


Condensed Matter Physics
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Lecture - 09
The Free Electron Theory of Metals-Worked Examples

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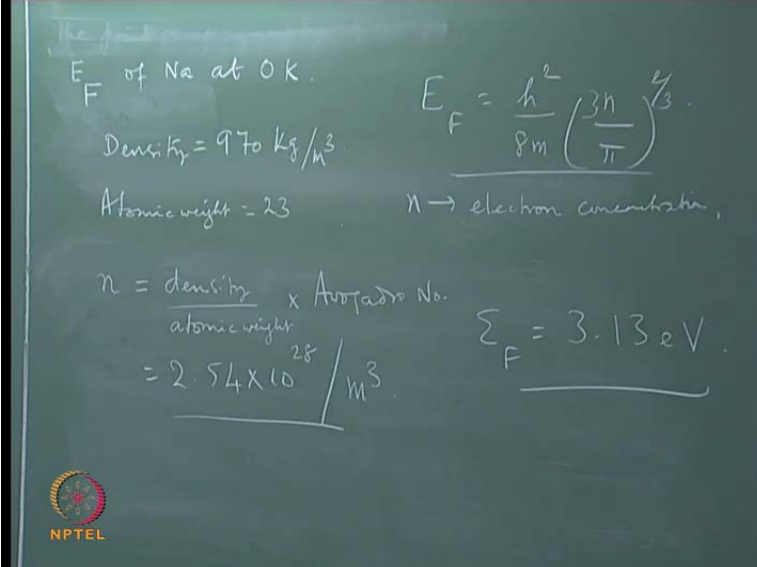
Problem 23

Calculate the Fermi energy of sodium at 0 K given the density of sodium is 970 kg/m^3 and its atomic weight is 23.

11

Now, we will move on to some questions relating to electrons in solids, the free electrons in metals in particular.

(Refer Slide Time: 00:32)



The slide shows a handwritten solution on a chalkboard. It starts with the question: "E_F of Na at 0K." and lists the given data: "Density = 970 kg/m³" and "Atomic weight = 23". The Fermi energy formula is written as $E_F = \frac{h^2}{8m} \left(\frac{3n}{\pi} \right)^{2/3}$, with a note that $n \rightarrow$ electron concentration. The electron concentration is calculated as $n = \frac{\text{density}}{\text{atomic weight}} \times \text{Avogadro's No.} = 2.54 \times 10^{28} / \text{m}^3$. Finally, the Fermi energy is calculated as $E_F = 3.13 \text{ eV}$. The NPTEL logo is visible in the bottom left corner.

The problem that we will discuss is we are asked to calculate the Fermi energy of sodium at 0 K, where given the density of sodium is 970 kilograms per meter cube, and the atomic weight is 23 as we know. We know that the basic expression for the Fermi energy is $\frac{h^2}{8m} \left(\frac{3n}{\pi} \right)^{2/3}$, where n is the electron concentration, $3n$ by π .

(Refer Slide Time: 01:43)


Solution:

$$E_{F_0} = \frac{h^2}{8m} \left(\frac{3n}{\pi} \right)^{2/3}$$

To determine n for sodium:


$$n = \text{density} \times \left(\frac{\text{Avogadro number}}{\text{atomic weight}} \right)$$

$$= 970 \left(\frac{6.023 \times 10^{26}}{23} \right) = 2.54 \times 10^{28} / \text{m}^3$$

 12

So, we are required to find n for which we take the density and divide by the atomic weight and multiplied by Avogadro number. And that the density and the atomic weight are given here, Avogadro number is known the result of this calculation is 2.54×10^{28} electron per meter cube. We are assuming that in sodium is monovalent that this is really the number of atoms per unit volume and assuming that each atom donates one conduction electron, we get the number of electrons per unit volume as this.

(Refer Slide Time: 02:51)

$$\begin{aligned} E_{F_0} &= \frac{(6.63 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31}} \left(\frac{3}{\pi}\right)^{2/3} n^{2/3} \\ &= 5.802 \times 10^{-38} \times (n)^{2/3} \\ &= 5.802 \times 10^{-38} \times (2.54 \times 10^{28})^{2/3} \\ &= 5.01369 \times 10^{-19} \text{ J} \\ &= 3.13 \text{ eV} \end{aligned}$$


13


And therefore, substituting this value of n , we get the Fermi energy as 3.13 electron volts this is a just a question of substituting this expression is. So, that is the Fermi energy of sodium at zero Kelvin.

