Master Nanosciences Nanotechnologies: "Solid state, electrons and phonons"

Exercises. Thursday 17th, September 2020

(Xavier Blase, 2020)

I) Density of states of free electrons in a 2-dimensional (2D) box

A few materials (graphene, boron-nitride, dichalcogenides, etc.) are 2-dimensional (2D). We assume here N free electrons confined in a 2D box (or square) of side L and surface S=L×L . The constant potential V_0 in the box is set to zero.

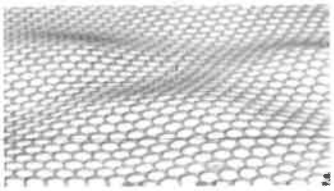
a) Provide the Schrödinger equation, eigenstates and corresponding energies for this system.

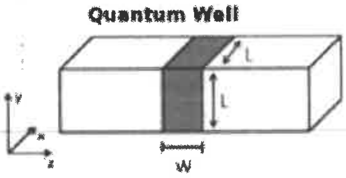
b) What are the Fermi wavevector $\vec{k}_F$ and Fermi energy ϵ_F as a function of N and S ?

c) Show that the density of states $D(\epsilon)$ - where $D(\epsilon)d\epsilon$ is the number of quantum states with energy within $[\epsilon, \epsilon + d\epsilon]$ - is independent of the energy ϵ.

d) In graphene, a 2D carbon-based material, going beyond the free electron approximation within the tight-binding formalism leads to a linear dispersion relation: $\epsilon = \gamma k$, with γ a constant and k the norm of the wavevector $\vec{k}$. What is now $D(\epsilon)$?

e) What happens if the material is not strictly 2D but has a finite width W smaller than the in-plane length L as in a Quantum Well (figure below on the right) ?





II) Wiedemann and Franz law (1853)

Wiedemann and Franz demonstrated in 1853 that the ratio of the thermal to the electric conductivity increases linearly with the temperature. The thermal conductivity κ relates the heat current J_T to the thermal gradient. Elementary kinetic theory shows that: $\kappa = cvl/3$, where c is the electronic heat capacity per unit volume, v the electron velocity and l the mean-free-path. Derive the classical (Drude) and quantum ratio (κ/σ) where σ is the electronic conductivity. Show that both are proportional to $(k_B/e)^2$T, where T is the temperature, thanks to a cancellation of errors in the classical case.

Hint: Show first that the density of states at the Fermi level reads: $D(\varepsilon_F) = (3N/2?_F)$

III) A simple model for negatively charged 1D carbon chains

Adapted from "Problèmes quantiques", Basdevant, Dalibard, Editions Ecole Polytechnique.

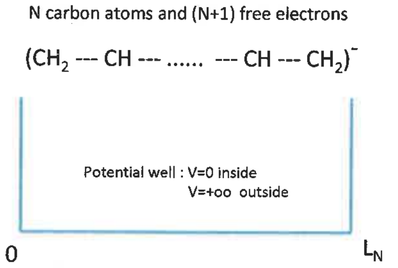
Conjugated polymers anions (negatively charged) derived from polyethylene can be modelled by a 1D box of length L_N where N is the number of carbon atoms, with $L_N = (N-1)d + 2b$ where d is the carbon-carbon distance ($d \simeq 1.40\ \mathring{A}$) and $b \simeq d/2$ represents the "extension" of the electronic wavefunction beyond the last atoms of the chain.

a) What are the energy levels ε_n for free electrons in this 1D box ?

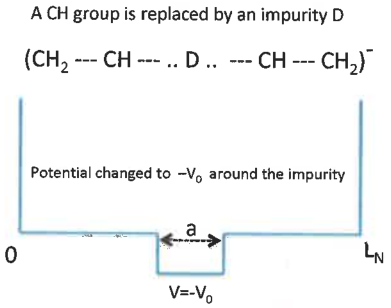
b) What is the lowest possible (ground-state) total energy E_0 for (N+1) non-interacting electrons in the box ? What is the energy of the first excited state E_1 ? We will use the mathematical formula $= \sum_{n=1}^{p} n^2 = p(p+1)(2p+1)/6$ and assume that (N+1) is even.

c) What is the wavelength λ_N of the light adsorbed in a transition from the ground-state to the first excited-state ? We recall the formula relating photon energy to its wavelength: $E = hc/\lambda$. One can further use the relation $a_0 = \hbar/(m_e c \alpha)$ where $a_0 = 0.529177\mathring{A}$ is the Bohr radius, m_e, c and α the electron mass, the speed of light and the fine structure constant $\alpha = 1/137$.

d) One observe experimentally that the ions with N=9, N=11, and N=13 absorb the light in the blue ($\lambda_N \simeq 4700\mathring{A}$ for N=9), the orange yellow ($\lambda_N \simeq 6000\mathring{A}$ for N=11) and the red ($\lambda_N \simeq 7300\mathring{A}$ for N=13). Can you comment on the quality of the model developed in the previous questions ?



