$). Labels corresponding to `point_label_type='SC'` are shown on the left, those corresponding to `point_label_type='BI'` on the right.

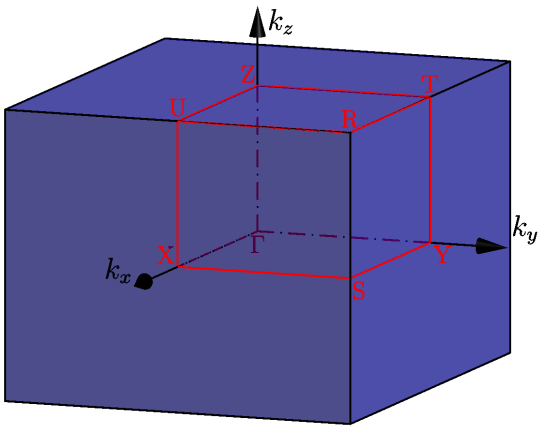
1.8 `ibrav=8`, simple orthorhombic lattice

The primitive vectors of the direct lattice are:

$$\begin{aligned} \mathbf{a}_1 &= a(1,0,0), \\ \mathbf{a}_2 &= a(0,\frac{b}{a},0), \\ \mathbf{a}_3 &= a(0,0,\frac{c}{a}), \end{aligned}$$

while the reciprocal lattice vectors are:

$$\begin{aligned} \mathbf{b}_1 &= \frac{2\pi}{a}(1,0,0), \\ \mathbf{b}_2 &= \frac{2\pi}{a}(0,\frac{a}{b},0), \\ \mathbf{b}_3 &= \frac{2\pi}{a}(0,0,\frac{a}{c}). \end{aligned}$$



The figure has been obtained with $b/a = 1.2$ and $c/a = 1.5$.

1.9 `ibrav=9`, one-face centered orthorhombic lattice

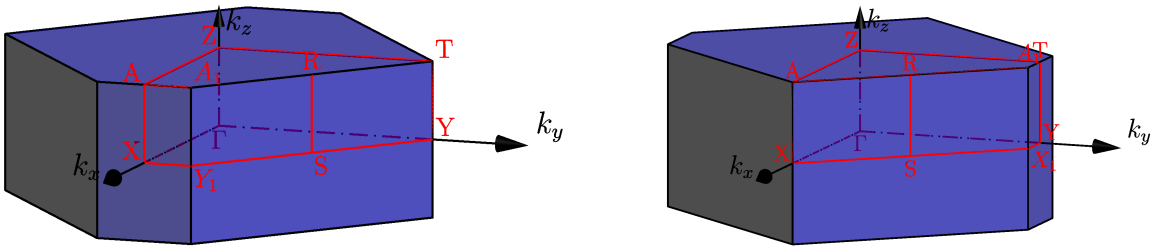
The direct lattice vectors are:

$$\begin{aligned}\mathbf{a}_1 &= \frac{a}{2}(1, \frac{b}{a}, 0),\\ \mathbf{a}_2 &= \frac{a}{2}(-1, \frac{b}{a}, 0),\\ \mathbf{a}_3 &= a(0, 0, \frac{c}{a}),\end{aligned}$$

while the reciprocal lattice vectors are

$$\begin{aligned}\mathbf{b}_1 &= \frac{2\pi}{a}(1, \frac{a}{b}, 0),\\ \mathbf{b}_2 &= \frac{2\pi}{a}(-1, \frac{a}{b}, 0),\\ \mathbf{b}_3 &= \frac{2\pi}{a}(0, 0, \frac{a}{c}).\end{aligned}$$

There is one shape that can have two orientations depending on the ratio between of a and b:



The figures have been obtained with $b/a = 0.8$ and $c/a = 1.4$ (left part $b < a$) and $b/a = 1.2$ and $c/a = 1.4$ (right part $b > a$).

1.10 `ibrav=10`, face centered orthorhombic lattice

The direct lattice vectors are:

$$\begin{aligned}\mathbf{a}_1 &= \frac{a}{2}(1, 0, \frac{c}{a}),\\ \mathbf{a}_2 &= \frac{a}{2}(1, \frac{b}{a}, 0),\\ \mathbf{a}_3 &= \frac{a}{2}(0, \frac{b}{a}, \frac{c}{a}).\end{aligned}$$

while the reciprocal lattice vectors are

$$\begin{aligned}\mathbf{b}_1 &= \frac{2\pi}{a}(1, -\frac{a}{b}, \frac{a}{c}),\\ \mathbf{b}_2 &= \frac{2\pi}{a}(1, \frac{a}{b}, -\frac{a}{c}),\\ \mathbf{b}_3 &= \frac{2\pi}{a}(-1, \frac{a}{b}, \frac{a}{c}).\end{aligned}$$