(Refer Slide Time: 03:18)

Problem 24

Find the energy level in sodium for which the probability of occupation at 300 K is (i) 0.5 (ii) 0.75 (iii) 0.25.

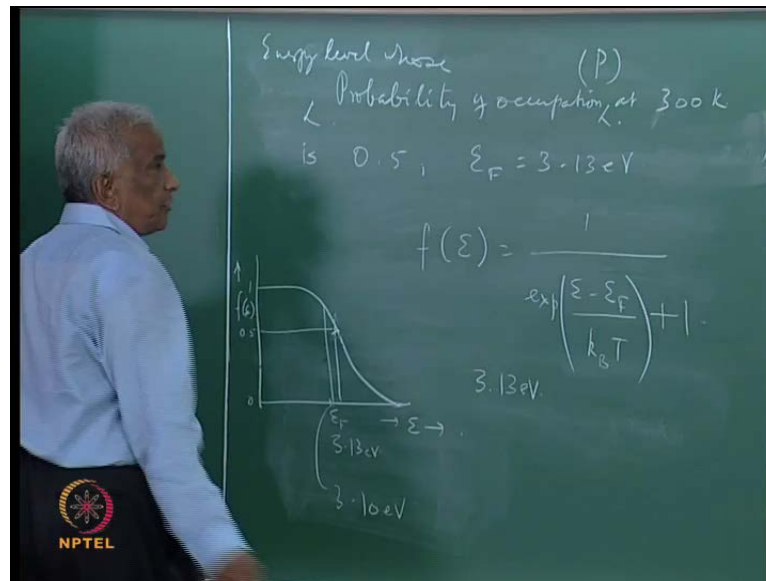
The Fermi energy of sodium is 3.13 eV.



14

In the next problem, we again deal with sodium we are asked to find the energy level in sodium at absolute zero, no, not at absolute zero.

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But probability of occupation of this energy level at a temperature of 300 Kelvin is 0.5. Energy level whose probability of occupation since here from given the result of the previous problem that E_f the Fermi energy at zero k is at 3.13 electron volts. For this we go back to the Fermi Dirac distribution function which finite temperatures as they form like this, we have discussed all these already. So, that is the shape of Fermi Dirac distribution function and therefore, we know that the probability of occupation at 300 k becomes half exactly at the Fermi level.

(Refer Slide Time: 05:09)

(i)
$$0.5 = \frac{1}{e^{(E-E_F)/k_B T} + 1}$$
$$e^{(E-E_F)/k_B T} = (1/0.5) - 1$$
$$= 2 - 1 = 1$$
$$(E - E_F) = 0$$
$$E = E_F$$

The energy at which the probability of occupation is 0.5 is the Fermi energy $E_F = 3.13$ eV. This is true at any temperature, for all metals

So, we can find this we can readily see that this has to be at an energy of 3.13 electron volts.

(Refer Slide Time: 05:23)

(ii)

$$0.75 = \frac{1}{e^{(E-E_f)/k_B T} + 1}$$

$$e^{(E-E_f)/k_B T} = (1/0.75) - 1$$

$$= 0.3333$$

$$E - E_f = \ln 0.3333 \times k_B T$$

$$E/E_f = (\ln 0.3333 \times k_B T / E_f) + 1$$

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This is true in general of all metals. The value of half for the probability of half occupation occurs at the Fermi energy. In the same way, we can find the values energy at which the probability of occupation becomes for example, 0.75.

(Refer Slide Time: 05:44)

(P)
Occupation at 300k
 $E_f = 3.13 \text{ eV}$
 $f(E) = \frac{1}{\exp\left(\frac{E}{k_B T}\right) + 1}$
3.13 eV

(ii)
 $P = 0.75$
 $0.75 = \frac{1}{\exp\left(\frac{E - 3.13}{k_B \cdot 300}\right) + 1}$
 $E \rightarrow 3.10 \text{ eV}$
 $P = 0.25$
 $E \rightarrow 3.16 \text{ eV}$

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So, that is the second question we have to find. So, substituting 0.75 equal to 1 by exponential e minus 3.13 by k B into 300 plus 1 substituting in this we can readily see that the E happens to be something like 3.10 electron volts.