N carbon atoms and (N+1) free electrons



A CH group is replaced by an impurity D

e) We now replace the central (CH) group by an impurity atom labeled D. The effect of this change is modelled by lowering the average potential by $-V_0$ on a distance (a/2) on each side of the impurity, with $a/d << 1$. Using 1st order perturbation theory, express to lowest order in (a/d) the variation $\delta\varepsilon_n$ of the electronic energy levels induced by the impurity. We recall that within first-order perturbation theory, a quantum state characterized by its energy ε_n and wavefunction ϕ_n sees its energy modified by $\delta\varepsilon_n = \langle\phi_n|\delta V|\phi_n\rangle$ when the system is perturbed by a potential δV. What do you observe when (n) is even or (n) is odd. How can you explain this ?

Hint: change $\phi_n(x)$ in $\phi_n(y + L_N/2)$ with (x = y + $L_N/2$), y varying between (-$L_N/2$) and (+$L_N/2$). For the normalization factor of the ϕ_n eigenstates, one may use the trigonometric relation: $sin^2(z) = [1 - cos(2z)]/2$.

Correction Exo. 1 September 2020

① Free electrons in a 2D box

a) $$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + \cancel{V_0}^{\,0}\right]\varphi(x) = \varepsilon\,\varphi(x)$$

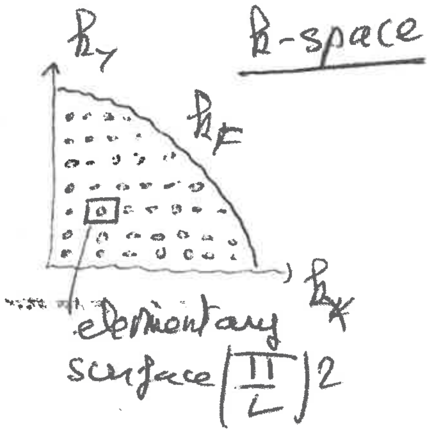
with $\varphi(x) = A(\sin k_x x)(\sin k_y y)$

$$\Rightarrow \varepsilon(k_x,k_y) = \frac{\hbar^2}{2m_e}(k_x^2+k_y^2) = \frac{\hbar^2 k^2}{2m_e}$$

Boundary conditions $\left|\begin{array}{l}\sin k_x L = 0\\ \sin k_y L = 0\end{array}\right. \Rightarrow \begin{cases} k_x = n\left(\frac{\pi}{L}\right)\\ k_y = m(\pi/L)\end{cases}$

(n,m) positive integers

b)



All levels with $|k| < k_F$ are occupied and accomodate N electrons:

$$\Rightarrow N = \underset{\overset{\nearrow}{\text{spin}}}{2} \times \underbrace{\frac{1}{4}}_{k_x>0,\ k_y>0} \times \frac{\pi k_F^2}{(\pi/L)^2}$$

$$\Rightarrow \boxed{k_F^2 = 2\pi\Big(\underbrace{\frac{N}{S}}_{\text{density}}\Big)} \quad \Rightarrow \quad \boxed{\varepsilon_F = \frac{\hbar^2}{2m_e}\left(2\pi\frac{N}{S}\right)}$$

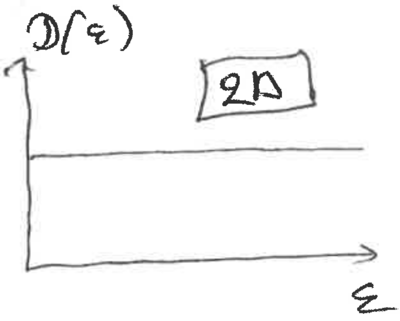
c) Identically, the number $\mathcal{N}(k)$ of quantum states with momentum lower than $|k|$ is:

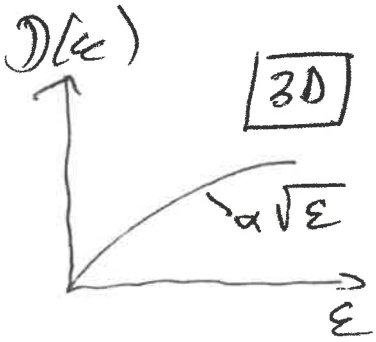
$$\mathcal{N}(k) = 2 \times \frac{1}{4} \times \frac{\pi k^2}{(\pi/L)^2} = \frac{S}{2\pi}k^2$$

and the number of states with energy lower than ε is:

$$\mathcal{N}(\varepsilon) = \left(\frac{S}{2\pi}\right)\left(\frac{2m_e\,\varepsilon}{\hbar^2}\right) = \frac{S\,m_e}{\pi\hbar^2}\,\varepsilon$$

$$\Rightarrow \mathcal{D}(\varepsilon) = \frac{d\mathcal{N}(\varepsilon)}{d\varepsilon} = \boxed{S\frac{m_e}{\pi\hbar^2}}$$ independent of ε.





d) In graphene $\varepsilon = \gamma k$ $\quad k = |\vec{k}|$

$$\Rightarrow \mathcal{N}(k) = \frac{S}{2\pi^2}k^2$$ (unchanged)

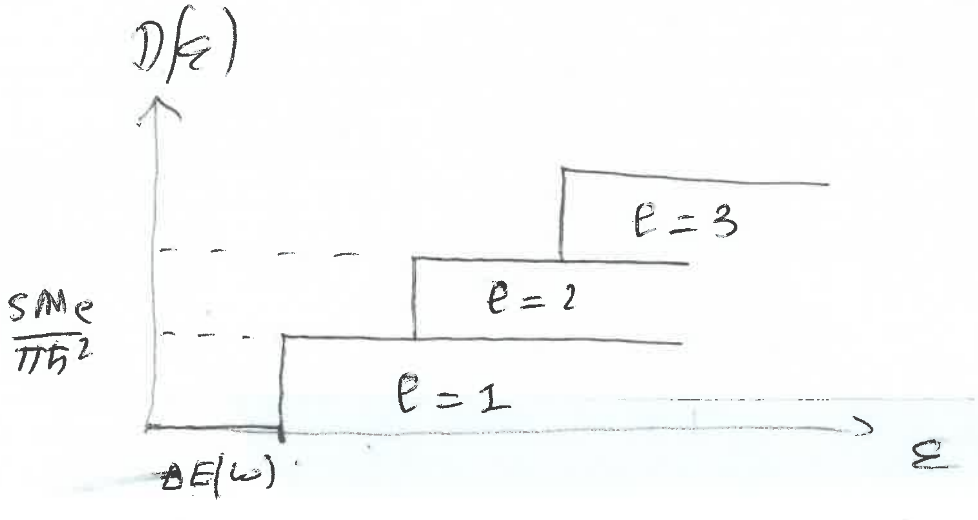
$$\Rightarrow \mathcal{N}(\varepsilon) = \frac{S}{2\pi^2}\left(\frac{\varepsilon}{\gamma}\right)^2$$

$$\Rightarrow \mathcal{D}(\varepsilon) = \frac{S}{(\gamma\pi)^2}\varepsilon$$ linear in ε

The free electron model with a quadratic relation $\varepsilon = \frac{\hbar^2 k^2}{2m}$ cannot explain the properties of graphene.

e) $$\varepsilon = \frac{\hbar^2 k^2}{2m_e} = \underbrace{\frac{\hbar^2}{2m_e}\left(\frac{\pi}{L}\right)^2}_{\text{small}}(n^2+m^2) + \underbrace{\frac{\hbar^2}{2m_e}\left(\frac{\pi}{W}\right)^2}_{\substack{\text{large}\\ \Delta E(w)}}\ell^2$$

k



Exercise #2 Thursday 17/09/2020 SSP

(Xavier Blase)

$$N = \int_0^{\varepsilon_F} \mathcal{D}(\varepsilon)\, d\varepsilon = \alpha \frac{\varepsilon_F^{3/2}}{3/2}$$

Using class formula concerning the model of free electrons in a box, we show first that:

$$\frac{\mathcal{D}(\varepsilon_F)}{N} = \frac{\frac{\Omega}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon_F}}{\frac{\Omega}{3\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\varepsilon_F^{3/2}} = \frac{3}{2\,\varepsilon_F}$$

