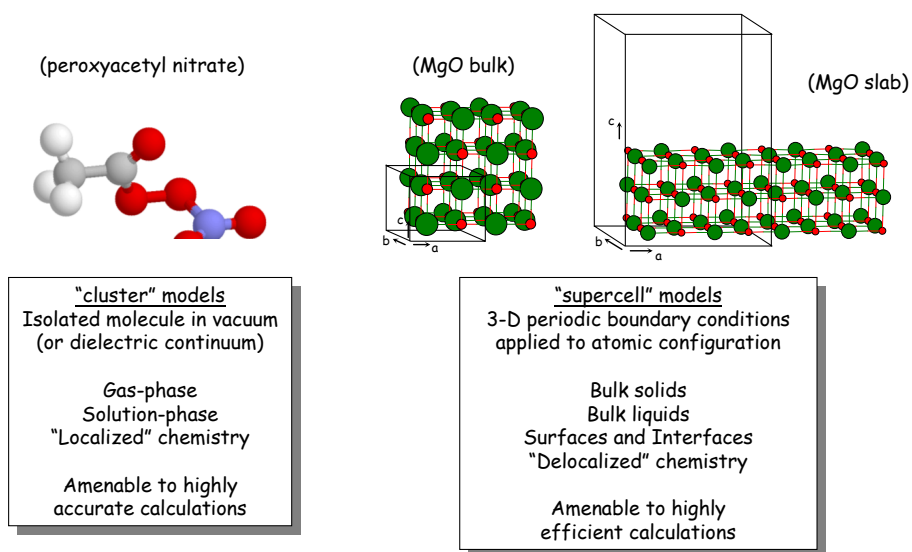## 1. Isolated vs. periodic systems

How to model things that are *not* molecular, like a metal or semiconductor or the surface of something? Could create a very large chunk, or "cluster," of the material, but this can be both expensive and not always clear how to create and terminate the chunk. Alternative is to create infinitely repeated, *periodic boundary condition* models. Is this easier? Yes, in particular in the context of DFT.

(peroxyacetyl nitrate)   (MgO bulk)   (MgO slab)

| "cluster" models	"supercell" models
Isolated molecule in vacuum (or dielectric continuum)	3-D periodic boundary conditions applied to atomic configuration
Gas-phase Solution-phase "Localized" chemistry	Bulk solids Bulk liquids Surfaces and Interfaces "Delocalized" chemistry
Amenable to highly accurate calculations	Amenable to highly efficient calculations

A *critical* difference between these supercells for bulk materials like MgO and the previous atom and molecule examples above, is that in the former case the bonding extends *across the boundaries of the box*. In brief, any particular ao or mo inside the supercell becomes an *infinite* number of states indexed by the real vector **k**.

2. Bloch's theorem and qualitative band structure

Have to learn some new language, derived from the solid state physics community, to understand the "band structure" model of electronic structure. Has a tradition at least as rich as molecular orbital/quantum chemistry. Pictures in this section borrowed liberally from Hoffmann, *Angew. Chemie* **1987**, *26*, 846.

Consider cyclic chain of increasing length of H atoms. Boundary condition (Born-van Karman) that wavefunctions connect at the end of the chain.
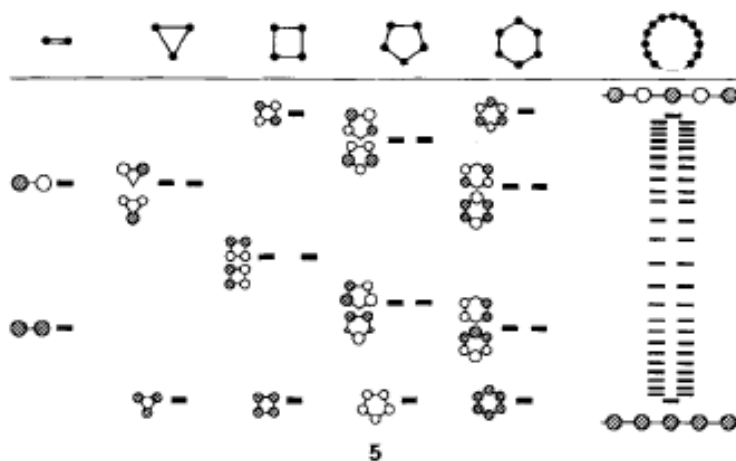
How would we solve this? Basis of single *s* (or *p*) function on each center, construct secular matrix and diagonalize (e.g., Hückel model). Get same number of output molecular orbitals as input atom orbitals.

As ring increases, number of states gets commensurately larger, but spreading out is seen to saturate. As number $\rightarrow \infty$, get continuous *band* of energy levels.

Note there is some regularity to the energy levels, number of nodes increases in a regular way. Each H atom here is identical to every other; the electrons in the orbital states "see" the same attractive potential near each atom. Define a lattice constant *a*.
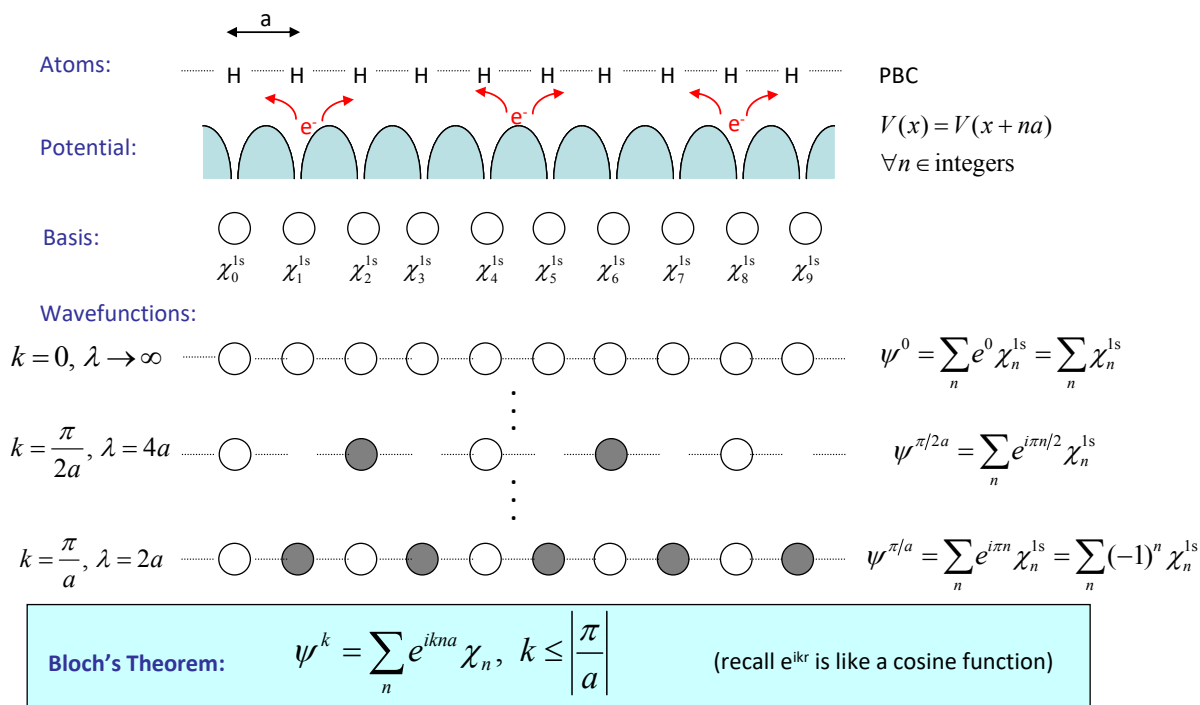

Bloch's theorem says that the periodic wavefunctions can be written as the product of a cell-invariant part (the H 1s functions here) and a cell-periodic part. The periodic part is indexed by the *wavevector k*. *k* takes as many values as there are periodic units *N*.
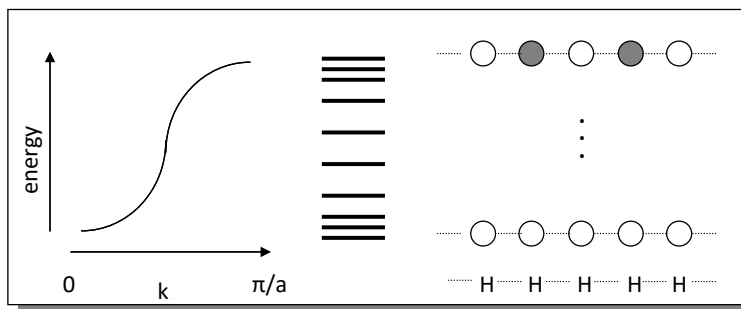
$$k = \frac{\pi}{a}\frac{n}{N}, \quad n = -\frac{N-1}{2}, ..., 0, ..., \frac{N-1}{2}$$

If *n* is infinite, than *k* is a continuous and real variable, and it exists within *reciprocal space* (note *k* has dimensions 1/length). The space of unique values of *k* is called the *first Brillouin zone*. The periodic phases of the basis functions correspond to an underlying wavelength associated with *k*: $\lambda_k = 2\pi/k$. By the de Broglie relationship, then, *k* relates to the *momentum* of an electron in that energy level. Each *k* is degenerate such that $E(k) = E(-k)$, as can be seen in the picture above.

