7th IIC-EMTCCM
European Master in Theoretical Chemistry and Computational Modelling
7th International Intensive Course

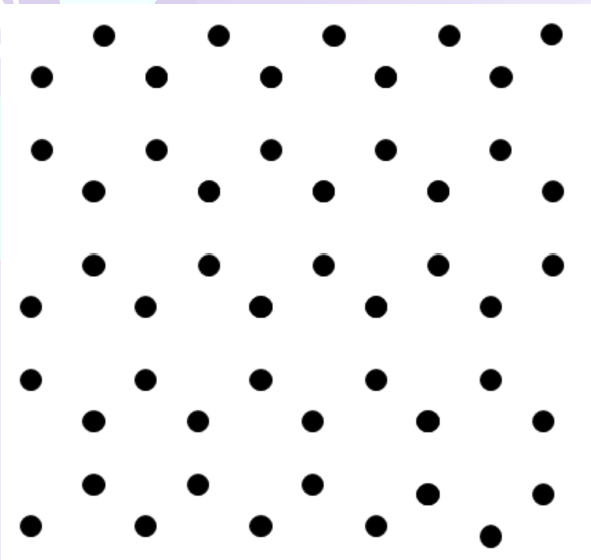
DIPARTIMENTO DI MATEMATICA E INFORMATICA

Outlook

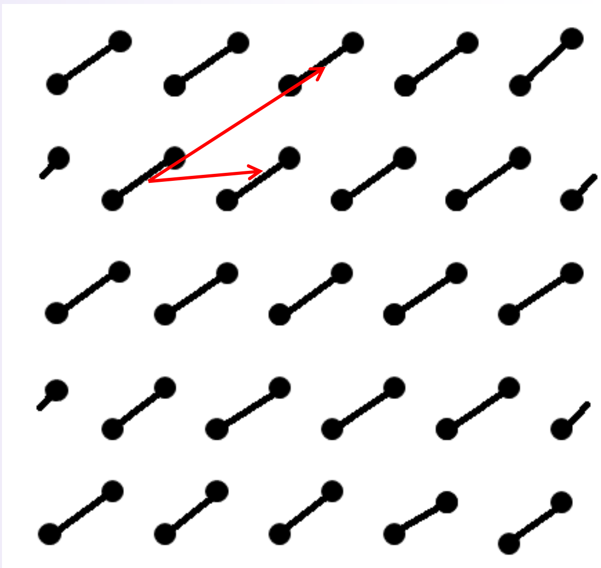
J. Planelles

UNIVERSITAT JAUME•I

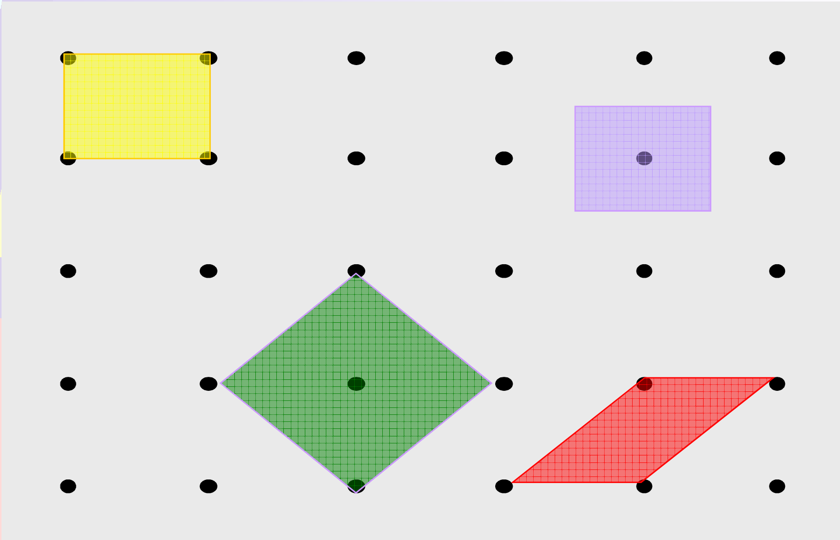
Is this a lattice?



Is this a lattice?

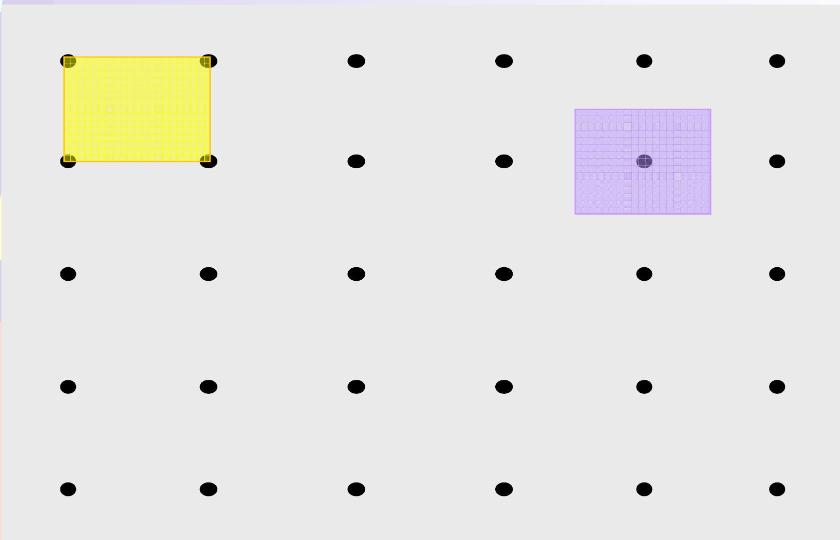


Unit cell: a region of the space that fills the entire crystal by translation



Primitive?