In this case there are three different shapes that can be rotated in different ways depending on the relative sizes of a, b, and c. If a is the shortest side, there are three different shapes according to

$$\frac{1}{a^2} \lessgtr \frac{1}{b^2} + \frac{1}{c^2}, \tag{1}$$

if b is the shortest side there are three different shapes according to

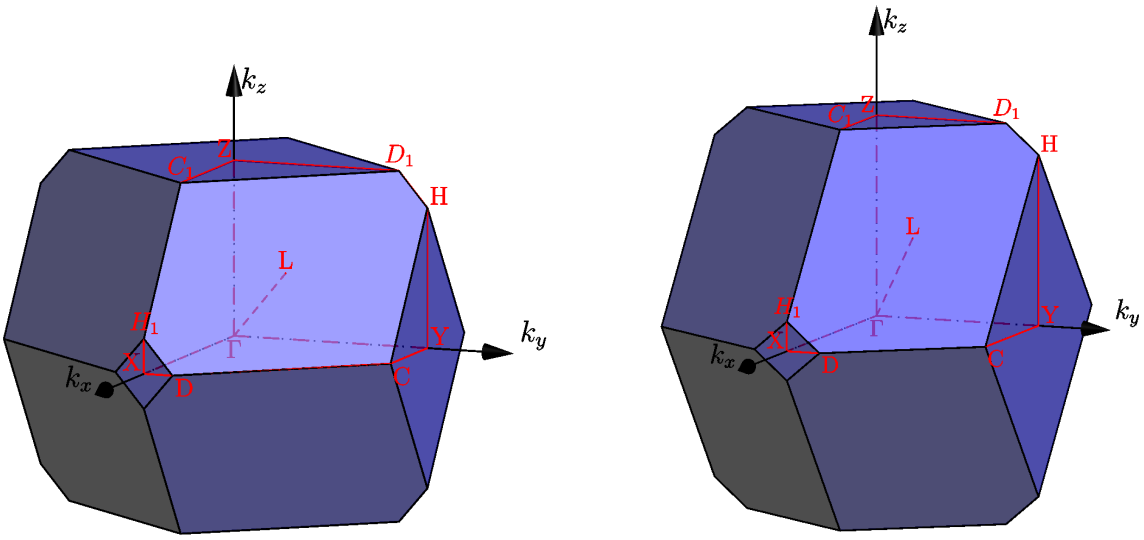
$$\frac{1}{b^2} \lessgtr \frac{1}{a^2} + \frac{1}{c^2}, \tag{2}$$

and if c is the shortest side there are three different shapes according to

$$\frac{1}{c^2} \lessgtr \frac{1}{a^2} + \frac{1}{b^2}. \tag{3}$$

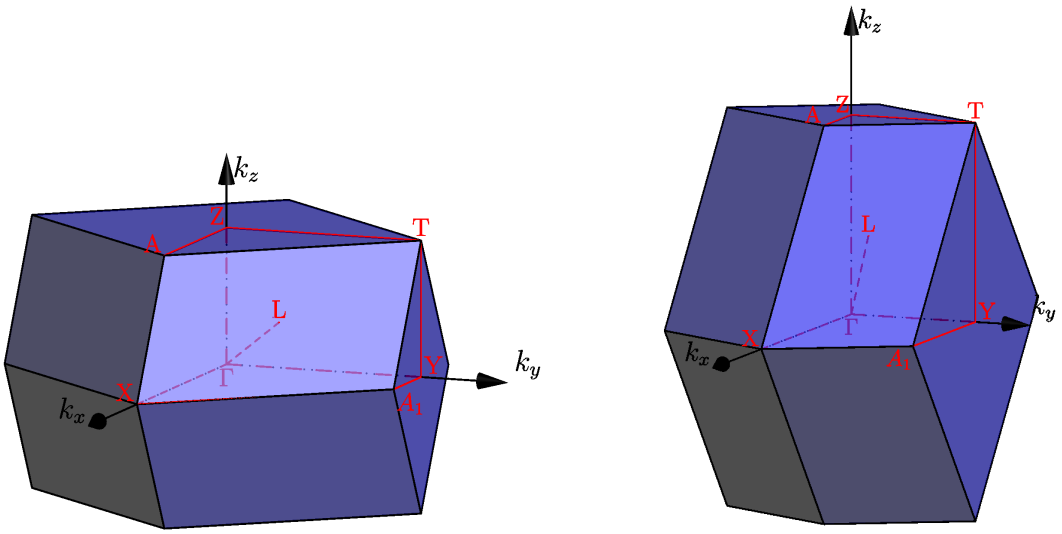
For each case there are two possibilities. If a is the shortest side, we can have $b < c$ or $b > c$, if b is the shortest side, we can have $a < c$ or $a > c$, and finally if c is the shortest side we can have $a < b$ or $a > b$. In total we have 18 distinct cases. Not all cases give different BZ. All the cases with the $<$ sign in Eqs. 1, 2, 3 give the same shape of the BZ that differ for the relative sizes of the faces. All the cases with the $>$ sign in Eqs. 1, 2, 3 give the same shape with faces of different sizes and oriented in different ways. Finally the particular case with the $=$ sign in Eqs. 1, 2, 3 give another shape with faces of different size and different orientations. We show all the 18 possibilities and the labels used in each case.