The space of continuous energy levels in *k* is called the *band structure*. By convention, structure is plotted against |k|. The width, or *dispersion*, of the energy band is determined by the overlap between adjacent periodic cells. Bottom of band is bonding, top is anti-bonding.
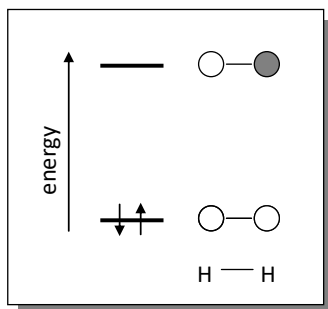
Molecular orbital diagram   Band structure diagram

The highest occupied energy level, in this particular case $k = \pi/2a$, is called the *Fermi energy*. Dispersion of bands depends on overlap via spacing between cells, and direction depends on topology of orbitals:
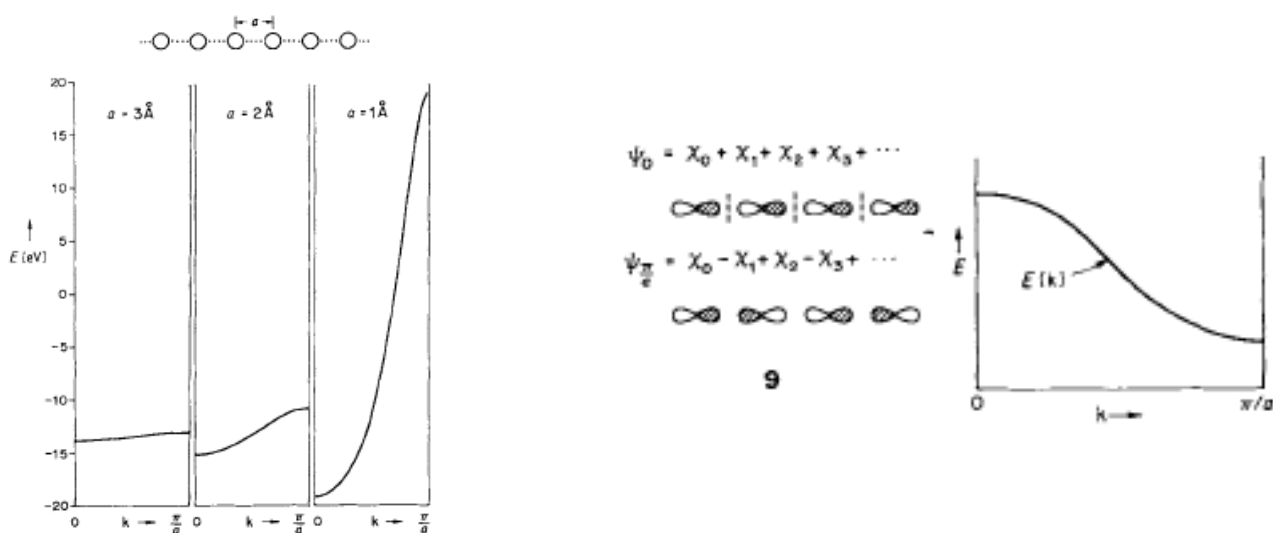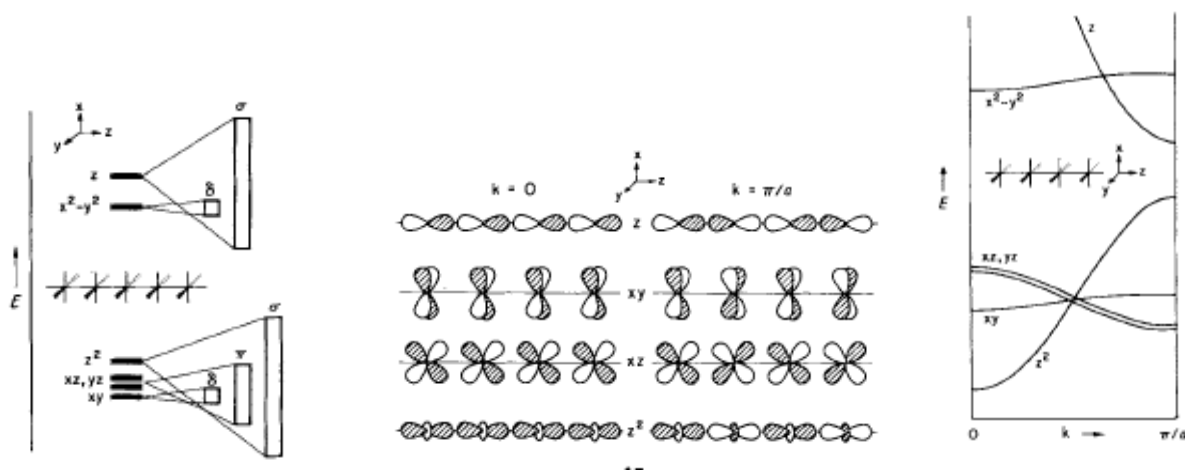

Fig. 1. The band structure of a chain of H atoms spaced 3, 2, and 1 Å apart. The energy of an isolated H atom is −13.6 eV.

If we had multiple basis functions on each center, would get multiple bands. Consider p_z and d orbitals from a chain of metal atoms:

Orbitals that overlap strongly give big dispersion, and bands run in directions determined by type of overlap. Extent of bonding depends on how many levels are filled.

Electrical properties related to band filling: partially filled bands at Fermi level → metallic behavior; "gap" at Fermi level → insulator. Analysis is domain of solid state physics.

3. Band folding

No reason we have to choose a single atom as the fundamental unit cell. Could e.g double the size of the cell, to create a *supercell*. Now basis is doubled in size and Brillouin zone is halved.
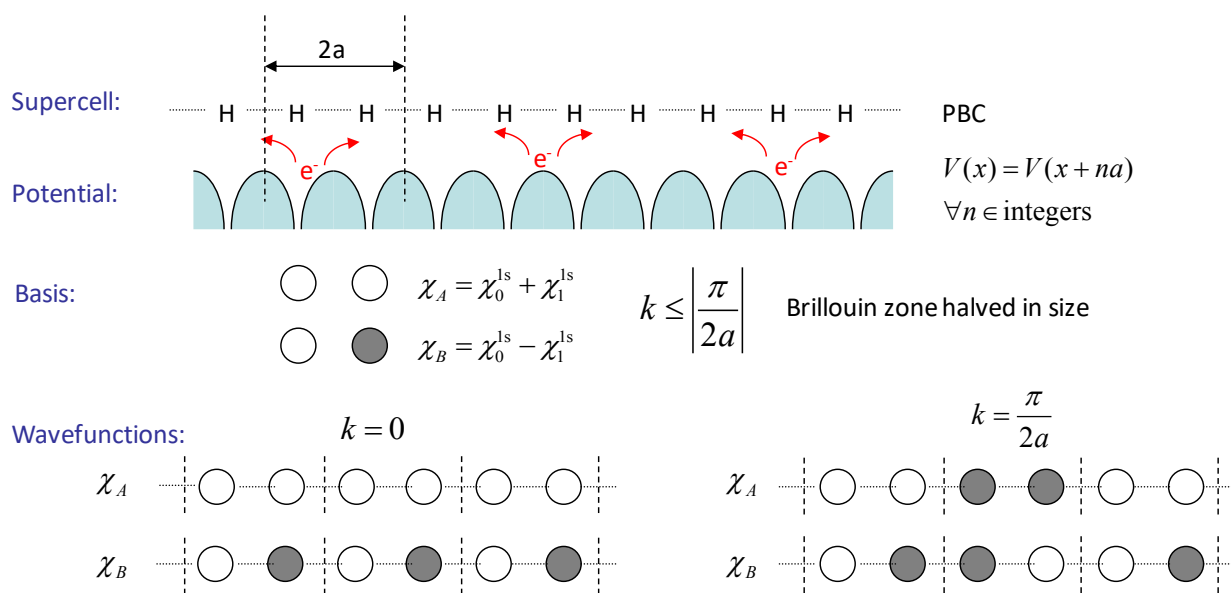