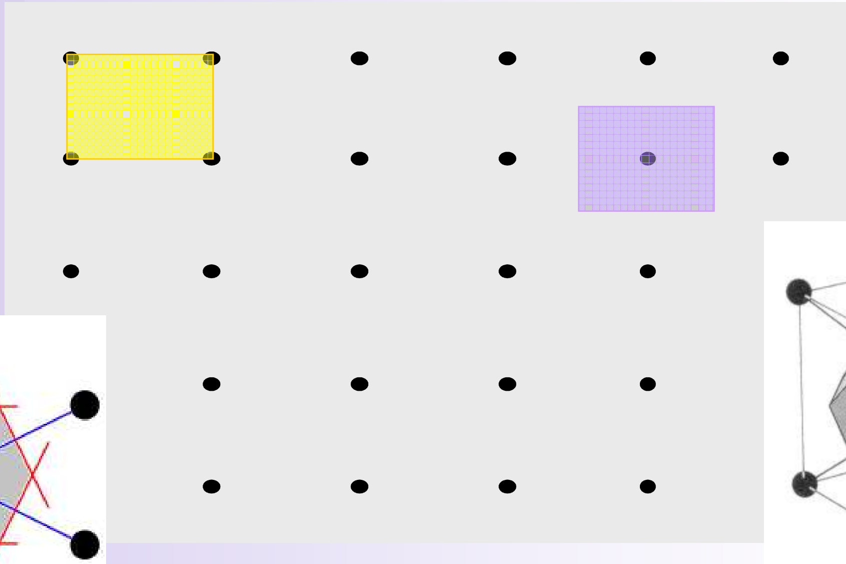
Primitives

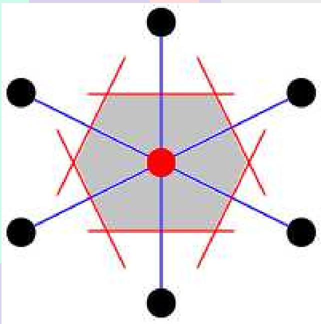


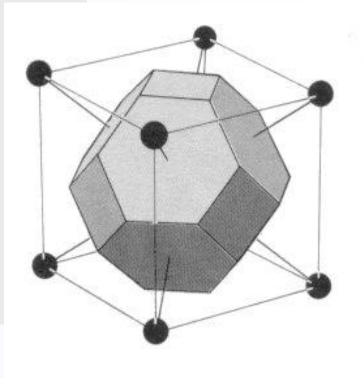
Primitive: smallest unit cells (1 point)

Wigner-Seitz unit cell: primitive and captures the point symmetry

Centered in one point. It is the region which is closer to that point than to any other.

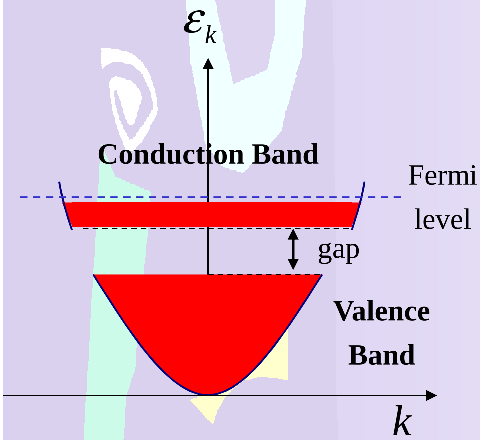






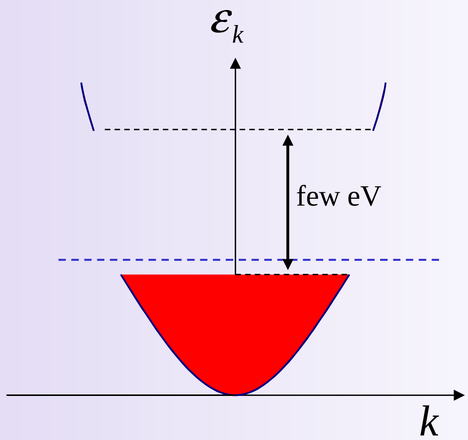
Body-centered cubic

Types of crystals



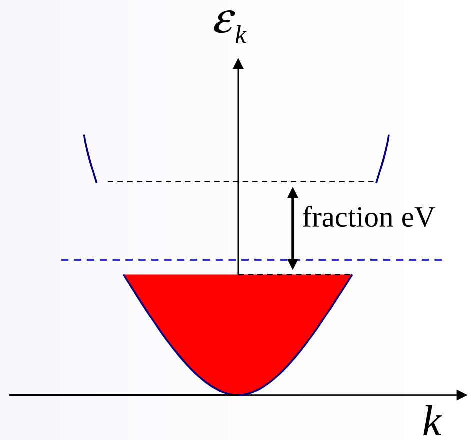
Metal

• Empty orbitals available at low-energy: high conductivity



Insulator

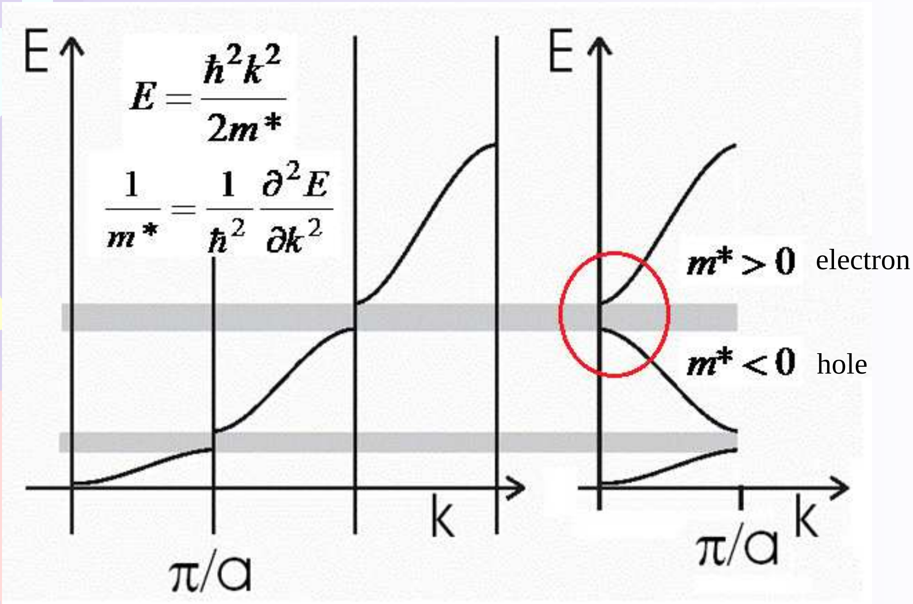
• Low conductivity



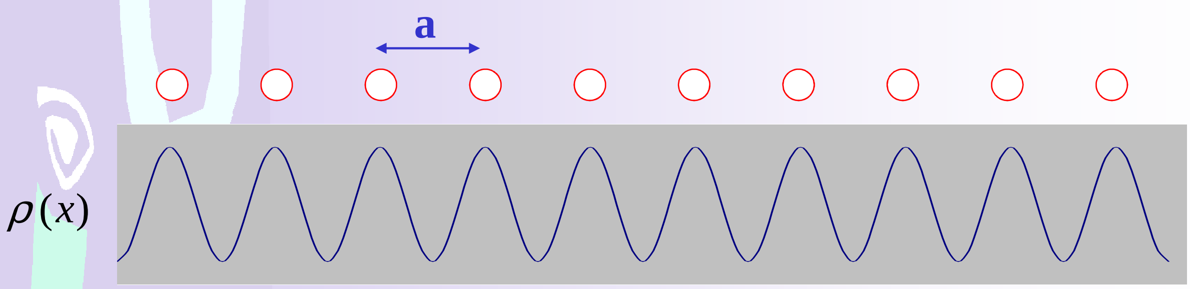
Semiconductor

• Switches from conducting to insulating at will

Positive /negative, lighter/heavier, effective mass



Translational symmetry



$$\rho(x) = \rho(x+na) \Leftrightarrow |f(x)|^2 = |f(x+na)|^2 \Rightarrow f(x+na) = e^{i\phi} f(x)$$

$$T_n f(x) = f(x+na) \rightarrow$$

$$\{T_n\} \rightarrow Translatio\ n\ \ Group$$

$$[T_n, T_m] = 0 \rightarrow Abelian\ Group$$

$$T_n = e^{i\,a\,n\,\hat{p}} = \sum_q \frac{(i\,a\,n)^q}{q!}\hat{p}^q$$

Bloch functions basis of irreps: $\Psi_{\mathbf{k}}(\mathbf{r}) = e^{i\,\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r});\quad u(\mathbf{r}+\mathbf{a}) = u(\mathbf{r})$

