Física Quântica (2009-2010)

dúvidas	qualquer dia	9h00-18h00 (gab D43)
entregar	quarta feira 9/12	(gab D43)

22. Um gás de fermiões, *gás de Fermi* ou *gás de electrões livres*, termos usados para descrever um conjunto de electrões não interactivos, é a versão de um gás ideal da Mecânica Quântica para o caso de partículas fermiónicas. Electrões em metais e semicondutores podem aproximadamente ser considerados gases de Fermi.
A distribuição da energia dos fermiões num gás de Fermi em equilíbrio térmico é determinada por sua densidade, pela temperatura e pelos estados disponíveis, através da estatística Fermi-Dirac.
Pelo princípio de exclusão de Pauli, nenhum estado quântico pode ser ocupado por mais de um fermião. Portanto, até à temperatura do zero absoluto a energia total do gás de Fermi é superior ao produto do número de partículas vezes a energia do estado fundamental.

a Considere uma partícula (massa m) livre, *i.e.* sem contribuição de qualquer forma de energia potencial ao Hamiltoniano, mas confinada a uma caixa unidimensional (fronteiras $x = 0$ e $x = L > 0$). Utilizando as condições fronteiras $\psi(x = 0) = \psi(x = L) = 0$, mostre que os níveis energéticos disponíveis à partícula são dados por (http://en.wikipedia.org/wiki/Particle_in_a_box)

$$E_n = \frac{1}{2m}\, n^2 \, \left(\frac{\pi\hbar}{L}\right)^2 \quad .$$

b Determine a energia total para um conjunto que consiste num número de $2N$ electrões (http://mathforum.org/library/drmath/view/56920.html) e mostre que quando $N \gg 1$ o resultado pode ser aproximado por

$$E(2N) \approx \frac{1}{3m}\, N^3 \, \left(\frac{\pi\hbar}{L}\right)^2 \quad .$$

c Explique porque o resultado da alínea **b** também pode ser obtido através a seguinte integração.

$$E(2N) \approx 2 \int_0^N dn\; E_n \quad .$$

Solution:

a. The Hamiltonian for a stationary state of a free particle is in one dimension given by

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \quad ,$$

whereas the corresponding Schrödinger equation ($H\psi = E\psi$) is given by

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x) \quad .$$

Acceptable solution are

$$\psi_n(x) = \mathcal{N}\sin(k_n x) \quad \text{with} \quad E_n = \frac{\hbar^2 k_n^2}{2m} \quad ,$$

where $\mathcal{N} = \sqrt{2/L}$ is a normalization factor.
Those solutions automatically obey the boundary condition $\psi_n(x = 0) = 0$. For the boundary condition at $x = L$ one has ($n = 1, 2, 3, ...$)

$$\sin(k_n L) = 0 \quad \Longleftrightarrow \quad k_n L = n\pi \quad .$$

Hence, the particle can only have energies E_1 (ground state), E_2 (first excitation), E_3 (second excitation), ... with

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 \quad .$$

b. From the Pauli principle we learn that only two electrons can ocupy the same energy level. Consequently, for $2N$ electrons we need at least N different levels: E_1, ..., E_N, each occupied with two electrons. The total energy of such system is then given by the sum

$$E(2N) = 2E_1 + 2E_2 + \ldots + 2E_N =$$

$$= 2\frac{1}{2m}\left(\frac{\pi\hbar}{L}\right)^2 + 2\frac{4}{2m}\left(\frac{\pi\hbar}{L}\right)^2 + \ldots + 2\frac{N^2}{2m}\left(\frac{\pi\hbar}{L}\right)^2 = 2\frac{1}{2m}\left(\frac{\pi\hbar}{L}\right)^2 \sum_{n=1}^{N} n^2.$$