χ_A band runs up in energy, χ_B runs down. Note that χ_A is always bonding and χ_B always antibonding *within* the supercell, but depending on k, they are either bonding or anti-bonding *between* cells. The two bands are degenerate (identical) at right edge of BZ. Plot energies:
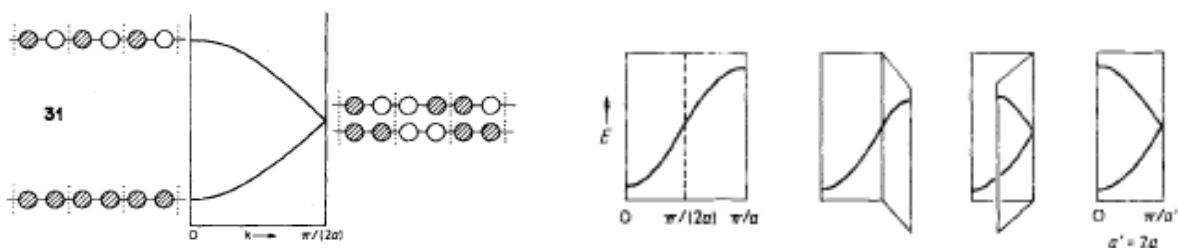
New band structure is identical to the old, but the band is folded in half. One *k*-point now contains information about two different bands. Could continue, BZ keeps getting smaller, bands keep multiplying, eventually return to MOs of one big molecule.

Notice in this particular case, since there is one electron/H that the Fermi level is right at the point where the two bands meet. This is an unstable situation: a high symmetry degenerate state. The energy can be lowered by allowing the hydrogens to pair up, causes states near Fermi level to separate. This is termed a *Peierl's distortion*, and is analogous to a *Jahn-Teller distortion* in molecules. Of course we knew that a chain of H atoms would want to make H_2 molecules!
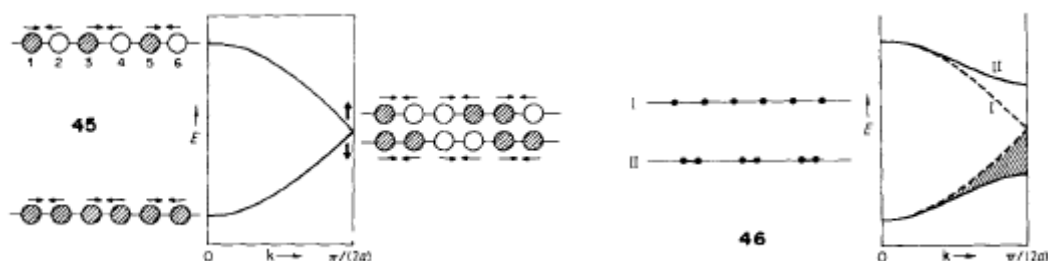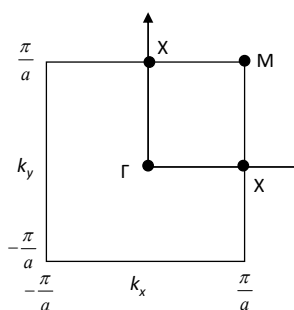

4. Multi-dimensional periodicity

Same ideas can be generalized to crystals with 2-D and 3-D periodicity. All points on lattice can be defined in terms of lattice vectors that define the unit cell. *k* becomes a *wavevector* **k** defined within a 2- or 3-D reciprocal space.

Square lattice

$$\mathbf{a}_1 = a\hat{x}$$
$$\mathbf{a}_2 = a\hat{y}$$
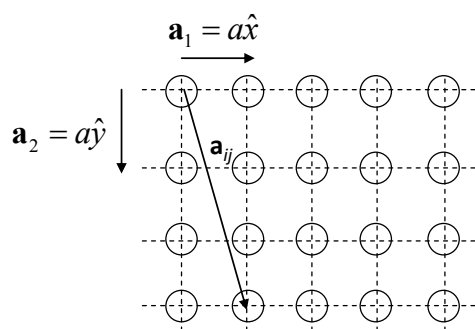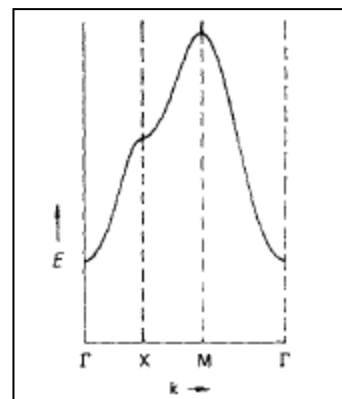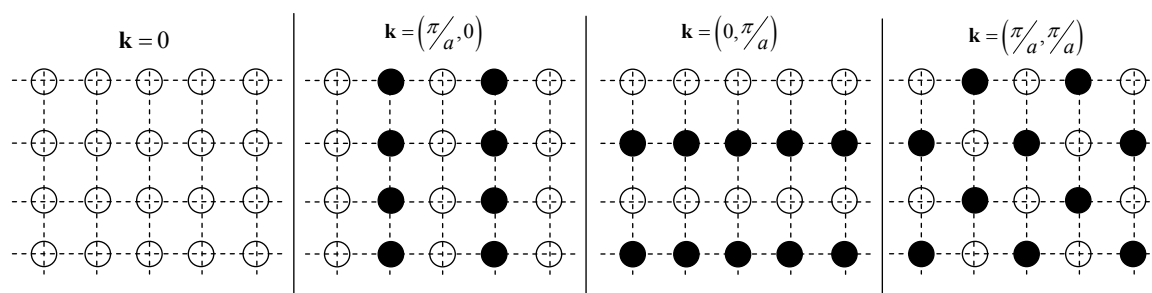
2-D Square Brillouin zone

Reciprocal lattice vectors

$$\mathbf{b}_1 = \left(\frac{2\pi}{a}\right)\hat{x} \qquad \mathbf{b}_2 = \left(\frac{2\pi}{a}\right)\hat{y} \qquad \mathbf{k} = k_x\mathbf{b}_1 + k_y\mathbf{b}_2$$

$$\psi^{\mathbf{k}} = \sum_{i,j} e^{i\mathbf{k}\cdot\mathbf{a}_{ij}} \chi_{ij}, \qquad k_x \leq \left|\frac{\pi}{a}\right|, k_y \leq \left|\frac{\pi}{a}\right|$$

Some sample 2-D wavefunctions:

Band structure $E(\mathbf{k})$ is now multi-dimensional, and it is customary to plot energy along special directions in reciprocal space.