Now using: $K = \frac{1}{3} c v \ell = \frac{1}{3} c v^2 \underset{\text{scattering time}}{\tau}$

we consider the case where electrons are "classical" (Drude) and the quantum case:

classical

$$c = \frac{1}{\Omega}\frac{\partial}{\partial T}\left(\underset{\text{thermal energy}}{\frac{3}{2} N k_B T}\right)$$

$$= \underbrace{\left(\frac{N}{\Omega}\right)}_{n\ \text{density}} \frac{3}{2} k_B$$

$$\frac{K}{\sigma} = \frac{1}{3}\frac{\left(n \frac{3}{2} k_B\right) v^2 \tau}{n e^2 \tau / m_e}$$

$$= \underbrace{\left(\frac{1}{2} m_e v^2\right)}_{3/2\, k_B T} \frac{k_B}{e^2}$$

$$= \frac{3}{2}\left(\frac{k_B}{e}\right)^2 T$$

quantum

$$c = \frac{\pi^2}{3} \underbrace{\mathcal{D}(\varepsilon_F)}_{\frac{3N}{2\varepsilon_F}} k_B^2 T \underset{\text{per volume}}{\left(\frac{1}{\Omega}\right)}$$

$$c = \frac{\pi^2}{2} n \frac{k_B^2 T}{\varepsilon_F}$$

$$\frac{K}{\sigma} = \frac{1}{3}\frac{\frac{\pi^2}{2} n \frac{k_B^2 T}{\varepsilon_F} v_F^2 \tau}{n e^2 \tau / m_e}$$

$$= \frac{\pi^2}{3} \underbrace{\left(\frac{1/2\, m_e v_F^2}{\varepsilon_F}\right)}_{1} \frac{k_B^2 T}{e^2}$$

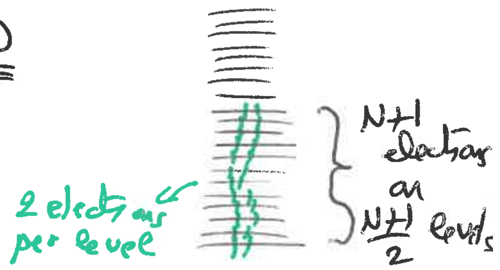
$$= \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T$$

same scaling with T

Exercise 3 – TD 17 september 2020

a) $\mathcal{E} = \dfrac{\hbar^2 k^2}{2m_e}$ $\qquad k = n\dfrac{\pi}{L} \quad (n>0)$ in $\underline{\underline{1D}}$

$$\Rightarrow \mathcal{E}_n = \frac{\hbar^2}{2m_e}\left(\frac{\pi}{L}\right)^2 n^2 \qquad n>0$$



b) We sum the (kinetic) energy of all electrons

$$E_0 = \underset{\substack{\text{spin}\\(2e^- \text{ per level})}}{2} \sum_{n=1}^{(N+1)/2} \frac{\hbar^2}{2m_e}\left(\frac{\pi}{L}\right)^2 n^2$$

$$= \frac{\hbar^2}{m_e}\left(\frac{\pi}{L}\right)^2 \left(\frac{N+1}{2}\right)\left(\frac{N+3}{2}\right)\frac{(N+2)}{6}$$

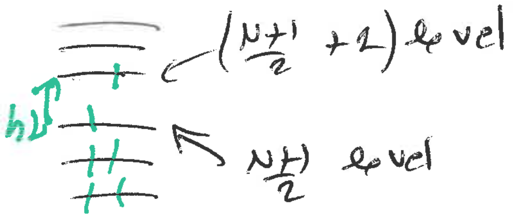
see formula with $p = \frac{N+1}{2}$

$$= \frac{\hbar^2}{24m_e}\left(\frac{\pi}{L}\right)^2 (N+1)(N+3)(N+2)$$

c) 1st excited state: the incoming photon promotes 1 electron from the highest occupied level to the lowest unoccupied

$$\Downarrow$$

$$\underset{h\nu}{\underbrace{\text{energy}}} = \frac{\hbar^2}{2m_e}\left(\frac{\pi}{L}\right)^2 \left[\left(\frac{N+1}{2}+1\right)^2 - \left(\frac{N+1}{2}\right)^2\right]$$



$$= \frac{\hbar^2}{2m_e}\left(\frac{\pi}{L}\right)^2 (N+2)$$

$$\Rightarrow \frac{hc}{\lambda} = \frac{\hbar^2}{2m_e}\left(\frac{\pi}{L}\right)^2 (N+2)$$

$h = 2\pi\hbar$

$$\Rightarrow \lambda = \frac{4}{\pi\alpha}\,\frac{1}{a_0}\,\frac{L^2}{N+2}$$

$\alpha = 1/137$

$a_0 = 0.529177\,\text{Å}$

Now $L = (N-1)d + d = Nd$

$$\Rightarrow \lambda_N = \frac{4}{\pi\alpha}\,\frac{d^2}{a_0}\,\frac{N^2}{N+2}$$

d)

N	model λ	exp. λ	error %
9	4752 Å	4700	1.2
11	6013	6000	0.2
13	7279	7300	0.3