At http://mathforum.org/library/drmath/view/56920.html we find

$$\sum_{n=1}^{N} n^2 = \frac{1}{6}N(N+1)(2N+1) \quad .$$

The proof is easy:
For $N = 1$ we have

$$\sum_{n=1}^{1} n^2 = 1^2 = 1 = \frac{1}{6} \times 1 \times 2 \times 3 = \frac{1}{6} \times 1 \times (1+1) \times (2 \times 1 + 1) \quad ,$$

whereas for $N = 2$ we have

$$\sum_{n=1}^{2} n^2 = 1^2 + 2^2 = 5 = \frac{1}{6} \times 2 \times 3 \times 5 = \frac{1}{6} \times 2 \times (2+1) \times (2 \times 2 + 1) \quad .$$

Next, we perform the induction step

$$\sum_{n=1}^{N+1} n^2 = \sum_{n=1}^{N} n^2 + (N+1)^2 = \frac{1}{6}N(N+1)(2N+1) + 6(N+1)^2 =$$

$$= \frac{1}{6}\left\{(2N^3 + 3N^2 + N) + 6(N^2 + 2N + 1)\right\} = \frac{1}{6}\left\{2N^3 + 9N^2 + 13N + 6\right\}$$

$$= \frac{1}{6}(N+1)(N+2)(2(N+1)+1) \quad ,$$

which completes the proof.
Hence

$$E(2N) = 2\frac{1}{2m}\left(\frac{\pi\hbar}{L}\right)^2 \frac{1}{6}N(N+1)(2N+1) \quad .$$

Now for $N \gg 1$ one has $N+1 \approx N$ and $2N+1 \approx 2N$, consequently

$$E(2N) \approx 2\frac{1}{2m}\left(\frac{\pi\hbar}{L}\right)^2 \frac{1}{6}2N^3 = \frac{1}{3m}\left(\frac{\pi\hbar}{L}\right)^2 N^3 \quad .$$

c. By passing from discrete to continuous variables, one has here

$$\sum_{n=1}^{N} f(n) \quad \Longrightarrow \quad \int_0^N dn\, f(n) \quad .$$

In figures 1 and 2 we have depicted that process for $f(n) = n^2$.

In figure 1 we study the case $N = 4$. We observe that there is a substantial difference between the summation, which gives $1 + 4 + 9 + 16 = 30$, and the integration, which gives $4^3/3 = 21.3$. That is a difference of 8.7 in 30, some 29%.

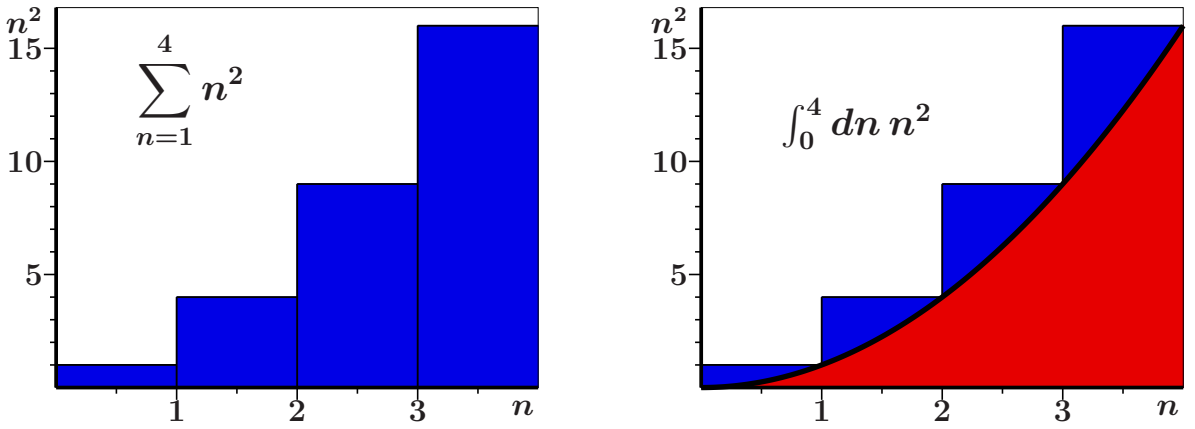

Figure 1: On the lefthand side we have depicted $\sum_{n=1}^{4} n^2$. The result is given by the area painted in blue. On the righthand side we have depicted $\int_0^4 dn\, n^2$. The result is given by the area painted in red. We observe a substantial difference (29%) between the blue and the red areas.