5. Density of states

Given multi-dimensional character of $\mathbf{k}$, it is convenient sometimes to average out the $\mathbf{k}$ contributions to bands. Density of states (DOS) provides a way:

$$\rho(E) = \frac{a}{2\pi} \int_{\pi/a}^{\pi/a} \delta(\epsilon_k - E)\,dk$$

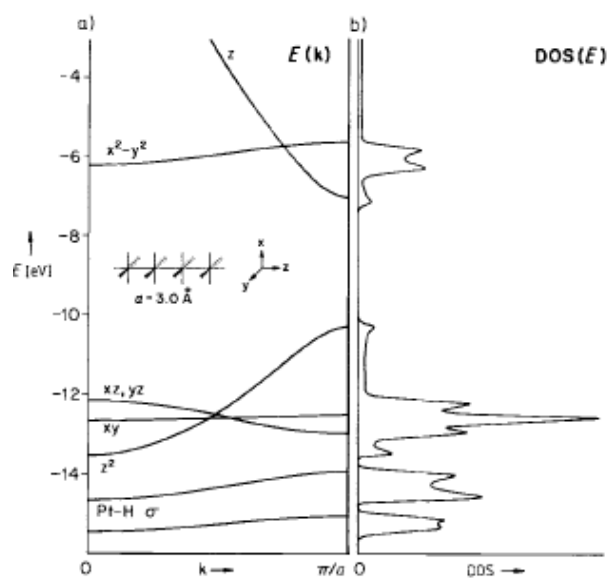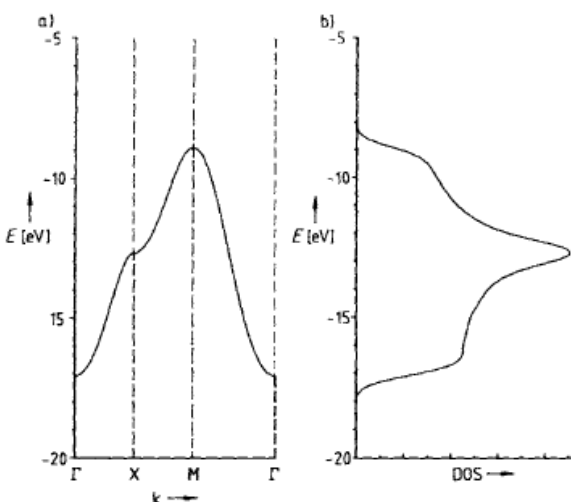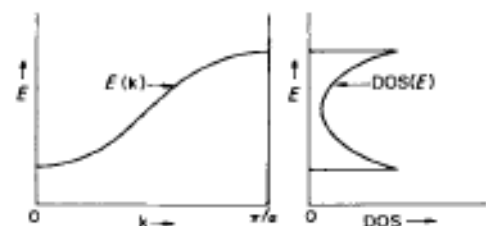: number of states in interval E to $E+dE$

Fig. 4. a) Band structure and b) density of states (DOS) for an eclipsed [PtH$_4$]$^{2\ominus}$ stack. The DOS curves are broadened so that the two-peaked shape of the xy peak in the DOS is not resolved.
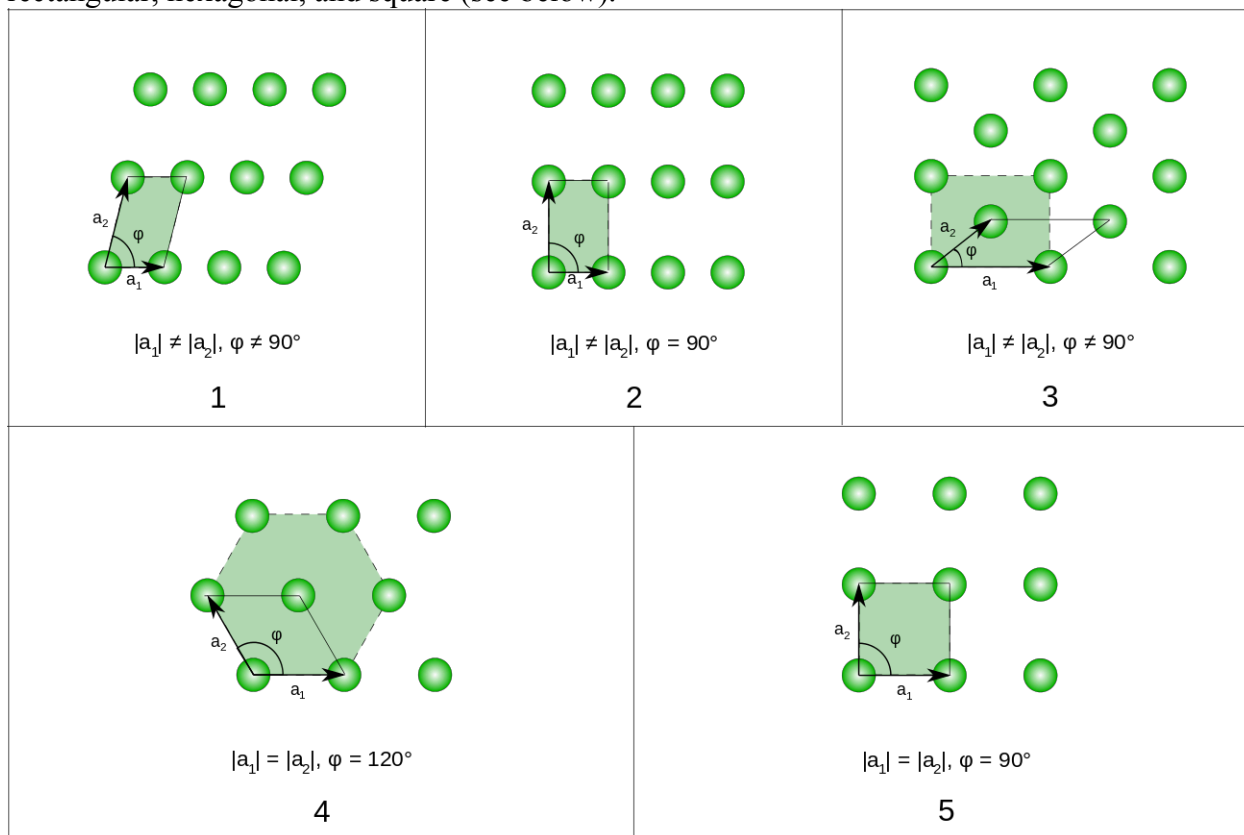
Recall a particular band (peak in DOS) is bonding or anti-bonding within the cell, but the width of the DOS peak spans from bonding to antibonding *between* cells.

6. Bravais lattices

In general, the translational symmetry can be characterized in terms of a *Bravais lattice*, which describes an infinite periodic array of units. The thing that is periodically replicated, the periodic unit, is called the *basis*. The basis could be an atom, a molecule, a fragment of a solid, a chunk of liquid, a banana, whatever.

In one dimension, there is only one type of Bravais lattice, defined by a single translation vector, **a**. Position of any lattice point can be given as some integer multiple of **a**, $\mathbf{R} = n\,\mathbf{a}$. Showed picture of this above.

In two dimensions, there are five distinct types of Bravais lattices, oblique, rectangular, centered rectangular, hexagonal, and square (see below).

$\lvert a_1\rvert \neq \lvert a_2\rvert$, $\varphi \neq 90°$	$\lvert a_1\rvert \neq \lvert a_2\rvert$, $\varphi = 90°$	$\lvert a_1\rvert \neq \lvert a_2\rvert$, $\varphi \neq 90°$
1	2	3
$\lvert a_1\rvert = \lvert a_2\rvert$, $\varphi = 120°$		$\lvert a_1\rvert = \lvert a_2\rvert$, $\varphi = 90°$
4		5
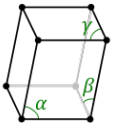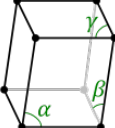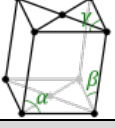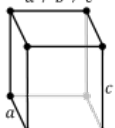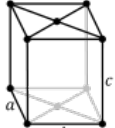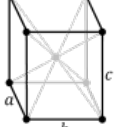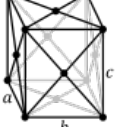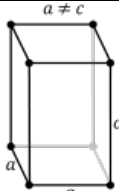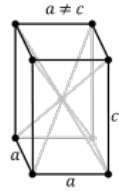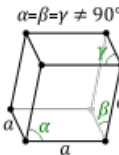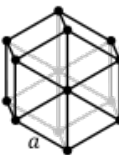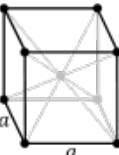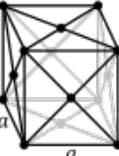
The lattice vectors define the *unit cell*. The unit cell is not unique; *primitive cell* contains exactly one Bravais lattice point. Larger unit cells can be constructed; show example of conventional cell for centered lattice.