We start with the case in which a is the shortest side and show on the left the case $b < c$ and on the right the case $b > c$. The first possibility is that $\frac{1}{a^2} < \frac{1}{b^2} + \frac{1}{c^2}$:



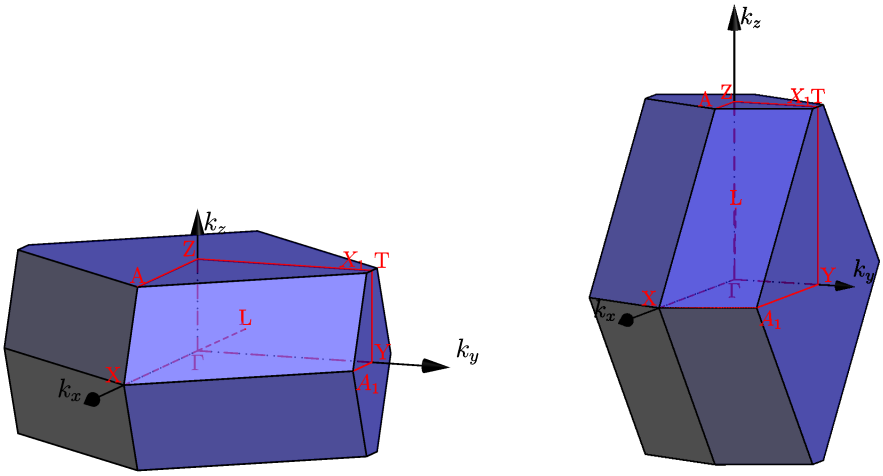
The figures have been obtained with $b/a = 1.2$ and $c/a = 1.4$ (left part $b < c$), and with $b/a = 1.4$ and $c/a = 1.2$ (right part $b > c$).

The second possibility is that $\frac{1}{a^2} = \frac{1}{b^2} + \frac{1}{c^2}$:



The figures have been obtained with $b/a = 1.2$ and $c/a = 1.80906807$ (left part $b < c$) and with $b/a = 1.80906807$ and $c/a = 1.2$ (right part $b > c$).

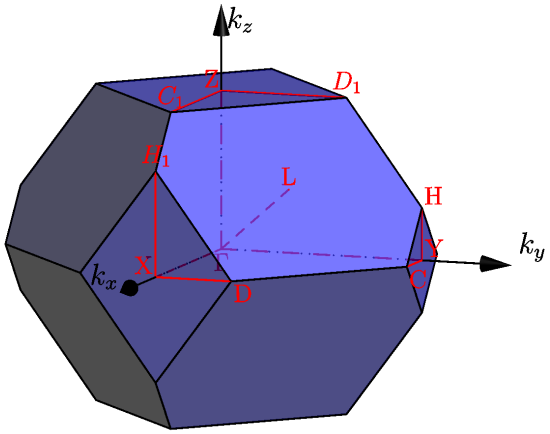
The third possibility is that $\frac{1}{a^2} > \frac{1}{b^2} + \frac{1}{c^2}$:

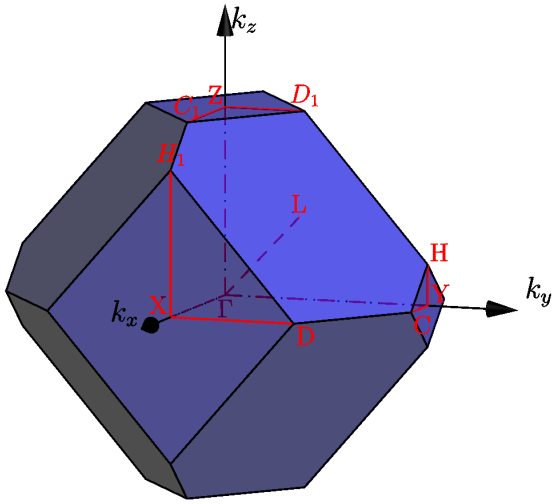


The figures have been obtained with $b/a = 1.2$ and $c/a = 2.4$ (left part $b < c$), and with $b/a = 2.4$ and $c/a = 1.2$ (right part $b > c$).

Then we consider the cases in which b is the shortest side and show on the left the case in which $a < c$ and on the right the case $a > c$.