The case $N = 50$ is studied in figure 2. There we find for the summation the result $50 \times (50 + 1) \times (2 \times 50 + 1)/6 = 42925$, whereas for the integration we obtain $50^3/3 = 41667$. That gives a difference of 1258 in 42925, which is some 3%.

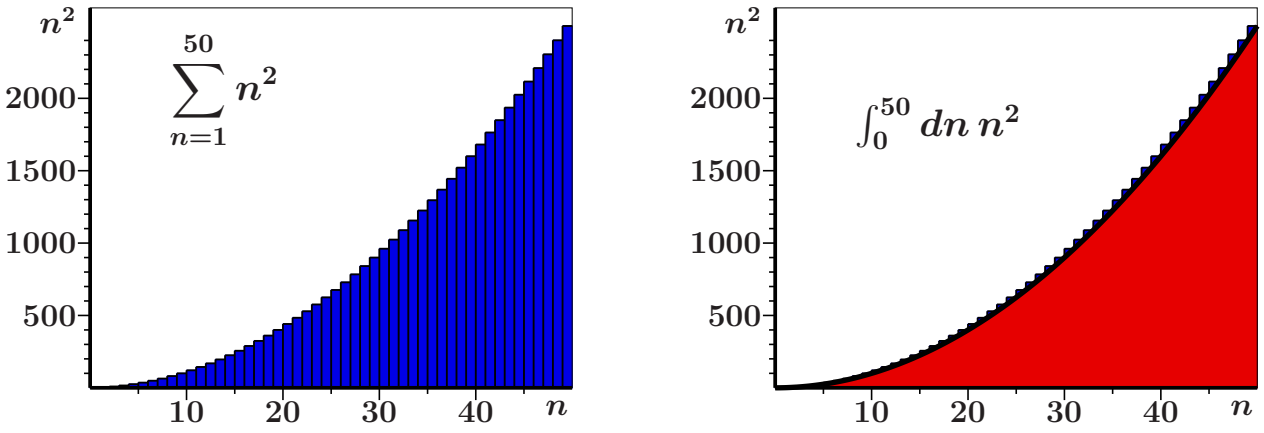

Figure 2: On the lefthand side we have depicted $\sum_{n=1}^{50} n^2$. The result is given by the area painted in blue. On the righthand side we have depicted $\int_0^{50} dn\, n^2$. The result is given by the area painted in red. We observe an almost negligible difference (3%) between the blue and the red areas.

We can easily make an estimate of the importance of the difference

$$\sum_{n=1}^{N} n^2 \; - \; \int_0^N dn\, n^2 \quad ,$$

by determining

$$\frac{\sum_{n=1}^{N} n^2 \; - \; \int_0^N dn\, n^2}{\int_0^N dn\, n^2} = \frac{\frac{1}{6}N(N+1)(2N+1) \; - \; \frac{1}{3}\, N^3}{\frac{1}{3}\, N^3} = \frac{N(3N+1)}{2N^3} \quad .$$

For large values of N one has

$$\frac{N(3N+1)}{2N^3} \approx \frac{N(3N)}{2N^3} = \frac{3}{2N} \quad .$$

For example, for $N = 50$ we find then that the difference is of some $3/100 = 3\%$, the same as we obtained before.

Also from the figures it may be clear that for $N = 10^{20}$, which is of the order of the number of free electrons in 0.01 cm^3 of conductor material, the fraction

$$\frac{\text{difference}}{\text{result}}$$

becomes much smaller than any experimental accuracy, namely 1.5×10^{-20}, hence negligible.

Furthermore, in general, integration is much easier than summation.