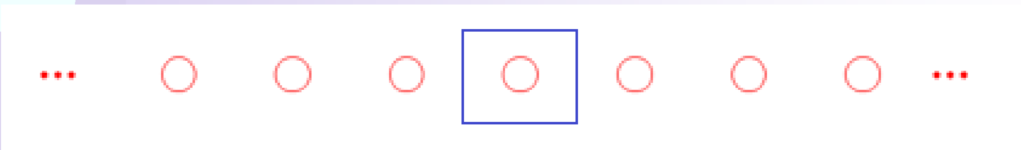
$$T_{\mathbf{n}}\Psi_{\mathbf{k}}(\mathbf{r}) = e^{i\,\mathbf{k}\cdot(\mathbf{r}+n\mathbf{a})}u(\mathbf{r}+n\mathbf{a}) = \underbrace{e^{i\,\mathbf{k}n\mathbf{a}}}_{character}\; e^{i\,\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r})$$

	E	$\cdots$	T_n	$\cdots$	$basis$
$\vdots$	$\vdots$	$\cdots$	$\vdots$	$\cdots$	$\vdots$
k	1	$\cdots$	e^{ikna}	$\cdots$	$u(r)\,e^{ikr}$
$\vdots$	$\vdots$	$\cdots$	$\vdots$	$\cdots$	$\vdots$

$$T_n = e^{i\,a\,n\,\hat{p}} = \sum_q \frac{(i\,a\,n)^q}{q!}\hat{p}^q$$

Solving Schrödinger equation for a crystal: BCs?

For crystals are infinite we use periodic boundary conditions:

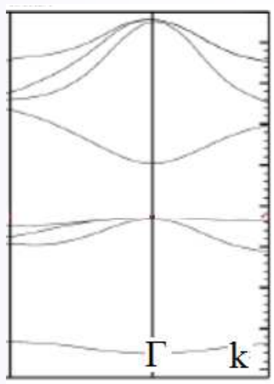


Group of translations:

$T_{\mathbf{a}}\Psi_{\mathbf{k}}(\mathbf{r}) = e^{i\,\mathbf{k}\cdot\mathbf{a}}\,\Psi_{\mathbf{k}}(\mathbf{r})$

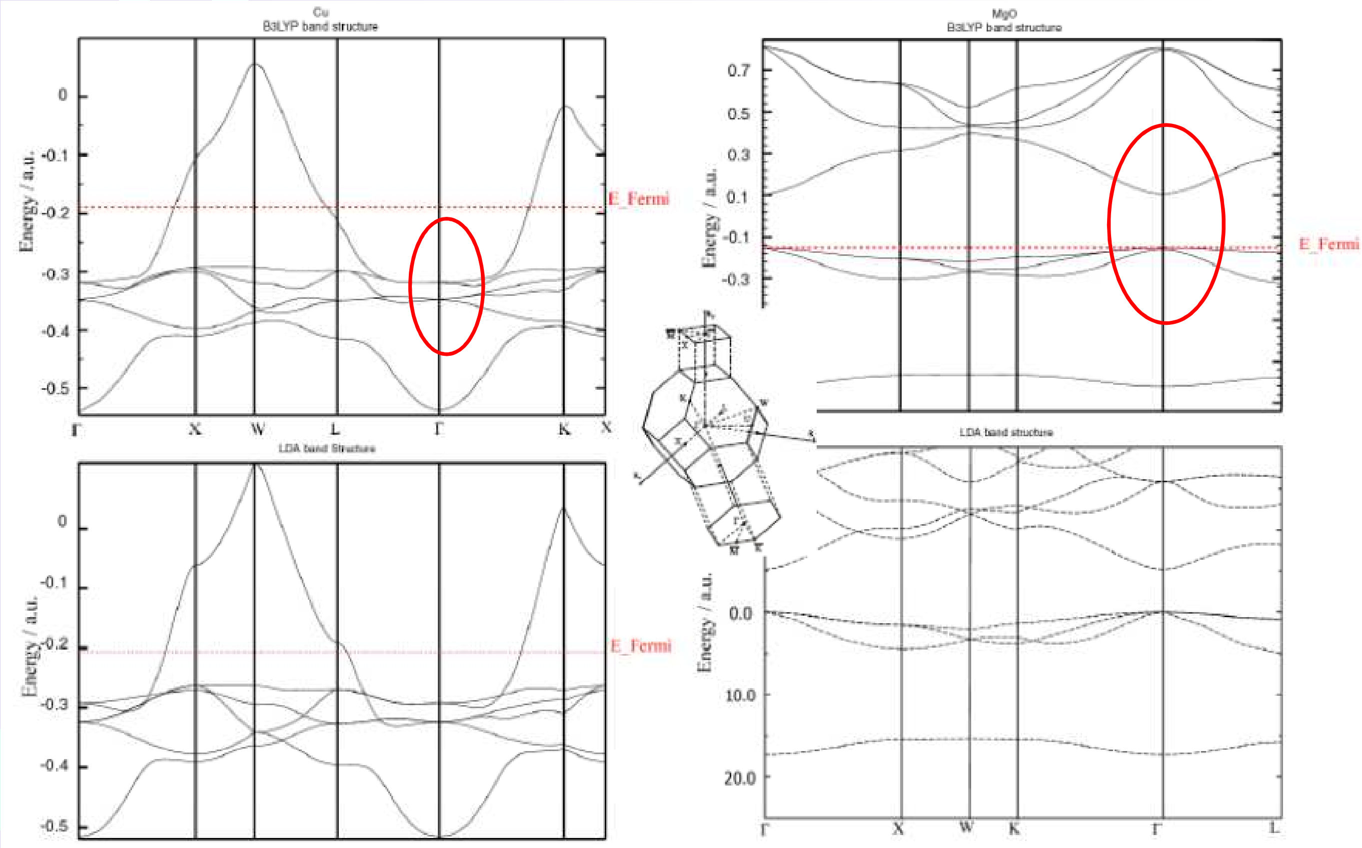
$\Psi_{\mathbf{k}}(-a/2) = e^{i\,\phi}\Psi_{\mathbf{k}}(a/2),\quad \phi\in[-\pi,\pi];$ $\mathbf{k} \in$ 1rst Brillouin zone

(Wigner-Seitz cell of the reciprocal lattice)



*We solve the Schrödinger equation **for each k value**:*

*The plot $E_n(k)$ represents an **energy band***



How does the wave function look like?