Wigner-Seitz cell is most compact cell possible, formed by region created by bisectors to all neighbors. Show example above.

In three dimensions, defined by three lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$, which defines an infinite periodic array of units. Position of any lattice point can be given by three integers, $\mathbf{R} = n_1\,\mathbf{a}_1 + n_2\,\mathbf{a}_2\,n_3\,\mathbf{a}_3$.

There are 14 Bravais lattices in three dimensions, combination of 7 crystal systems and four types of centerings, Primitive (P), Body Centered (I), Face Centered (F), and Base Centered (C) (not all 28 combinations are unique). (Images courtesy Wikipedia). Our POSCARs will always fall into one of these 14 types. In order of roughly increasing symmetry:

	Triclinic			
1	Primitive	$a \neq b \neq c$ $\alpha, \beta, \gamma \neq 90°$	$\alpha, \beta, \gamma \neq 90°$ 	$\boldsymbol{a_1} = a \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad \boldsymbol{a_2} = b \begin{pmatrix} \cos\gamma \\ \sin\gamma \\ 0 \end{pmatrix} \quad \boldsymbol{a_3} = c \begin{pmatrix} \cos\beta \\ \cos\alpha' \sin\beta \\ \sin\alpha' \sin\beta \end{pmatrix}$ $\sin\alpha' = \dfrac{\sqrt{\sin^2\gamma - \cos^2\beta - \cos^2\alpha + 2\cos\alpha\cos\beta\cos\gamma}}{\sin\beta\sin\gamma}$ $\cos\alpha' = \dfrac{\cos\alpha - \cos\beta\cos\gamma}{\sin\beta\sin\gamma}$

	Monoclinic			
2	Primitive	$a \neq b \neq c$ $\alpha = \beta = 90°$ $\gamma \neq 90°$	$\alpha \neq 90°$ $\beta, \gamma = 90°$ 	$\boldsymbol{a_1} = a \begin{pmatrix} \sin\gamma \\ \cos\gamma \\ 0 \end{pmatrix} \quad \boldsymbol{a_2} = \begin{pmatrix} 0 \\ b \\ 0 \end{pmatrix} \quad \boldsymbol{a_3} = \begin{pmatrix} 0 \\ 0 \\ c \end{pmatrix}$
3	Base Centered		$\alpha \neq 90°$ $\beta, \gamma = 90°$ 	$t_1 = +\dfrac{1}{2}a_1 - \dfrac{1}{2}a_2$ $t_2 = +\dfrac{1}{2}a_1 + \dfrac{1}{2}a_2$ $t_3 = +\dfrac{1}{2}a_3$ (I think)

	Orthorhombic			
4	Primitive	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	$a \neq b \neq c$ 	$\boldsymbol{a_1} = \begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix} \quad \boldsymbol{a_2} = \begin{pmatrix} 0 \\ b \\ 0 \end{pmatrix} \quad \boldsymbol{a_3} = \begin{pmatrix} 0 \\ 0 \\ c \end{pmatrix}$
5	Base Centered		$a \neq b \neq c$ 	$t_1 = +\dfrac{1}{2}a_1 - \dfrac{1}{2}a_2$ $t_2 = +\dfrac{1}{2}a_1 + \dfrac{1}{2}a_2$ $t_3 = +\dfrac{1}{2}a_3$
6	Body Centered		$a \neq b \neq c$ 	$t_1 = -\dfrac{1}{2}a_1 + \dfrac{1}{2}a_2 + \dfrac{1}{2}a_3$ $t_2 = +\dfrac{1}{2}a_1 - \dfrac{1}{2}a_2 + \dfrac{1}{2}a_3$ $t_3 = +\dfrac{1}{2}a_1 + \dfrac{1}{2}a_2 - \dfrac{1}{2}a_3$
7	Face Centered		$a \neq b \neq c$ 	$t_1 = +\dfrac{1}{2}a_2 + \dfrac{1}{2}a_3$ $t_2 = +\dfrac{1}{2}a_1 + \dfrac{1}{2}a_3$ $t_3 = +\dfrac{1}{2}a_1 + \dfrac{1}{2}a_2$

	Tetragonal			

8	Primitive	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$		$\boldsymbol{a}_1 = \begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix} \quad \boldsymbol{a}_2 = \begin{pmatrix} 0 \\ b \\ 0 \end{pmatrix} \quad \boldsymbol{a}_3 = \begin{pmatrix} 0 \\ 0 \\ c \end{pmatrix}$
9	Body Centered			$\boldsymbol{t}_1 = -\frac{1}{2}\boldsymbol{a}_1 + \frac{1}{2}\boldsymbol{a}_2 + \frac{1}{2}\boldsymbol{a}_3$ $\boldsymbol{t}_2 = +\frac{1}{2}\boldsymbol{a}_1 - \frac{1}{2}\boldsymbol{a}_2 + \frac{1}{2}\boldsymbol{a}_3$ $\boldsymbol{t}_3 = +\frac{1}{2}\boldsymbol{a}_1 + \frac{1}{2}\boldsymbol{a}_2 - \frac{1}{2}\boldsymbol{a}_3$
	Rhombohedral/Trigonal			
10	Primitive	$a = b = c$ $\alpha = \beta = \gamma \neq 90°$		Treat as hexagonal with basis of $(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$ and $(\frac{1}{3}, \frac{2}{3}, \frac{2}{3})$
	Hexagonal			
11	Primitive	$a = b \neq c$ $\alpha = \beta = 90°$ $\gamma = 120°$		$\boldsymbol{a}_1 = a \begin{pmatrix} \frac{\sqrt{3}}{2} \\ -\frac{1}{2} \\ 0 \end{pmatrix} \quad \boldsymbol{a}_2 = a \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad \boldsymbol{a}_3 = c \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix},$
	Cubic			
12	Primitive	$a = b = c$ $\alpha = \beta = \gamma = 90°$		$\boldsymbol{a}_1 = \begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix} \quad \boldsymbol{a}_2 = \begin{pmatrix} 0 \\ b \\ 0 \end{pmatrix} \quad \boldsymbol{a}_3 = \begin{pmatrix} 0 \\ 0 \\ c \end{pmatrix}$
13	Body Centered			$\boldsymbol{t}_1 = -\frac{1}{2}\boldsymbol{a}_1 + \frac{1}{2}\boldsymbol{a}_2 + \frac{1}{2}\boldsymbol{a}_3$ $\boldsymbol{t}_2 = +\frac{1}{2}\boldsymbol{a}_1 - \frac{1}{2}\boldsymbol{a}_2 + \frac{1}{2}\boldsymbol{a}_3$ $\boldsymbol{t}_3 = +\frac{1}{2}\boldsymbol{a}_1 + \frac{1}{2}\boldsymbol{a}_2 - \frac{1}{2}\boldsymbol{a}_3$
14	Face Centered			$\boldsymbol{t}_1 = +\frac{1}{2}\boldsymbol{a}_2 + \frac{1}{2}\boldsymbol{a}_3$ $\boldsymbol{t}_2 = +\frac{1}{2}\boldsymbol{a}_1 + \frac{1}{2}\boldsymbol{a}_3$ $\boldsymbol{t}_3 = +\frac{1}{2}\boldsymbol{a}_1 + \frac{1}{2}\boldsymbol{a}_2$

Any of the "centered" ones can be defined as a conventional with a basis larger than 1.

NEED TO MAKE POSCARS OF ALL OF THESE!

7. Quantitative supercell calculations

Want to solve Kohn-Sham equation quantitatively:

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{Coulomb}}(\mathbf{r}) + v_{\text{xc}}[\rho(\mathbf{r}')] \right] \psi_i = \epsilon_i \psi_i$$

where the potential terms have the periodicity of a Bravais lattice, $v(\mathbf{r}) = v(\mathbf{r} + \mathbf{R})$ for all $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$. i indexes the various energy levels.