23. Em virtude de se estar a estudar um gás de Fermi mais realista é preciso de considerar o movimento de electrões livres em três dimensões.

a Considere uma caixa cúbica com um volume de $V = L^3$. Mostre que a energia própria de uma função de onda admissível da forma

$$\sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \quad ,$$

é dada por $E\left(n_x, n_y, n_z\right) = \frac{1}{2m}\, n^2 \, \left(\frac{\pi\hbar}{L}\right)^2$ com $n^2 = n_x^2 + n_y^2 + n_z^2$.

b Os níveis energéticos disponíveis aos electrões podem ser representados por pontos (vectores) com três coordenadas $n_x = 1,\ 2,\ 3,\ \ldots$, $n_y = 1,\ 2,\ 3,\ \ldots$ e $n_z = 1,\ 2,\ 3,\ \ldots$. Para um certo valor máximo $n_{\max}$ da grandeza n estes pontos encham um oitavo de uma esfera com raio $n_{\max}$.
Utilizando a integração em três dimensões

$$\int_{\text{oitavo da esfera}} d^3n \;=\; \frac{1}{8}\, 4\pi \, \int_0^{n_{\max}} n^2 dn \quad ,$$

determine a relação entre o número de estados N e o "raio" da esfera $n_{\max}$.

c Determine a energia total $E(n_{\max})$ para um conjunto de $2N$ electrões que se movem livremente dentro da caixa cúbica acima referida e mostre que o resultado é igual a

$$E(2N) = \frac{6N\hbar^2}{10m} \, \left(\frac{6\pi^2 N}{V}\right)^{2/3} \quad .$$

Solution:

a. In the three-dimensional case we obtain for the Hamiltonian for a stationary state of a free particle

$$H = -\frac{\hbar^2}{2m}\bigtriangledown^2 = -\frac{\hbar^2}{2m}\left\{\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right\} \quad ,$$

whereas the corresponding Schrödinger equation ($H\psi = E\psi$) is given by

$$-\frac{\hbar^2}{2m}\left\{\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right\}\psi(x,y,z) = E\psi(x,y,z) \quad .$$

It easily follows that

$$\psi_{k_x,k_y,k_z}(x,y,z) = \mathcal{N}^3 \sin\left(k_x x\right) \sin\left(k_y y\right) \sin\left(k_z z\right) \quad ,$$

with $\mathcal{N} = \sqrt{2/L}$, is a solution of the Schrödinger equation

$$-\frac{\hbar^2}{2m}\left\{\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right\}\psi_{k_x,k_y,k_z}(x,y,z) =$$

$$= -\frac{\hbar^2}{2m}\mathcal{N}^3 \left\{\left[\frac{d^2}{dx^2}\sin\left(k_x x\right)\right] \sin\left(k_y y\right) \sin\left(k_z z\right) \;+\right.$$

$$+\sin(k_x x)\left[\frac{d^2}{dy^2}\sin(k_y y)\right]\sin(k_z z)+\sin(k_x x)\sin(k_y y)\left[\frac{d^2}{dz^2}\sin(k_z z)\right]\Big\}$$

$$=-\frac{\hbar^2}{2m}\mathcal{N}^3\Big\{\left[-k_x^2\sin(k_x x)\right]\sin(k_y y)\sin(k_z z)\ +$$

$$+\sin(k_x x)\left[-k_y^2\sin(k_y y)\right]\sin(k_z z)+\sin(k_x x)\sin(k_y y)\left[-k_z^2\sin(k_z z)\right]\Big\}$$

$$=\frac{\hbar^2}{2m}\left\{k_x^2+k_y^2+k_z^2\right\}\mathcal{N}^3\sin(k_x x)\sin(k_y y)\sin(k_z z)=\frac{\hbar^2}{2m}\left\{k_x^2+k_y^2+k_z^2\right\}\ \psi_{k_x,k_y,k_z}(x,y,z)$$

for

$$E(k_x,k_y,k_z)=\frac{\hbar^2}{2m}\left\{k_x^2+k_y^2+k_z^2\right\}\quad .$$

Furthermore it automatically satisfies the boundary conditions $\psi=0$ at the faces $x=0$, $y=0$ and $z=0$ of the cube. Moreover, at the other three faces $x=L$, $y=L$ and $z=L$ of the cube we must have $\sin(k_x L)=0$, $\sin(k_y L)=0$ and $\sin(k_z L)=0$, respectively, in order for the wave function to vanish at those faces as well. This leads to

$$k_x L=n_x\pi\quad,\quad k_y L=n_y\pi\quad\text{and}\quad k_z L=n_z\pi\quad,$$

for $n_x=1,\,2,\,3,\,\ldots$, $n_y=1,\,2,\,3,\,\ldots$ and $n_z=1,\,2,\,3,\,\ldots$.