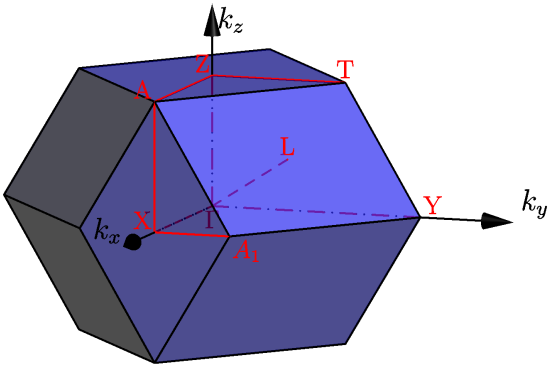
We have the same three possibilities as before. The first possibility is that $\frac{1}{b^2} < \frac{1}{a^2} + \frac{1}{c^2}$:

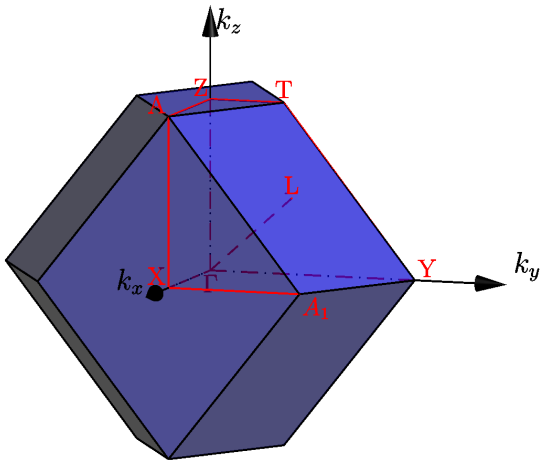




The figures have been obtained with $b/a = 0.9$ and $c/a = 1.2$ (left part $a < c$) and $b/a = 0.75$ and $c/a = 0.95$ (right part $a > c$).

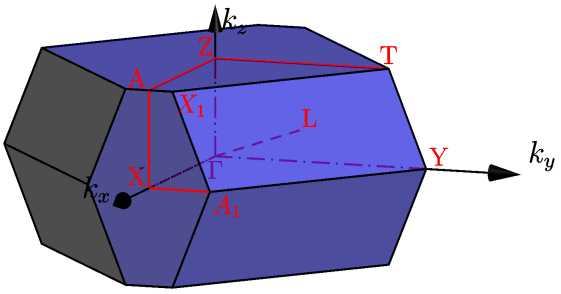
The second possibility is that $\frac{1}{b^2} = \frac{1}{a^2} + \frac{1}{c^2}$:

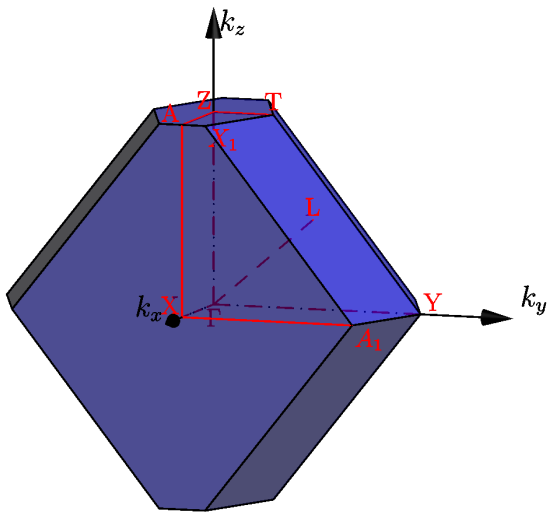




The figures have been obtained with $b/a = 0.8$ and $c/a = 1.33333333333$ (left part $a < c$), and $b/a = 0.6$ and $c/a = 0.75$ (right part $a > c$).

The third possibility is than $\frac{1}{b^2} > \frac{1}{a^2} + \frac{1}{c^2}$:

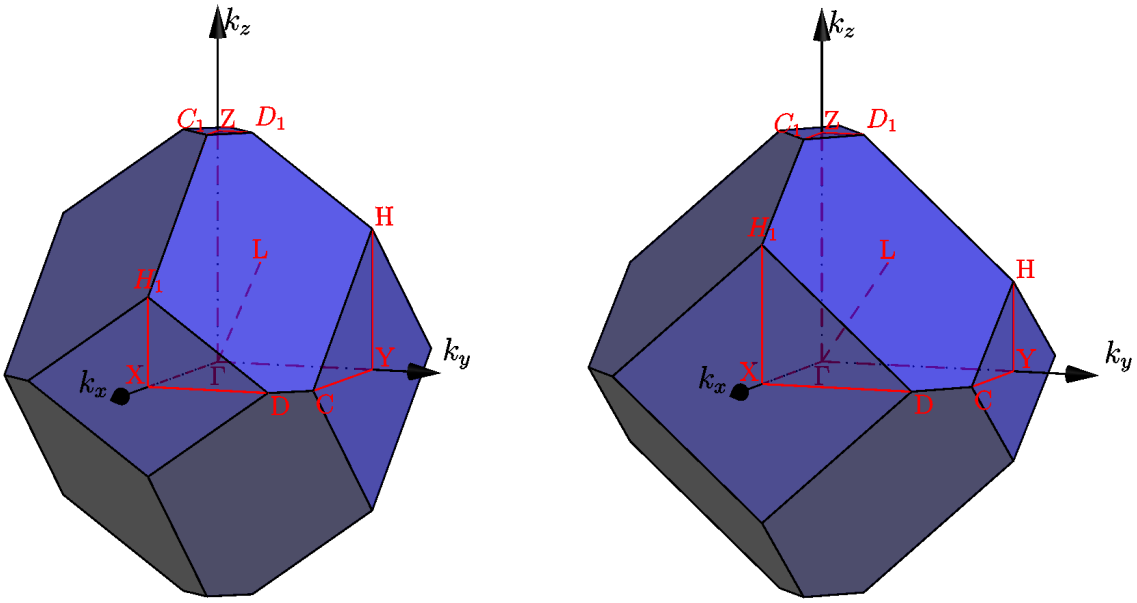




The figures have been obtained with $b/a = 0.8$ and $c/a = 2.0$ (left part $a < c$), and with $b/a = 0.4$ and $c/a = 0.5$ (right part $a > c$).

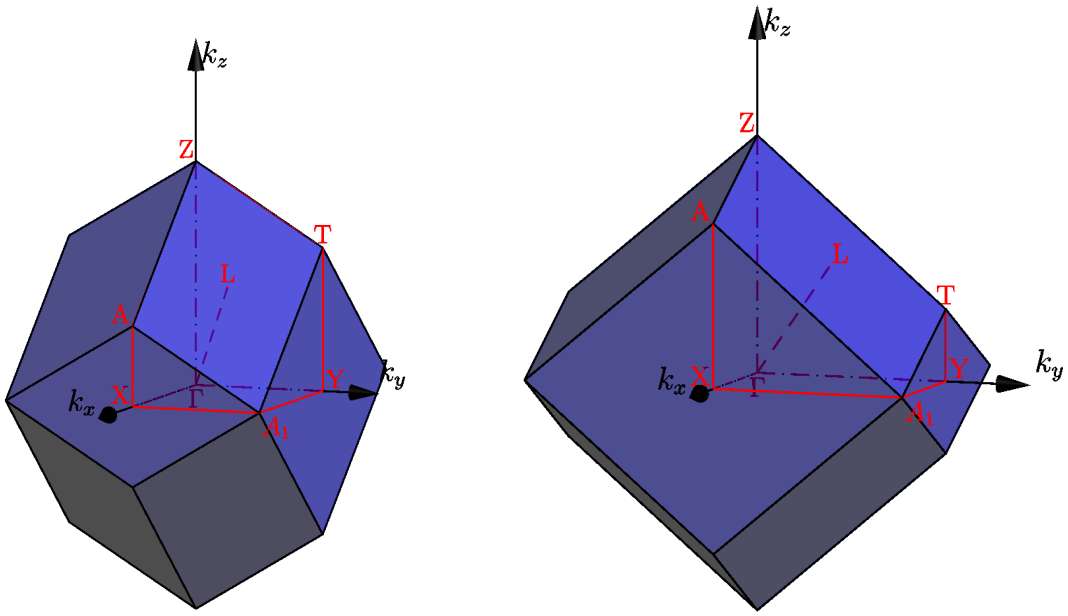
Finally we consider the case in which c is the shortest side and show on the left the case in which $a < b$ and on the right the case in which $a > b$.

The first possibility is that $\frac{1}{c^2} < \frac{1}{a^2} + \frac{1}{b^2}$:



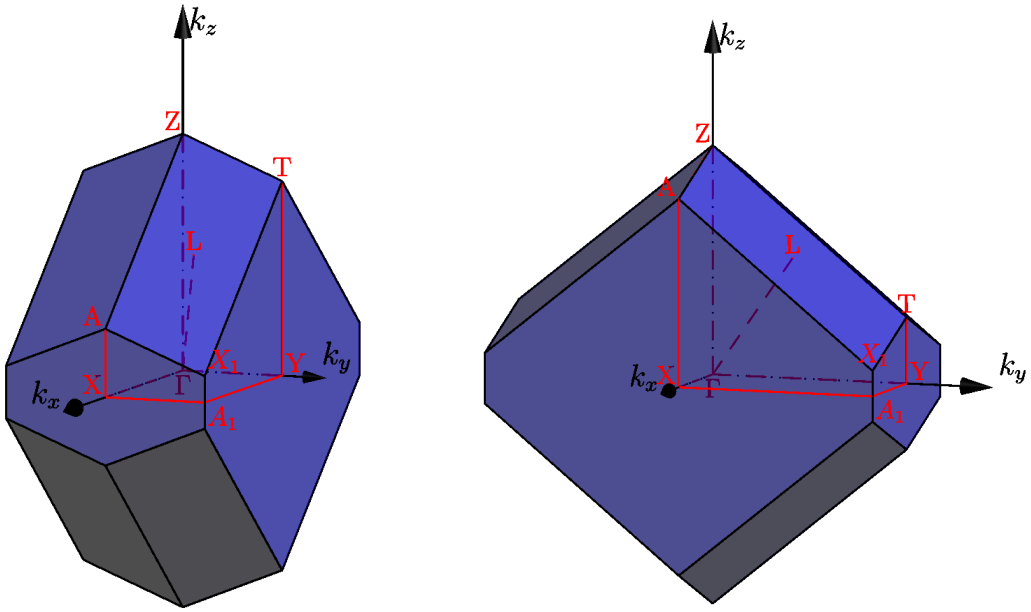
The figures have been obtained with $b/a = 1.2$ and $c/a = 0.85$ (left part $a < b$) and $b/a = 0.85$ and $c/a = 0.75$ (right part $a > b$).

The second possibility is that $\frac{1}{c^2} = \frac{1}{a^2} + \frac{1}{b^2}$:



The figures have been obtained with $b/a = 1.333333333$ and $c/a = 0.8$ (left part $a < b$) and with $b/a = 0.66$ and $c/a = 0.5508422$ (right part $a > b$).

Finally the third possibility is that $\frac{1}{c^2} > \frac{1}{a^2} + \frac{1}{b^2}$:



The figures have been obtained with $b/a = 2.0$ and $c/a = 0.8$ (left part $a < b$), and $b/a = 0.5$ and $c/a = 0.4$ (right part $a > b$).

1.11 `ibrav=11`, body centered orthorhombic lattice

The direct lattice vectors are:

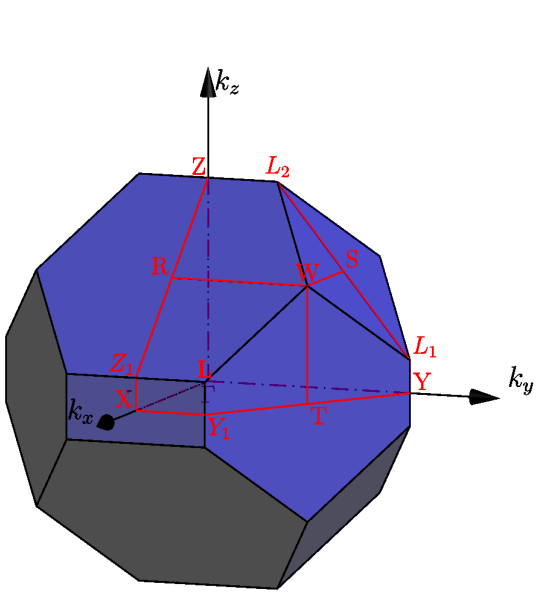
$$\begin{aligned}
\mathbf{a}_1 &= \frac{a}{2}(1, \frac{b}{a}, \frac{c}{a}), \\
\mathbf{a}_2 &= \frac{a}{2}(-1, \frac{b}{a}, \frac{c}{a}), \\
\mathbf{a}_3 &= \frac{a}{2}(-1, -\frac{b}{a}, \frac{c}{a}).
\end{aligned}$$

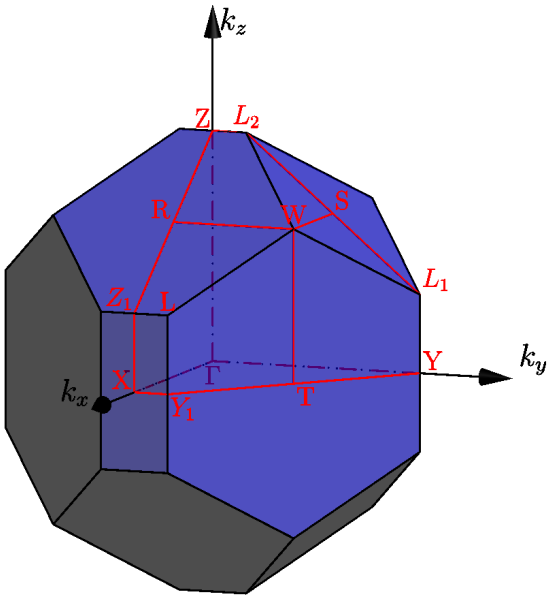
while the reciprocal lattice vectors are:

$$\begin{aligned}
\mathbf{b}_1 &= \frac{2\pi}{a}(1, 0, \frac{a}{c}), \\
\mathbf{b}_2 &= \frac{2\pi}{a}(-1, \frac{a}{b}, 0), \\
\mathbf{b}_3 &= \frac{2\pi}{a}(0, -\frac{a}{b}, \frac{a}{c}).
\end{aligned}$$

In this case the BZ has one shape that can be rotated in different ways depending on the relative sizes of a, b, and c. Similar orientations and BZ that differ only for the relative sizes of the faces are obtained for the cases that have in common the longest side. Therefore we distinguish the cases in which a is the longest side and $b < c$ or $b > c$, the cases in which b is the longest side and $a < c$ or $a > c$ and the cases in which c is the longest side and $a < b$ or $a > b$. We have 6 distinct cases.