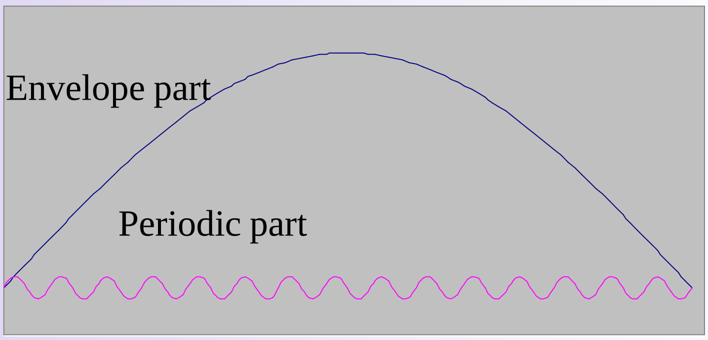
$$\Psi_k(\vec{r}) = e^{i\vec{k}\vec{r}}\, u_k(\vec{r})$$

Bloch function

Envelope part

Periodic (unit cell) part

$$u_k(\vec{r}+\vec{t}) = u_k(\vec{r})$$



k·p Theory

$$\hat{H}=\left(\frac{\vec{p}^2}{2m}+V_c(\vec{r})\right) \qquad \Psi_k(\vec{r})=e^{i\vec{k}\vec{r}}\,u_k(\vec{r})$$

$$e^{-i\vec{k}\vec{r}}\;\hat{H}\;\Psi_k(\vec{r})=\varepsilon_k\,e^{-i\vec{k}\vec{r}}\;\Psi_k(\vec{r})$$

$$\left(\frac{\vec{p}^2}{2m}+V_c(\vec{r})+\frac{\hbar^2 k^2}{2m}+\hbar\frac{\vec{k}\cdot\vec{p}}{m}\right)u_k(\vec{r})=\varepsilon_k\,u_k(\vec{r})$$

The k·p Hamiltonian

$$u_k^n(\vec{r})=\sum_n^{\infty} c_{nk}\,u_0^n(\vec{r})$$

Expansion in a basis **AND** perturbational correction

One-band Hamiltonian for the conduction band

$$\left\langle u_0^n\middle|\hat{H}_{kp}\middle|u_0^{n'}\right\rangle=\left(\varepsilon_0^n+\frac{\hbar^2|\vec{k}|^2}{2m}\right)\delta_{n,n'}+\hbar\frac{\vec{k}}{m}\left\langle u_0^n\middle|\vec{p}\middle|u_0^{n'}\right\rangle$$

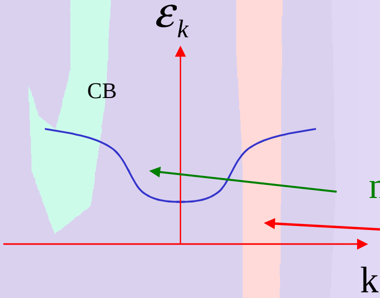
$$\varepsilon_k^{cb}=\varepsilon_0^{cb}+\frac{\hbar^2|\vec{k}|^2}{2m}$$

Crude approximation... including remote bands perturbationally:

$$\varepsilon_k^{cb}=\varepsilon_0^{cb}+\sum_{\alpha=x,y,z}\frac{\hbar^2|k_\alpha|^2}{2m}+\frac{\hbar^2}{m^2}|k_\alpha|^2\sum_{n\neq cb}\frac{\left|\left\langle u_0^{cb}\middle|p_\alpha\middle|u_0^n\right\rangle\right|^2}{\varepsilon_0^{cb}-\varepsilon_0^n}$$

1/m*

Effective mass



Free electron — m=1 a.u.

InAs — m*=0.025 a.u.

negative mass

$$\frac{1}{m^*}=\frac{1}{\hbar^2}\frac{\partial\varepsilon_k^{cb}}{\partial k^2}$$

$$\varepsilon_k^{cb}=\varepsilon_0^{cb}+\frac{\hbar^2 k_\alpha^{\,2}}{2m_\alpha^*}$$

Theory of invariants

(Determining the Hamiltonian (up to constants) by **symmetry** considerations)

1. Second order perturbation: H second order in k: $H = \sum_{i \geq j}^{3} M_{ij} k_i k_j$

2. H must be an invariant under point symmetry (T_d ZnBl, D_{6h} wurtzite)

A·B is invariant (A_1 symmetry) if A and B are of the same symmetry

e.g. (x, y, z) basis of T_2 of T_d: $x \cdot x + y \cdot y + z \cdot z = r^2$ basis of A_1 of T_d

Theory of invariants (machinery)

1. **k** basis of T_2

2. $k_i\, k_j$ basis of $T_2 \otimes T_2 = A_1 \oplus E \oplus T_2 \oplus [T_1]$

3. Character Table:

$$A_1 \rightarrow k_x^2 + k_y^2 + k_z^2$$
$$E \rightarrow \{2k_z^2 - k_x^2 - k_y^2, k_x^2 - k_y^2\}$$
$$T_2 \rightarrow \{k_x k_y, k_x k_z, k_y k_z\}$$
$$T_1 \rightarrow NO\ (k_i k_j\ \textit{symmetric tensor})$$

notation: elements of these basis: k_i^Γ .

4. Invariant: sum of invariants: $H = \sum_i^{\dim(\Gamma)} \sum_\Gamma a_\Gamma N_i^\Gamma k_i^\Gamma$

irrep

basis element

fitting parameter (not determined by symmetry)

Machinery (cont.)

How can we determine the N_i^Γ matrices?

(J_x, J_y, J_z) *basis of* T_1, *and* $T_2 \otimes T_2 = T_1 \otimes T_1$

$\rightarrow$ **we can use symmetry-adapted J_iJ_j products**

Example: 4-th band model: $\{|3/2, 3/2>, |3/2, 1/2>, |3/2, -1/2>, |3/2, -3/2>\}$

$$\mathbb{J}_x = \begin{bmatrix} 0 & \sqrt{3}/2 & 0 & 0 \\ \sqrt{3}/2 & 0 & 1 & 0 \\ 0 & 1 & 0 & \sqrt{3}/2 \\ 0 & 0 & \sqrt{3}/2 & 0 \end{bmatrix}$$

$$\mathbb{J}_z = \begin{bmatrix} 3/2 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & 0 \\ 0 & 0 & -1/2 & 0 \\ 0 & 0 & 0 & -3/2 \end{bmatrix}$$

$$\mathbb{J}_y = \begin{bmatrix} 0 & -i\sqrt{3}/2 & 0 & 0 \\ i\sqrt{3}/2 & 0 & -i & 0 \\ 0 & i & 0 & -i\sqrt{3}/2 \\ 0 & 0 & i\sqrt{3}/2 & 0 \end{bmatrix}$$

$$\mathbb{J}^2 = \tfrac{3}{2}(\tfrac{3}{2}+1)\mathbb{I}_{4\mathrm{x}4} = \tfrac{15}{4}\mathbb{I}_{4\mathrm{x}4}$$

$$\{\mathbb{J}_x, \mathbb{J}_y\} = \tfrac{1}{2}(\mathbb{J}_x\mathbb{J}_y + \mathbb{J}_y\mathbb{J}_x)$$

$\mathbb{J}_x^2$ $\mathbb{J}_y^2$ $\mathbb{J}_z^2$

Machinery (cont.)