For the eigenenergy of the state ψ_{n_x,n_y,n_z} we obtain then

$$E(n_x,n_y,n_z)=\frac{1}{2m}\,n^2\,\left(\frac{\pi\hbar}{L}\right)^2\quad\text{with}\quad n^2=n_x^2+n_y^2+n_z^2\quad.$$

b. In figure 3 we show for a two-dimensional "cube" how the states can be represented by points. Each dot represents one state and ocupies 1 unit in each dimension. Hence, the number of states

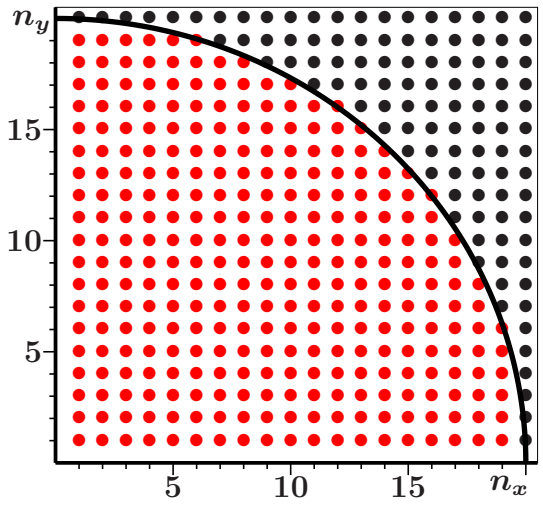

Figure 3: In two dimensions for $n_x\le 20$ and $n_y\le 20$ we represent all possible states by dots. The states which are represented by the red dots inside the "octant" have eigenenergies $\le\frac{1}{2m}\,20^2\,\left(\frac{\pi\hbar}{L}\right)^2$.

N inside one octant of a sphere with radius $n_{\max}$ equals

$$N \;=\; \int_{\text{oitavo da esfera}} d^3n\; 1 \;=\; \frac{1}{8}\int d\Omega \int_0^{n_{\max}} n^2 dn \;=\; \frac{1}{8}\,4\pi\,\frac{1}{3}\,n_{\max}^3 = \;\frac{\pi}{6}\,n_{\max}^3 \quad .$$

Consequently

$$n_{\max} = \left(\frac{6N}{\pi}\right)^{1/3} \quad .$$

c. Each state can be ocupied by two electrons with opposite directions of the spin z component. The energy contribution of a state with quantum numbers $\vec{n} = (n_x, n_y, n_z)$ is given by $E\,(n_x, n_y, n_z) = \frac{1}{2m}\,n^2\,\left(\frac{\pi\hbar}{L}\right)^2$.

Summing over all states with energies equal or less than $\frac{1}{2m}\,n_{\max}^2\,\left(\frac{\pi\hbar}{L}\right)^2$ gives

$$E(2N) = 2\int_{\text{octant}} d^3n\; E\,(n_x, n_y, n_z) = 2\,\frac{1}{8}\int d\Omega \int_0^{n_{\max}} n^2 dn\; E_n =$$

$$= 2\,\frac{1}{8}\,4\pi \int_0^{n_{\max}} n^2 dn \left\{\frac{1}{2m}\,n^2\,\left(\frac{\pi\hbar}{L}\right)^2\right\} = \frac{\pi}{2m}\,\left(\frac{\pi\hbar}{L}\right)^2 \int_0^{n_{\max}} dn\, n^4$$

$$= \frac{\pi}{2m}\,\left(\frac{\pi\hbar}{L}\right)^2\,\frac{1}{5}\,n_{\max}^5 = \frac{\pi}{10m}\,\left(\frac{\pi\hbar}{L}\right)^2\,\left(\frac{6N}{\pi}\right)^{5/3} = \frac{\pi}{10m}\,\left(\frac{\pi\hbar}{L}\right)^2\,\left(\frac{6N}{\pi}\right)\left(\frac{6N}{\pi}\right)^{2/3}$$