Convenient to define the *reciprocal lattice*, $\mathbf{b}$, defined in general by $\mathbf{b}^T\mathbf{a} = 2\pi\mathbf{1}$ (where columns of matrix correspond to lattice vectors). In 1 dimension, $b = 2\pi/a$. In 3 dimensions, can be shown to be

$$\mathbf{b}_1 = 2\pi\frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \qquad \mathbf{b}_2 = 2\pi\frac{\mathbf{a}_1 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \qquad \mathbf{b}_3 = 2\pi\frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \qquad \mathbf{k} = k_x\mathbf{b}_1 + k_y\mathbf{b}_2 + k_z\mathbf{b}_3$$

The Wigner-Seitz cell of the reciprocal lattice is the first Brillouin zone. Reciprocal lattice important for two reasons:

(1) <u>Fourier transforms</u>: Any function (like the potential, $v(\mathbf{r})$) that has the periodicity of the Bravais lattice can be written as a Fourier series whose only non-zero terms are elements of the reciprocal lattice, $\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$:

$$v(\mathbf{G}) = \frac{1}{\Omega_{\text{cell}}} \int_{\Omega_{\text{cell}}} v(\mathbf{r})e^{i\mathbf{G}\cdot\mathbf{r}}d\mathbf{r}$$

$$v(\mathbf{r}) = \sum_{\mathbf{G}} v(\mathbf{G})e^{i\mathbf{G}\cdot\mathbf{r}}$$

Can take advantage of this fact to efficiently evaluate matrix elements.

(2) <u>Bloch's theorem, rigorously</u>: The eigenstates ψ_i can be chosen to have the form of plane waves times a function with the periodicity of the Bravais lattice:

$$\psi_i^{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\chi_i^{\mathbf{k}}(\mathbf{r}), \text{ where } \chi_i^{\mathbf{k}}(\mathbf{r}) = \chi_i^{\mathbf{k}}(\mathbf{r} + \mathbf{R})$$

where the vectors $\mathbf{k}$ are within the first Brillouin zone. Kohn-Sham equation can then be written:

$$\boxed{\left[-\frac{1}{2}(\nabla + i\mathbf{k})^2 + v_{\text{Coulomb}}(\mathbf{r}) + v_{\text{xc}}[\rho(\mathbf{r}')] \right] \chi_i^{\mathbf{k}} = \epsilon_i^{\mathbf{k}}\chi_i^{\mathbf{k}}}$$

Have to solve this for all the orbitals *i and* for all possible (infinity!) values of $\mathbf{k}$, get the band structure $\epsilon_i^{\mathbf{k}}$ and wavefunctions inside the periodic cell, $\chi_i^{\mathbf{k}}$ and, of course, the total energy E.

Now we are back to where we were in the previous lecture. Can in principle expand χ_i^k in whatever basis we want, but based on (1) above, particularly convenient to describe using <u>plane-waves</u>, that is, to do a Fourier expansion:

$$\chi_i^{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{i\mathbf{G}}^{\mathbf{k}}e^{i\mathbf{G}\cdot\mathbf{r}}$$

The *c* are our variational parameters to solve for. In one dimension, $b = \dfrac{2\pi}{a}$:

$$\chi_i^k(x) = \frac{1}{\sqrt{a}}\sum_m c_{im}^k e^{iG_m x}, \qquad G_m = mb = \frac{2\pi m}{a}$$
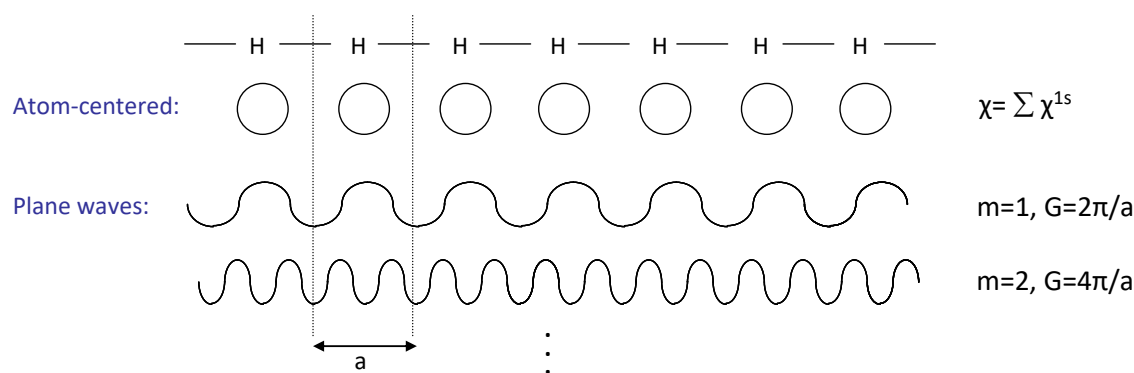
If we could let m range from $-\infty$ to ∞, we'd have an exact expansion. Can't do that, of course, and in practice the sum is truncated such that

$$\frac{\hbar^2}{2m_e}\left|k+G_m\right|^2 = \frac{\hbar^2}{2m_e}\left|G_{cut}\right|^2 < E_{cutoff}$$

Again, the *cutoff* controls the size of the basis set. Bigger the absolute value, higher the maximum frequency and higher the kinetic energy of the basis function.

Substituting into Bloch's theorem,
$$\psi_i^k(x) = e^{ikx}\sum_m c_{im}^k e^{iG_m x} = \sum_m c_{im}^k e^{i(k+G_m)x}$$

For a given value of k, have to evaluate matrix elements of $e^{i(k+G_m)x}$.

Kinetic energy: Diagonal in basis functions…easy!
$$\left\langle e^{i(k+G_m)x}\left|-\frac{1}{2}\frac{d^2}{dx^2}\right|e^{i(k+G_{m'})x}\right\rangle = \frac{1}{2}\left(k+G_m\right)^2 \delta_{mm'}$$

Potential energy terms: Since potential terms have the periodicity of the system, it is possible to Fourier transform them:
$$v(x) = \sum_m v(G_m)e^{iG_m x} \qquad v(G_m) = \frac{1}{a}\int v(x)e^{-iGx}dx$$

Transforms require real space/reciprocal space grids. Once transformed, though, evaluation is rapid:

$$\left\langle e^{i(k+G_m)x}\left|v(x)\right|e^{i(k+G_{m'})x}\right\rangle = \sum_{m''}v(G_{m''})\left\langle e^{i(k+G_m)x}\left|e^{iG_{m''}x}\right|e^{i(k+G_{m'})x}\right\rangle = v(G_{m'-m})$$

These matrix elements are components of FT of potential, and thus can be evaluated quickly with plane waves. Efficient code depends on being able to evaluate some of the potential terms in "real space" and some parts in "reciprocal space." Just need to be able to do fast discrete Fourier transforms of the potential.

Trade-off is that individual plane waves aren't very good basis functions, so we'll need a lot of them. End up with a large (# PW) × (# PW) matrix to diagonalize for the coefficients.

Have to do this for each **k** point. So how do the **k** points couple to each other? Through the charge density, which ultimately determines the potentials:

$$\rho(\mathbf{r}) = \sum_i occ_i^k \int \left|\psi_i^k(\mathbf{r})\right|^2 dk = \sum_i f_i^k \int \left|\psi_i^k(\mathbf{r})\right|^2 dk \, ,$$

Efficient evaluation requires Fourier transforms here as well. Can show that the exact Fourier expansion has to include terms up to $2G_{cut}$.

Note integration over all **k** in the first Brillouin zone. *This integration cannot be done analytically*; have to use numerical quadrature over **k** points. And since the coefficients are not known ahead of time, equations have to be solved iteratively, SCF-like.

Would be nice to work this 1-D case out more explicitly. Show step function, error in integration over it.