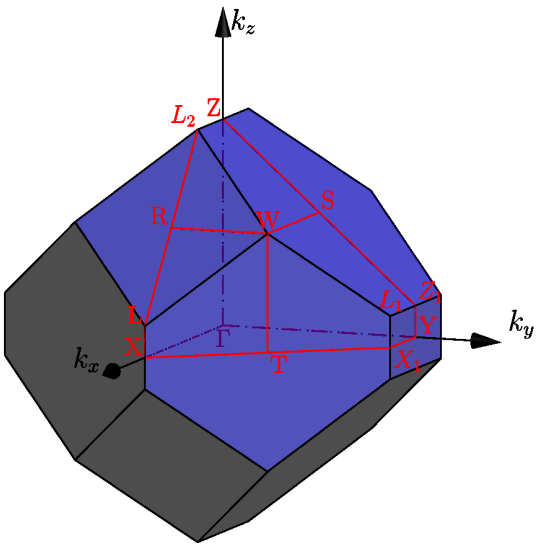
First we take a as the longest side and show on the left the case $b < c$ and on the right the case $b > c$:

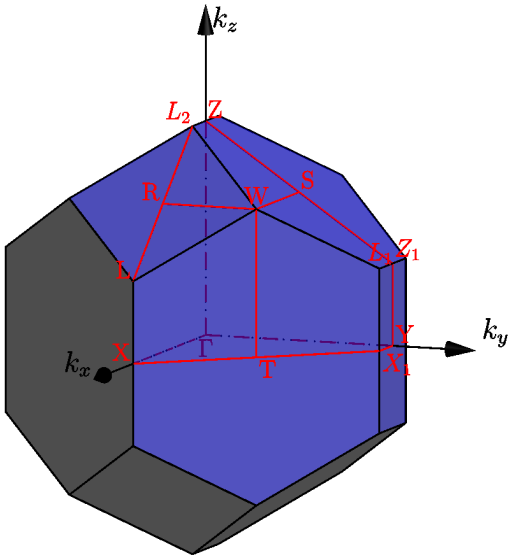




The figures have been obtained with $b/a = 0.7$ and $c/a = 0.85$ (left part $b < c$) and $b/a = 0.85$ and $c/a = 0.7$ (right part $b > c$).

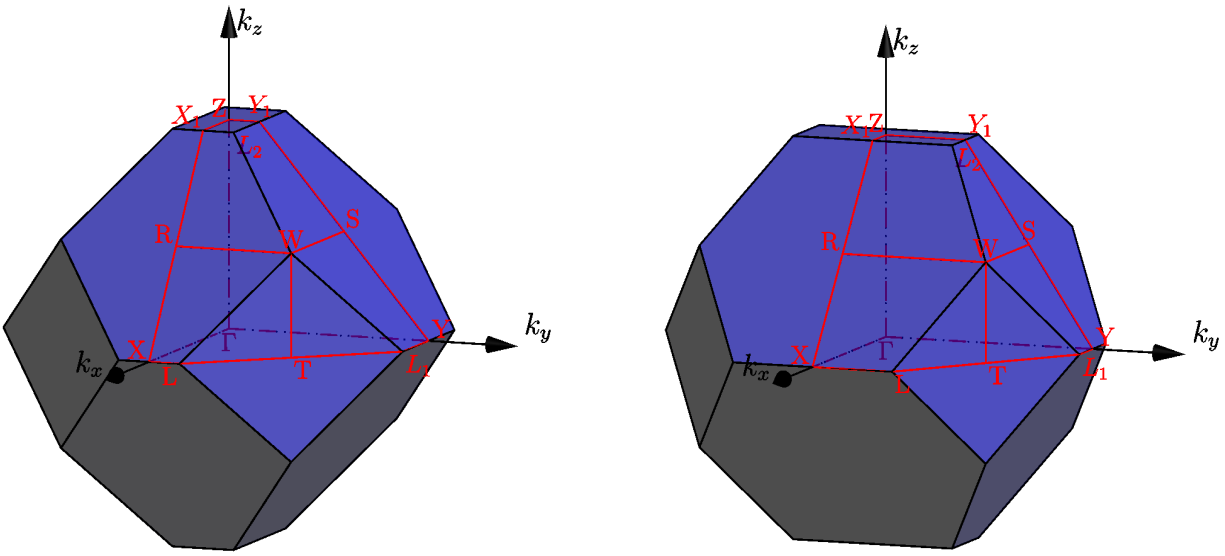
Then we take b as the longest side and show on the left the case in which $a < c$ and on the right the case in which $a > c$:





The figures have been obtained with $b/a = 1.4$ and $c/a = 1.2$ (left part $a < c$) and $b/a = 1.2$ and $c/a = 0.8$ (right part $a > c$).