Form the following invariants

$$A_1: \quad X_{A_1} = \mathbb{I}\cdot(k_x^2+k_y^2+k_z^2) = k^2 \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} k^2 & 0 & 0 & 0 \\ 0 & k^2 & 0 & 0 \\ 0 & 0 & k^2 & 0 \\ 0 & 0 & 0 & k^2 \end{bmatrix}$$

$$E: \quad X_E = \tfrac{1}{\sqrt{6}}(2\mathbb{J}_z^2 - \mathbb{J}_y^2 - \mathbb{J}_x^2)\tfrac{1}{\sqrt{6}}(2k_z^2 - k_y^2 - k_x^2) + \tfrac{1}{\sqrt{2}}(\mathbb{J}_x^2 - \mathbb{J}_y^2)\tfrac{1}{\sqrt{2}}(k_x^2 - k_y^2)$$

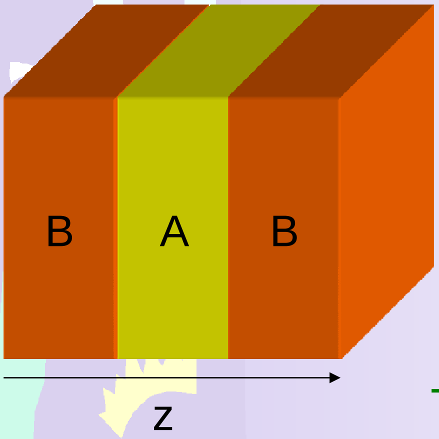
$$T_2: \quad X_{T_2} = \tfrac{1}{2}(\mathbb{J}_x\mathbb{J}_y + \mathbb{J}_y\mathbb{J}_x)k_xk_y + \tfrac{1}{2}(\mathbb{J}_y\mathbb{J}_z + \mathbb{J}_z\mathbb{J}_y)k_yk_z + \tfrac{1}{2}(\mathbb{J}_z\mathbb{J}_x + \mathbb{J}_x\mathbb{J}_z)k_zk_x$$

And build the Hamiltonian

$$\mathbb{H} = -\frac{\hbar^2}{2m_0}\left[(\gamma_1 + \frac{5}{2}\gamma_2)X_{A_1} - 2\gamma_2 X_E + 4\gamma_3 X_{T_2}\right]$$

Luttinger parameters: determined by fitting

Heterostructures: e.g. QW



How do we study it?

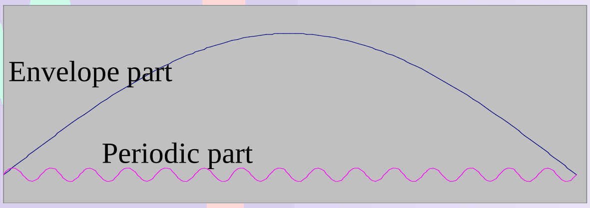
If A and B have:
- the same crystal structure
- similar lattice constants
- no interface defects

...we use the "envelope function approach"

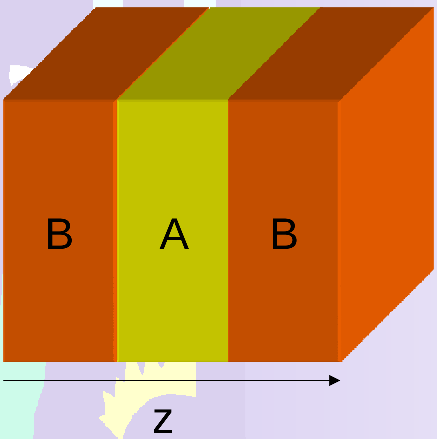
$$\sout{\Psi_k(\vec{r}) = e^{i\vec{k}\vec{r}}\, u_k(\vec{r})} \rightarrow \Psi_k(\vec{r}) = e^{i\vec{k}_\perp \vec{r}_\perp}\, \chi(z)\, u_k(\vec{r})$$

Project H_{kp} onto $\{\Psi_{nk}\}$, considering that:

$$\int_\Omega f(r)\, u_{nk}(r)\, dr \approx \frac{1}{\Omega} \int_{unit\,cell} u_{nk}(r)\, dr \cdot \int_\Omega f(r)\, dr \cdot$$



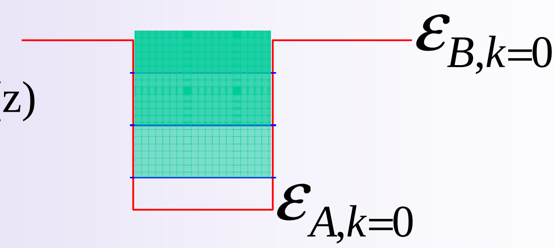
Heterostructures



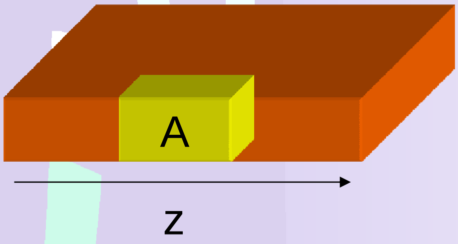
In a one-band model we finally obtain:

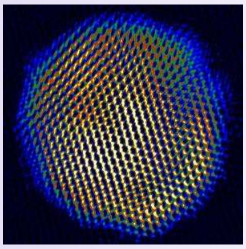
$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dz^2} + V(z) + \frac{\hbar^2 k_\perp^2}{2m} \right) \chi(z) = \varepsilon\, \chi(z)$$

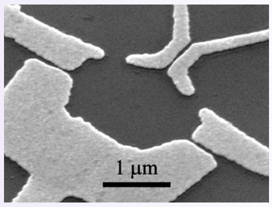
V(z)

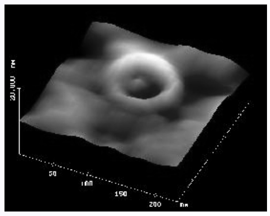


1D potential well: particle-in-the-box problem

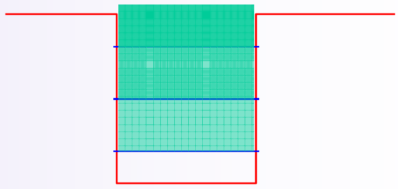








$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z)\right)\chi(x,y,z) = \varepsilon\,\chi(x,y,z)$$



Most prominent applications:

- Single electron transistor
- In-vivo imaging
- Photovoltaics
- LEDs
- Cancer therapy
- Memory devices
- Qubits?