Multiple dimensions follow the same basic idea. **k** is a vector, now, and have to do everything on 3-D grids. The basis functions *have* to fill the whole supercell, so there are basis functions even where you don't want them!

$$\chi^{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega^{1/2}} \sum_m c_{G_m}^{n\mathbf{k}} e^{i\mathbf{G}_m \cdot \mathbf{r}}, \qquad\qquad \mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3, \quad m \in I$$

$$\psi^{n\mathbf{k}}(r) = \frac{1}{\Omega^{1/2}} \sum_G c_G^{n\mathbf{k}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}$$

$$\rho(\mathbf{r}) = \sum_n occ_{n\mathbf{k}} \int \left|\psi^{n\mathbf{k}}(\mathbf{r})\right|^2 d\mathbf{k} = \sum_n f_{n\mathbf{k}} \int \left|\psi^{n\mathbf{k}}(\mathbf{r})\right|^2 d\mathbf{k}$$

$$f_{n\mathbf{k}} = \frac{1}{1 + e^{(\varepsilon_{n\mathbf{k}} - \varepsilon_{fermi})/k_B T}}, \quad \text{Fermi function}$$

8. k-point sampling

The total energy of a system given by

$$E_e = \frac{1}{N_k} \sum_{\vec{k},i} \left[\epsilon_i(\vec{k}) + \sum_{\vec{G}} \epsilon_{xc}(\vec{G})n(\vec{G}) + 2\pi \sum_{\vec{G}} \frac{n(\vec{G})^2}{G^2} \right]$$

The states *i* are discrete (like orbitals), the plane-waves **G** are determined by the plane wave cutoff, but there are an infinite **k** points to sum over. Can't calculate *every* **k** value, so have to replace integration of first BZ with a *discrete sampling* of **k** space. Quality of this sampling has a lot to do with quality of the calculation. Too few points, poor results, too many, calculation is too expensive. Handled in *Vasp* in KPOINTS file.

If bands are very flat (think H chain well spaced out) then a single point would be adequate. If dispersion is large then more are needed. Generally need to test.

How to choose **k** points to sample over? Most widely used approach is that of Monkhorst and Pack, which provides a formula for choosing uniform sets of points within first BZ:

$$\mathbf{k}_{n_1,n_2,n_3} = \sum_{i=1}^{3} \frac{2n_i - N_i - 1}{2N_i} \mathbf{G}_i$$

You specify total number of k points in each direction, N_i, and formula spreads them out. For example, in 1-dimensional case, say $N = 3$, then $k_1 = -1\ (\pi/a)$, $k_2 = 0\ (\pi/a)$, $k_3 = 1\ (\pi/a)$. This is gamma-centered (contains 0), and has 2 symmetry-distinct k.

Introduction

For many properties
(e.g.: density of states, charge density, matrix elements, response functions, ...)
integrals (I) over the Brillouin-zone are necessary:

$$I(\varepsilon) = \frac{1}{\Omega_{BZ}} \int_{BZ} F(\varepsilon)\delta(\varepsilon_{n\mathbf{k}} - \varepsilon)d\mathbf{k}$$

To evaluate computationally
integrals $\Rightarrow$ weighted sum over special k-points

$$\frac{1}{\Omega_{BZ}} \int_{BZ} \qquad \Rightarrow \qquad \sum_{\mathbf{k}} \omega_{\mathbf{k}_i}$$

A. Eichler, Sampling the Brillouin-zone   Page 3

Monkhorst and Pack (1976):

Idea: equally spaced mesh in Brillouin-zone.

Construction-rule:

$$\mathbf{k}_{prs} = u_p \mathbf{b}_1 + u_r \mathbf{b}_2 + u_s \mathbf{b}_3$$

$$u_r = \frac{2r - q_r - 1}{2q_r} \qquad r = 1, 2, \ldots, q_r$$

$\mathbf{b}_i$ reciprocal lattice-vectors

q_r determines number of
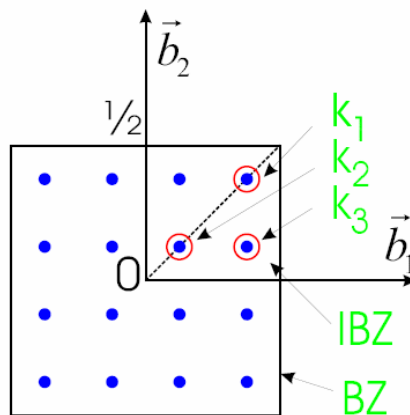
        k-points in r-direction

Example:

- quadratic 2-dimensional lattice

- $q_1 = q_2 = 4 \Rightarrow$ 16 k-points

- only 3 inequivalent k-points ($\Rightarrow$ IBZ)
  - $4 \times \mathbf{k}_1 = (\frac{1}{8}, \frac{1}{8}) \Rightarrow \omega_1 = \frac{1}{4}$
  - $4 \times \mathbf{k}_2 = (\frac{3}{8}, \frac{3}{8}) \Rightarrow \omega_2 = \frac{1}{4}$
  - $8 \times \mathbf{k}_3 = (\frac{3}{8}, \frac{1}{8}) \Rightarrow \omega_3 = \frac{1}{2}$

$\frac{1}{\Omega_{BZ}} \int\limits_{BZ} F(\mathbf{k}) d\mathbf{k} \Rightarrow \frac{1}{4} F(\mathbf{k}_1) + \frac{1}{4} F(\mathbf{k}_2) + \frac{1}{2} F(\mathbf{k}_3)$
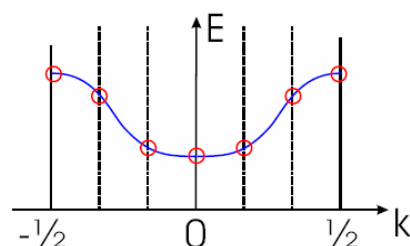
Interpretation:

representation of function $F(\mathbf{k})$ on a discrete equally-spaced mesh

$$\sum_{n=0}^{N} a_n \cos(2\pi nk)$$

density of mesh $\Leftrightarrow$ more Fourier-components $\Rightarrow$ higher accuracy

Common meshes :

Two choices for the center of the mesh

- centered on Γ ($\Rightarrow$ Γ belongs to mesh).

- centered around Γ. (can break symmetry !!)

Rules of thumb:

- Should keep density of k points ~ constant in each of three reciprocal lattice directions, $N_i |\mathbf{b}_i| \approx \text{constant}$.

- More total k points generally more precise results. Metallic systems require more than semiconductors or insulators.

- Number of k points does not necessarily scale with N. Even and odd grids, in particular, can scale differently because of symmetry.

- Odd grids will always contain the Γ point. Even grids can be "Γ-centered," or shifted, to contain the Γ point. Turned on using Gamma rather than Monkhorst in KPOINTS file.

- Symmetry can be used to reduce the number that actually need to be evaluated; get weighted by degeneracy.

- Generally need to test!

- Don't forget, k point sampling is necessary to account for bonding that extends *across* cell boundaries; no k point sampling necessary for atoms or molecules!

In *Vasp*, can either list k points explicitly in KPOINTS file (Cartesian option), or can specify using Monkhorst-Pack description.

The KPOINTS - file:

```
1> k-points for a metal
2>  0
3> Gamma point
4> 9 9 9
5> 0 0 0
```

1st line: comment

2nd line: 0 ($\Rightarrow$ automatic generation)

3rd line: *M*onkhorst or *G*ammapoint (centered)

4th line: mesh parameter

5th line: 0 0 0 (shift)

mesh parameter

- determine the number of intersections in each direction

- longer axes in real-space $\Leftrightarrow$ shorter axes in k-space

  $\Rightarrow$ less intersections necessary for equally spaced mesh

  Consequences:

  – molecules, atoms (large supercells)
    $\Rightarrow (1 \times 1 \times 1)(\equiv \Gamma)$ is enough.

  – surfaces (one long direction $\Rightarrow$ 2-D Brillouin-zone)
    $\Rightarrow (x \times y \times 1)$ for the direction corresponding to the long direction.