Finally we take c as the longest side and show on the left the case in which $a < b$ and on the right the case in which $b < a$:



The figures have been obtained with $b/a = 1.2$ and $c/a = 1.4$ (left part), and $b/a = 0.8$ and $c/a = 1.2$ (right part).

1.12 `ibrav=12`, simple monoclinic lattice, c unique

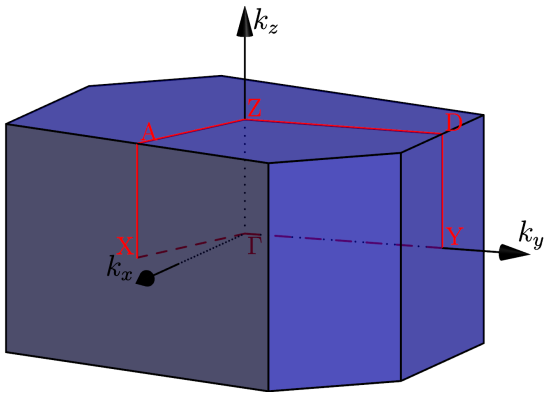
The direct lattice vectors are:

$$\begin{aligned}
\mathbf{a}_1 &= a(1,0,0), \\
\mathbf{a}_2 &= a(\frac{b}{a}\cos\gamma, \frac{b}{a}\sin\gamma, 0), \\
\mathbf{a}_3 &= a(0,0,\frac{c}{a}).
\end{aligned}$$

while the reciprocal lattice vectors are:

$$\begin{aligned}
\mathbf{b}_1 &= \frac{2\pi}{a}(1, -\frac{\cos\gamma}{\sin\gamma}, 0), \\
\mathbf{b}_2 &= \frac{2\pi}{a}(0, \frac{a}{b\sin\gamma}, 0), \\
\mathbf{b}_3 &= \frac{2\pi}{a}(0,0,\frac{a}{c}).
\end{aligned}$$

The Brillouin zone is:



The figure has been obtained with $b/a = 0.8$, $c/a = 1.4$ and $\cos\gamma = 0.3$.

1.13 `ibrav=-12`, simple monoclinic lattice, b unique

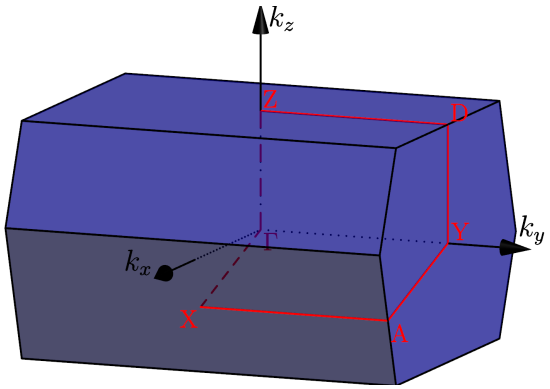
The direct lattice vectors are:

$$\begin{aligned}\mathbf{a}_1 &= a(1,0,0),\\ \mathbf{a}_2 &= a(0,\frac{b}{a},0),\\ \mathbf{a}_3 &= a(\frac{c}{a}\cos\beta,0,\frac{c}{a}\sin\beta),\end{aligned}$$

while the reciprocal lattice vectors are:

$$\begin{aligned}\mathbf{b}_1 &= \frac{2\pi}{a}(1,0,-\frac{\cos\beta}{\sin\beta}),\\ \mathbf{b}_2 &= \frac{2\pi}{a}(0,\frac{a}{b},0),\\ \mathbf{b}_3 &= \frac{2\pi}{a}(0,0,\frac{a}{c\sin\beta}).\end{aligned}$$

The Brillouin zone is:



The figure has been obtained with $b/a = 0.8$, $c/a = 1.4$ and $\cos\beta = 0.3$.

1.14 `ibrav=13,14`, one-base centered monoclinic, triclinic

These lattices are not supported by this feature, you have to give explicitly the coordinates of the path.

2 Bibliography

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[4] E.S. Tasci, G. de la Flor, D. Orobengoa, C. Capillas, J.M. Perez-Mato, M.I. Aroyo, "An introduction to the tools hosted in the Bilbao Crystallographic Server". EPJ Web of Conferences 22 00009 (2012).