Quantum dot

SUMMARY (keywords)

Lattice → Wigner-Seitz unit cell

Periodicity → Translation group → wave-function in Block form

Reciprocal lattice → k-labels within the 1rst Brillouin zone

Schrodinger equation → BCs depending on k; bands E(k); gaps

Gaps → metal, isolators and semiconductors

Machinery: kp Theory → effective mass

J character table

Theory of invariants: $\Gamma \otimes \Gamma \ni A_1$; $H = \sum N_i^{\Gamma} k_i^{\Gamma}$

Heterostructures: EFA

$$k \rightarrow \hat{p} = -i\nabla$$

$$confinement \rightarrow V_C = band\ \ offset$$

QWell QWire QDot

Magnetisme

Newton's Law

$$\frac{d}{dt}p - F = 0$$

Lagrange equation

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) - \frac{\partial L}{\partial q} = 0$$

$$p = \frac{\partial L}{\partial \dot{q}}$$

Canonical momentum

Conservative systems

$$V = V(q) \qquad F = -\frac{\partial V}{\partial q} \qquad L = T - V$$

kinematic momentum: $\pi_x = \dfrac{\partial T}{\partial \dot{x}} = m\dot{x}$

canonical momentum: $p_x = \dfrac{\partial L}{\partial \dot{x}} = \dfrac{\partial T}{\partial \dot{x}} = \pi_x$

Newton's Law

$$\frac{d}{dt}p - F = 0$$

$$p = \frac{\partial L}{\partial \dot{q}}$$

Lagrange equation

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) - \frac{\partial L}{\partial q} = 0$$

Velocity-dependent potentials: the case of the magnetic field: $\vec{B} = \vec{\nabla} \wedge \vec{A}(x,y,z)$

$$U = -e\,(\vec{v}\cdot\vec{A}) \qquad L = T - U \qquad F_x = -\frac{\partial U}{\partial x} + \frac{d}{dt}\frac{\partial U}{\partial \dot{x}}$$

kinematic momentum:

$$\pi_x = \frac{\partial T}{\partial \dot{x}} = m\,\dot{x} \qquad F_x = \dot{\pi}_x = \frac{d}{dt}\left(\frac{\partial T}{\partial \dot{x}}\right)$$

canonical momentum:

$$p_x = \frac{\partial L}{\partial \dot{x}} = \frac{\partial T}{\partial \dot{x}} - \frac{\partial U}{\partial \dot{x}} = \pi_x + e\,A_x$$

Hamiltonian:

Conservative systems

$$H = \sum_{i=x,y,z} p_i\,\dot{x}_i - L = \sum_{i=x,y,z} \pi_i\,\dot{x}_i - (T - V) = 2T - (T - V)$$

$$\Rightarrow \quad H = T + V = \frac{\pi^2}{2m} + V \equiv \frac{p^2}{2m} + V$$

kinetic + potential energy

$$\Rightarrow \quad \boxed{H = \frac{p^2}{2m} + V}$$

Hamiltonian:

Free particle in a magnetic field

$$H = \sum_{i=x,y,z} p_i \dot{x}_i - L = \sum_{i=x,y,z} (\pi_i \dot{x}_i + e \dot{x}_i A_i) - (T - U)$$

$$\Rightarrow \quad H = (2T - U) - (T - U) = T = \frac{\pi^2}{2m}$$

Just kinetic energy!

$$\Rightarrow \quad \boxed{H = \frac{1}{2m}(p - e A)^2}$$

Particle in a potential and a magnetic field:

$$\hat{\mathcal{H}} = \frac{(\hat{p} - eA)^2}{2m_e} + V$$

Gauge

$$\nabla \wedge (\nabla \chi) = 0$$

$$B = \nabla \wedge A_1 \; ; \; A = A_1 + \nabla \chi \quad \Rightarrow \quad B = \nabla \wedge A$$

Coulomb Gauge : $\nabla A = 0$

$$H = \frac{1}{2m}(p - e A)^2$$

$$\boxed{\hat{p} \rightarrow -i\hbar\nabla}$$ ***Always!***

$$H = \frac{1}{2m}(-i\hbar\nabla - e A)^2 = \frac{\hbar^2}{2m}\nabla^2 + \frac{i\hbar}{2m} e (\nabla A + A \nabla) + \frac{e^2}{2m} A^2$$

$$\boxed{H = \frac{\hat{p}^2}{2m} - \frac{e}{m} A \cdot \hat{p} + \frac{e^2}{2m} A^2}$$

Electron in an axial magnetic field

$$\hat{\mathcal{H}} = \frac{(\hat{p} - eA)^2}{2m_e}$$

Magnetic confining potential

$$\vec{B} = B_0 \vec{k} \qquad \vec{A} = (-\tfrac{1}{2} y\, B_0, \tfrac{1}{2} x\, B_0, 0)$$

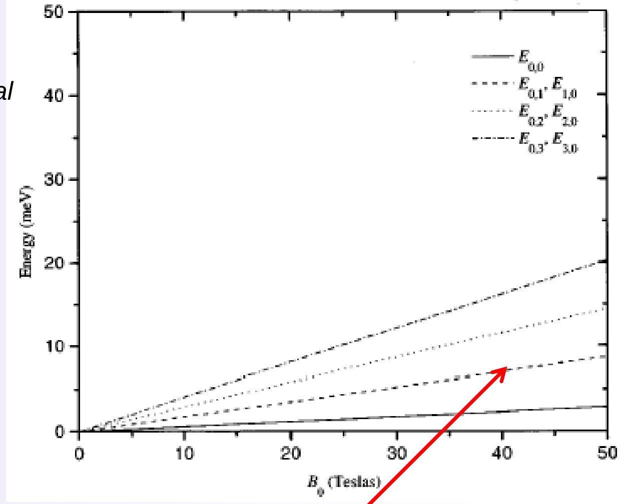
$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{eB}{2m_e}\hat{L}_z + \frac{e^2 B^2}{8m_e}\rho^2$$
$$= \frac{\hat{p}_z^2}{2m_e} + \hat{\mathcal{H}}_{HO}^{2D} - \frac{eB}{2m_e}\hat{L}_z$$