  – "typical" values (never trust them!):

metals:	$(9 \times 9 \times 9)$/atom
semiconductors:	$(4 \times 4 \times 4)$/atom

9. Fermi level smearing

A characteristic of insulators (like MgO) is that there is a gap at the Fermi level: bands below the gap are filled for all values of **k**, bands above are empty. Integrating over **k** works easily. Metal are more tricky. By definition the Fermi level cuts through some bands (as in the 1-D H chain above), and so occupancies change discontinuously with **k**, according to a sharp Fermi function. Integrations over **k** have to handle these discontinuities. For instance, think about ϵ_i^k contribution to total energy, changes discontinuously at Fermi level for any band that crosses Fermi level.

Possible to transform this integral into one that includes a delta function (as proposed by Methfessel and Paxton, PRB 40, 3616):

$$I = \int_{-\infty}^{\infty} [1 - \theta(E(\vec{k}) - E_F)] \int_{BZ} f(\vec{k})\delta(\epsilon - E(\vec{k}))d\epsilon$$

How to integrate a delta function? "Smear out" the discontinuity. ISMEAR and SIGMA parameters do this in INCAR.

ISMEAR = –1: Fermi smearing, very simple, introduces fictitious T ($\gg$ real T) that you can't get rid of

ISMEAR = 0: Gaussian smearing, changes delta into a Gaussian of width **SIGMA**. Similar to introducing a fictitious T, but this one you can extrapolate away.

ISMEAR > 0: Methfessel and Paxton integration, like Gaussian but expands delta function in a *n* functions.

ISMEAR = –4 or –5: Tetrahedron method, either without or with Blöchl corrections. Interpolates on **k** points, either linearly or quadratically. Most accurate, have to have enough **k** points to do an interpolation on.

Sigma = smearing parameter, in eV. Typically on order of 0.1 eV.

Smearing methods

Problem: in metallic systems Brillouin-zone integrals over functions that are discontinuous at the Fermi-level.
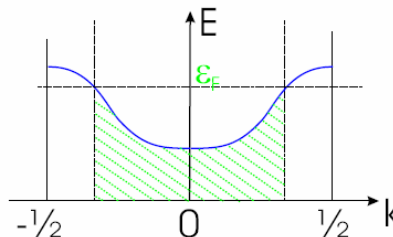
$\Rightarrow$ high Fourier-components $\Rightarrow$ dense grid is necessary.

Solution: replace step function by a smoother function.

Example: bandstructure energy

$$\sum_{n\mathbf{k}} \omega_{\mathbf{k}} \varepsilon_{n\mathbf{k}} \bar{\Theta}(\varepsilon_{n\mathbf{k}} - \mu)$$

$$\text{with:} \bar{\Theta}(x) = \begin{cases} 1 & x \le 0 \\ 0 & x > 0 \end{cases}$$

$$\Rightarrow \sum_{n\mathbf{k}} \omega_{\mathbf{k}} \varepsilon_{n\mathbf{k}} f\left(\frac{\varepsilon_{n\mathbf{k}} - \mu}{\sigma}\right)$$

necessary: appropriate function $f \Rightarrow f$ equivalent to partial occupancies.

Fermi-Dirac function

$$f\left(\frac{\varepsilon_{n\mathbf{k}} - \mu}{\sigma}\right) = \frac{1}{\exp\left(\frac{\varepsilon_{n\mathbf{k}} - \mu}{\sigma}\right) + 1}$$

consequence: energy is no longer variational with respect to the partial occupacies f.

$$(1) \qquad F = E - \sum_n \sigma S(f_n)$$

$$(2) \quad S(f) = -[f\ln f + (1 - f)\ln(1 - f)]$$

$$(3) \qquad \sigma = k_B T$$

F *free energy.*

  <u>new variational functional</u> - defined by (1).

$S(f)$ *entropy*

  of a system of non-interacting electrons at a finite temperature T.

σ *smearing parameter.*

  can be interpreted as finite temperature via (3).

     $\Rightarrow$ calculations at finite temperature are possible (Mermin 1965)

Gaussian smearing

broadening of energy-levels with Gaussian function.

$\Rightarrow f$ becomes an integral of the Gaussian function:

$$f\left(\frac{\varepsilon_{n\mathbf{k}}-\mu}{\sigma}\right) = \frac{1}{2}\left[1-\mathrm{erf}\left(\frac{\varepsilon_{n\mathbf{k}}-\mu}{\sigma}\right)\right]$$

no analytical inversion of the error-function erf exists

$\Rightarrow$ entropy and free energy cannot be written in terms of f.

$$S\left(\frac{\varepsilon-\mu}{\sigma}\right) = \frac{1}{2\sqrt{\pi}}\exp\left[-\left(\frac{\varepsilon-\mu}{\sigma}\right)^2\right]$$

- σ has no physical interpretation.
- variational functional $F(\sigma)$ differs from $E(0)$.
- forces are calculated as derivatives of the variational quantity $(F(\sigma))$.
  $\Rightarrow$ not necessarily equal to forces at $E(0)$.

Improvement: extrapolation to $\sigma \to 0$.

$$
\begin{aligned}
(1)\quad & F(\sigma) \approx E(0)+\gamma\sigma^2 \\[2mm]
(2)\quad & F(\sigma) = E(\sigma)-\sigma S(\sigma) \\[2mm]
(3)\quad & S(\sigma) = -\frac{\partial F(\sigma)}{\partial \sigma} \approx -2\gamma\sigma \\[2mm]
(1)-(3)\to(4)\quad & E(\sigma) \approx E(0)-\gamma\sigma^2 \\[2mm]
(1),(4)\quad & E(0) \approx \hat{E}(\sigma) = \tfrac{1}{2}\left(F(\sigma)+E(\sigma)\right)
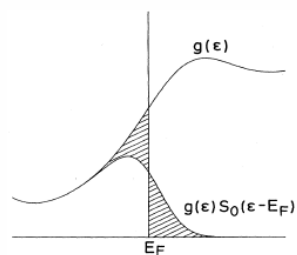\end{aligned}
$$

Method of Methfessel and Paxton (1989)

Idea:

expansion of stepfunction in a complete set of orthogonal functions

$\Rightarrow$ term of order 0 = integral over Gaussians

$\Rightarrow$ generalization of Gaussian broadening with functions of higher order.

Linear tetrahedron method

Idea:

1. dividing up the Brillouin-zone into tetrahedra

2. Linear interpolation of the function to be integrated X_n within these tetrahedra

3. integration of the interpolated function $\bar{X}_n$
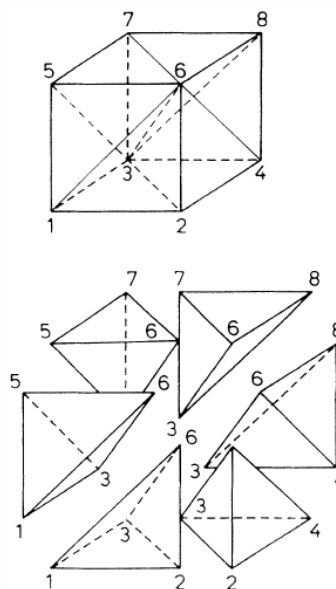
Corrections by Blöchl (1993)

Idea:

- linear interpolation under- or overestimates the real curve

- for full-bands or insulators these errors cancel

- for metals: correction of quadratic errors is possible:

$$\delta\omega_{\mathbf{k}n} \quad = \sum_{T} \tfrac{1}{40} D_T(\varepsilon_F) \sum_{j=1}^{4} (\varepsilon_{jn} - \varepsilon_{\mathbf{k}n})$$

j corners (k-point) of the tetrahedron T

$D_T(\mu)$ DOS for the tetrahedron T at ε_F.

What to do in practice

energy/DOS calculations:

linear tetrahedron method with Blöchl corrections

ISMEAR=-5

calculation of forces:

- semiconductors: Gaussian smearing (ISMEAR=0; SIGMA=0.1)

- metals : Methfessel-Paxton (N=1 or 2)

- always: test for energy with LT+Blöchl-corr.

in any case:

careful checks for k-point convergence are necessary

10.   Resources

R. Hoffmann, *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*, VCH: New York, 1988.
Ashcroft and Mermin, *Solid State Physics*
R. M. Martin, *Electronic Structure: Basic Theory and Practical Methods*

http://electronicstructure.org/