$$= \frac{6N\hbar^2}{10m}\,\left(\frac{\pi}{L}\right)^2\,\left(\frac{6N}{\pi}\right)^{2/3} = \frac{6\hbar^2 N}{10m}\,\left(\frac{\pi^3}{L^3}\right)^{2/3}\,\left(\frac{6N}{\pi}\right)^{2/3} = \frac{6N\hbar^2}{10m}\,\left(\frac{\pi^3}{L^3}\,\frac{6N}{\pi}\right)^{2/3}$$

$$= \frac{6N\hbar^2}{10m}\,\left(\frac{6\pi^2 N}{L^3}\right)^{2/3} = \frac{6N\hbar^2}{10m}\,\left(\frac{6\pi^2 N}{V}\right)^{2/3} \quad .$$

Note that $2N/V$ defines the density of free electrons in the box.

24. Mostre que a energia ε_F (energia de Fermi) dos níveis energéticos mais elevados de um conjunto de $2N$ electrões que se movem livremente dentro da uma caixa cúbica de volume V, é dada por

$$\varepsilon_F(2N) = \frac{\hbar^2}{2m}\,\left(\frac{6\pi^2 N}{V}\right)^{2/3} \quad .$$

a Determine as energias de Fermi de cobre (densidade de electrões livres = $8.50 \times 10^{28}/\mathrm{m}^3$), de sódio (densidade de electrões livres = $2.50 \times 10^{28}/\mathrm{m}^3$), de prata (densidade de electrões livres = $5.76 \times 10^{28}/\mathrm{m}^3$) e de ouro (densidade de electrões livres = $5.90 \times 10^{28}/\mathrm{m}^3$).

Literatura: Charles Kittel, *Thermal Physics*.
Capítulo 10: Enumeration of orbitals.
Capítulo 14: Fermi-Dirac distribution.

Solution:

The Fermi energy is the maximum possible energy (actually only at 0 Kelvin) for a set of $2N$ free electrons. Hence, we have

$$\varepsilon_F = E\left(n_{\max}\right) = \frac{1}{2m}\,n_{\max}^2\,\left(\frac{\pi\hbar}{L}\right)^2 \quad .$$

Also using the result of exercise (23b) and remembering that the density of free electrons equals $2N/V$, we obtain

$$\varepsilon_F = \frac{1}{2m}\,\left(\frac{6N}{\pi}\right)^{2/3}\,\left(\frac{\pi\hbar}{L}\right)^2 = \frac{\hbar^2}{2m}\,\left(\frac{6\pi^2 N}{L^3}\right)^{2/3} = \frac{\hbar^2}{2m}\,\left(\frac{6\pi^2 N}{V}\right)^{2/3} = \frac{\hbar^2 c^2}{2mc^2}\,\Big(3\pi^2 \times \text{density}\Big)^{2/3}.$$

In the tables of physical constants of the Particle Data Group (http://pdg.lbl.gov/2009/reviews/-rpp2009-rev-phys-constants.pdf) we find for electrons

$$\hbar c = 197.3269631 \pm 0.0000049 \text{ MeV fm} \quad \text{and} \quad m_e c^2 = 0.510998910 \pm 0.000000013 \text{ MeV} \quad .$$

So, the formula becomes (1 fm = 10^{-15} m)

$$\varepsilon_F = \frac{\hbar^2 c^2}{2mc^2}\,\Big(3\pi^2 \times \text{density}\Big)^{2/3} = 3.646450 \times 10^{-19} \text{ eV m}^2 \times \Big(\text{density in m}^{-3}\Big)^{2/3} \quad .$$

We obtain

Copper (Cu)	$d = 8.50 \times 10^{28}/\mathrm{m}^3$	$\varepsilon_F = 7.05$ eV
Sodium (Na)	$d = 2.50 \times 10^{28}/\mathrm{m}^3$	$\varepsilon_F = 3.12$ eV
Silver (Ag)	$d = 5.76 \times 10^{28}/\mathrm{m}^3$	$\varepsilon_F = 5.44$ eV
Gold (Au)	$d = 5.90 \times 10^{28}/\mathrm{m}^3$	$\varepsilon_F = 5.53$ eV