$$E_{HO}^{2D} = (2n + |M| + 1)\,\omega$$

$$\hat{H}' = \frac{B\hat{L}_z}{2m} \qquad E' = \frac{B}{2m} M = \omega M$$

$$[\hat{H}_{HO}^{2D}, \hat{H}'] = 0$$

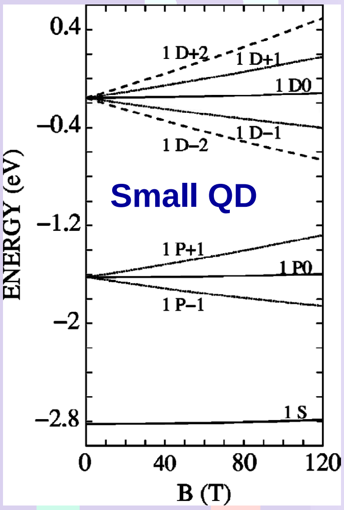
Rosas et al. AJP 68 (2000) 835

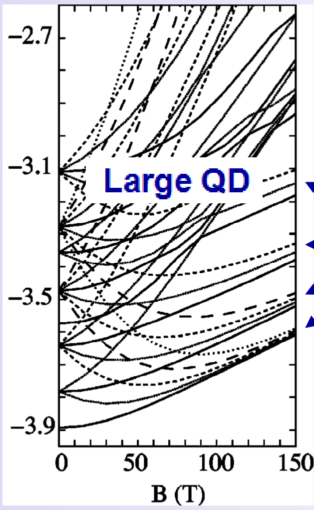


- **Landau levels *E(B)***
- **No crossings!**

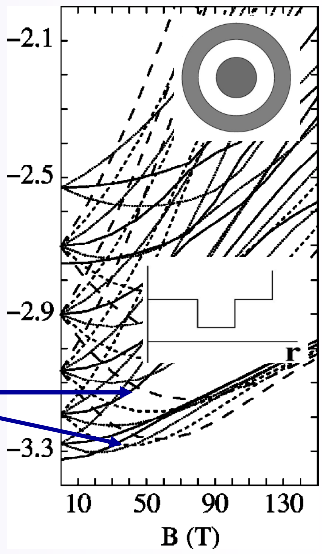
$$E(n, M) = (2n + |M| + M + 1)\frac{B}{2m}$$

Electron in a spherical QD pierced by a magnetic field

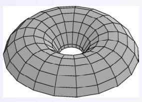




Landau levels limit



AB crossings



$$\left(-\frac{1}{2m_e}\nabla^2 + \frac{B^2}{8m_e}\rho^2 + \frac{BM}{2m_e} + V_e(\rho, z)\right)\Phi_{n,M} = E_{n,M}\Phi_{n,M}$$

Competition: quadratic vs. linear term

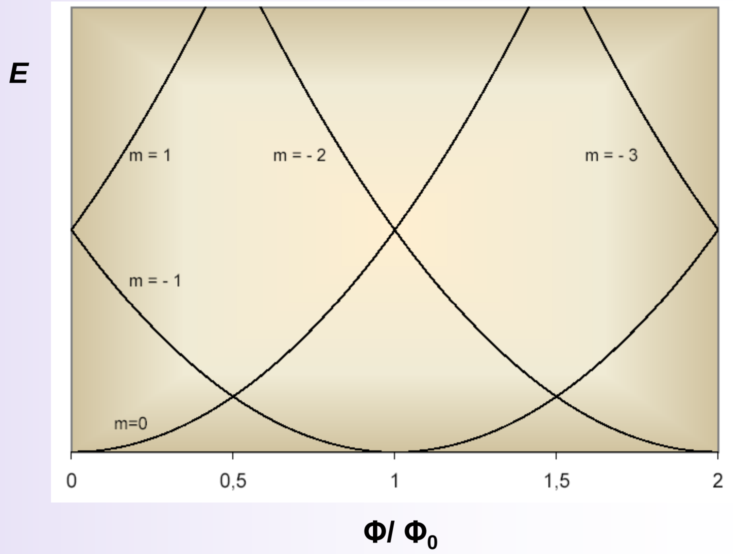
Aharonov-Bohm Effect

1D QR

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m_e R^2}\left(\frac{\partial}{\partial\phi} + i\frac{\Phi}{\Phi_0}\right)^2$$

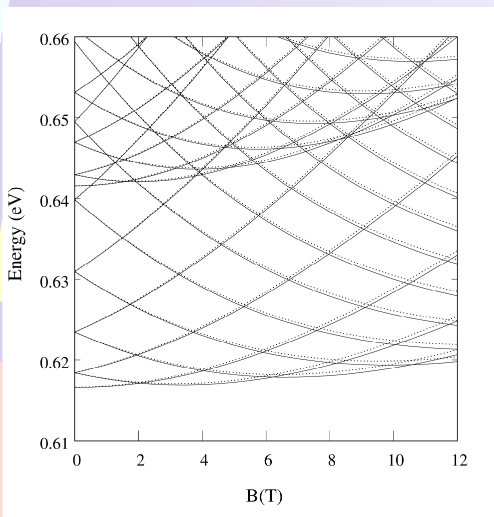
$$E_m = \frac{1}{2}(m+F)^2$$

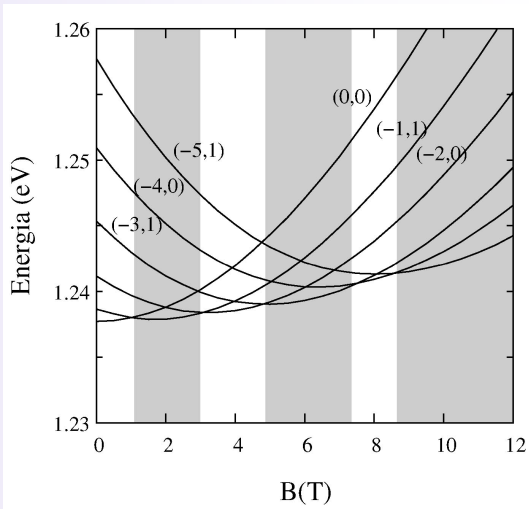
$$m = 0 \pm 1 \pm 2 ... \in \mathcal{Z}$$



- Periodic symmetry changes of the energy levels
- Energetic oscillations
- Persistent currents

Fractional Aharonov-Bohm Effect



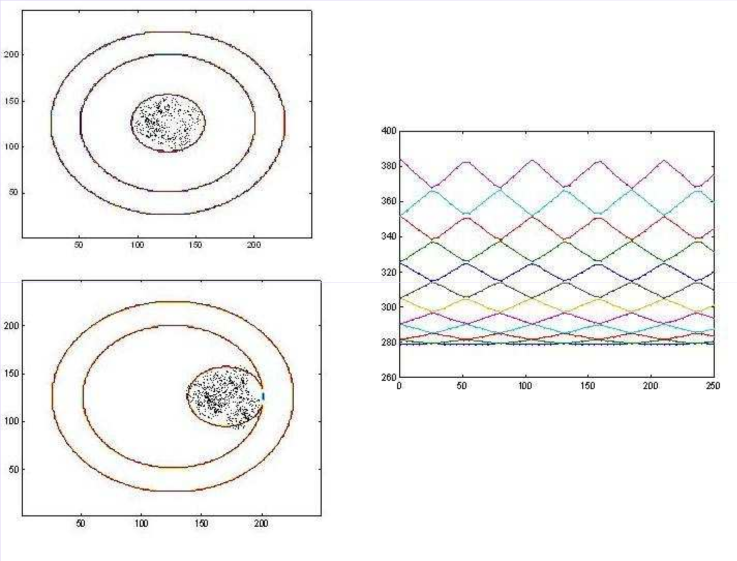


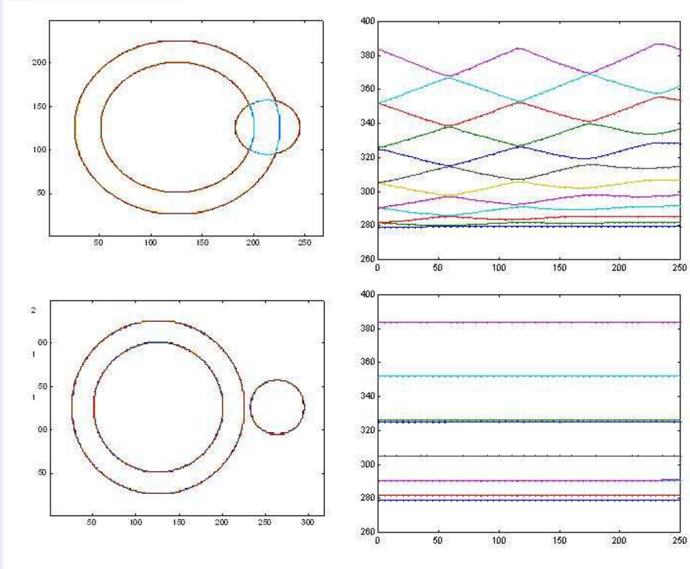
1 electron

2 electrons coulomb interaction

*J.I. Climente , J. Planelles and F. Rajadell,J. Phys. Condens. Matter **17** (2005) 1573*

The energy spectrum of a single or a many-electron system in a QR (complex topology) can be affected by a magnetic field despite the field strength is null in the region where the electrons are confined

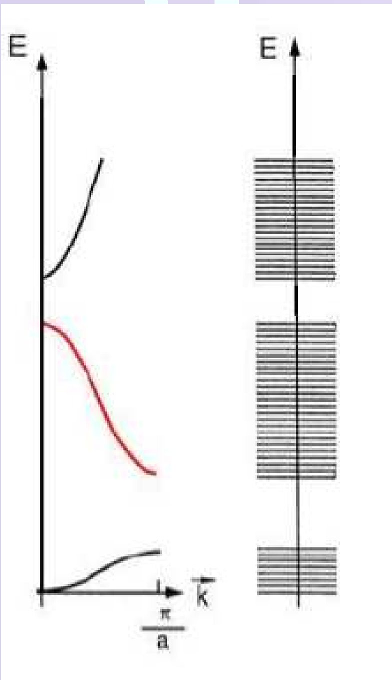


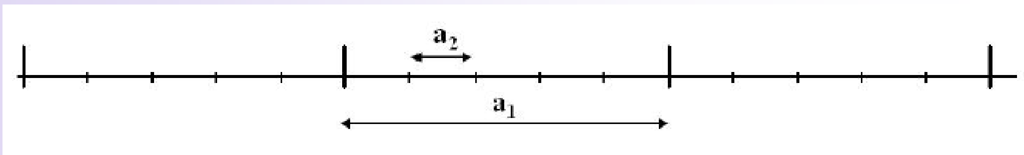


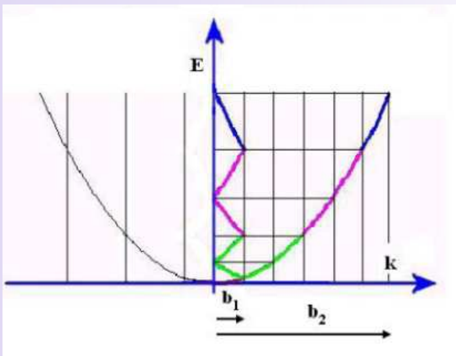
It is not the case for a QD (simple connected topology confining potential)

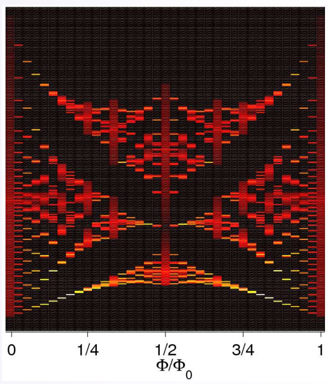
Translations and Magneto-translations

<u>Two-fold periodicity</u>: magnetic and spatial cells









Hofstadter butterfly

Summary

No magnetic monopoles: $\vec{\nabla}\vec{B} = 0$ → $\vec{B} = \vec{\nabla} \wedge \vec{A}$ *vector potential*

No conservative field: → *velocity-dependent potential:* $U = -e\left(\vec{v}\cdot\vec{A}\right)$

Lagrangian: $L = T - U$

kinematic momentum

Canonical momentum: $p_x = \frac{\partial L}{\partial \dot{x}} = \frac{\partial T}{\partial \dot{x}} - \frac{\partial U}{\partial \dot{x}} = \pi_x + e\,A_x$

Hamiltonian: $H = p\,\dot{x} - L = T = \frac{\pi^2}{2m} = \frac{1}{2m}(p - e\,A)^2$

Coulomb gauge: $\nabla A = 0$

Hamiltonian operator:

$$H = \frac{\hat{p}^2}{2m} - \frac{e}{m} A\cdot\hat{p} + \frac{e^2}{2m} A^2$$

Magnetic field: summary (cont.)

axial symmetry

$\vec{B} = B_0\vec{k}$ →

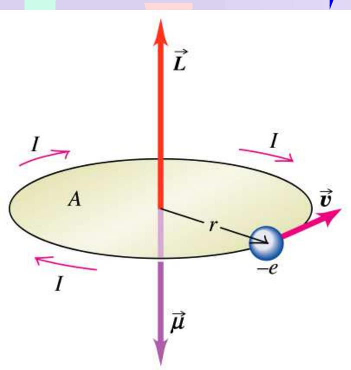
$$\hat{\mathcal{H}} = -\frac{1}{2m_e}\nabla^2 + \frac{B^2}{8m_e}\rho^2 + \frac{BM}{2m_e} + V_e(\rho, z)$$

Relevant at soft confinement (nanoscale and bulk)

dominates at strong confinement (atomic scale)

Spatial confinement

Aharonov-Bhom oscillations in non-simple topologies



$$\vec{\mu} = i\vec{S} = \frac{ev}{2\pi r}\pi r^2\vec{n} = \frac{evr}{2}\vec{n} = \frac{e}{2m_e}\vec{L}$$

$$W = -\vec{\mu}\vec{B} = -\frac{eB_0}{2m_e}M$$

Magnetic field: summary (cont.)

Periodicity and homogeneous magnetic field

↓

Magneto-translations and Super-lattices

↓

B-dependent (super)-lattice constant

↓

Fractal spectrum (Hofstadter butterfly)