(Refer Slide Time: 06:19)


At 300 K , $k_B T / E_F = 0.026 / 3.31 = 0.007855$

$$E / E_F = (-1.0987 \times 0.007855) + 1$$

$$E = 0.9914 \times E_F = 0.9914 \times 3.13$$

$$= 3.10 \text{ eV}$$

The probability of occupation of the energy level 3.10 eV ($E < E_F$) is 0.75



18

And that would be this is 3.13, and this will be somewhere here 3.10 electron volts in which we have a probability of occupation of 0.75. The next question concerns the same value for energy level for which the probability is 0.25.

(Refer Slide Time: 06:58)

(iii) $0.25 = \frac{1}{e^{(E-E_F)/k_B T} + 1}$

$$e^{(E-E_F)/k_B T} = (1/0.25) - 1 = 3$$

$$E - E_F = \ln 3 \times k_B T$$


$$E / E_F = (\ln 3 \times k_B T / E_F) + 1$$

$$E / E_F = (1.0986 \times 0.007855) + 1$$

$$= 1.008629$$

$$E = 1.008629 \times 3.13 = 3.16 \text{ eV}$$

The probability of occupation of energy level 3.16 eV ($E > E_F$) is 0.25.




19

And for following same procedure, we find the corresponding energy is 3.16 electron volts. In other words, we have the Fermi tail here and it is slightly above the Fermi level this is 3.16 electron volts and that is where the probability reduces further from 0.5 to 0.25, but still it is non-zero. So, states here are occupied with a probability of one-fourth.

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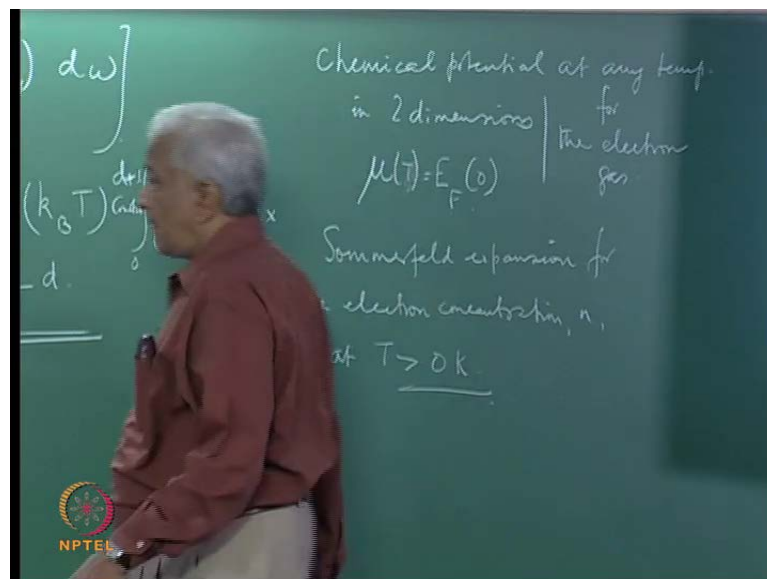
Problem 25

In two dimensions show that the chemical potential at any temperature is equal to the Fermi energy at $T = 0\text{K}$. (Hint: Start from the Sommerfeld expansion for the electron concentration at any temperature T above 0K .)



The next problem is about the chemical potential in two dimensions are at any temperature for the electron gas.

(Refer Slide Time: 07:39)



Chemical potential at any temp.
in 2 dimensions for the electron gas

$$\mu(T) = E_F(0)$$

Sommerfeld expansion for
electron concentration, n ,
at $T > 0\text{K}$.

And we are required to prove this is the standard symbol, for this is mu and this is we are required to prove that this is equal to E_f zero at this is the Fermi energy at T equal to zero k this is mu of t mu at any temperature. So, in order to prove this, we have to start from the slope called Sommerfeld expansion for the electron concentration in at any temperature T.

(Refer Slide Time: 09:14)

The Sommerfeld Expansion


The Sommerfeld expansion is applied to integrals of the form

$$\int_{-\infty}^{\infty} d\varepsilon H(\varepsilon) f(\varepsilon), \quad f(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/k_B T} + 1}, \quad \text{(Prob 25.1)}$$

where $H(\varepsilon)$ vanishes as $\varepsilon \rightarrow -\infty$ and diverges no more rapidly than some power of ε as $\varepsilon \rightarrow +\infty$. If one defines

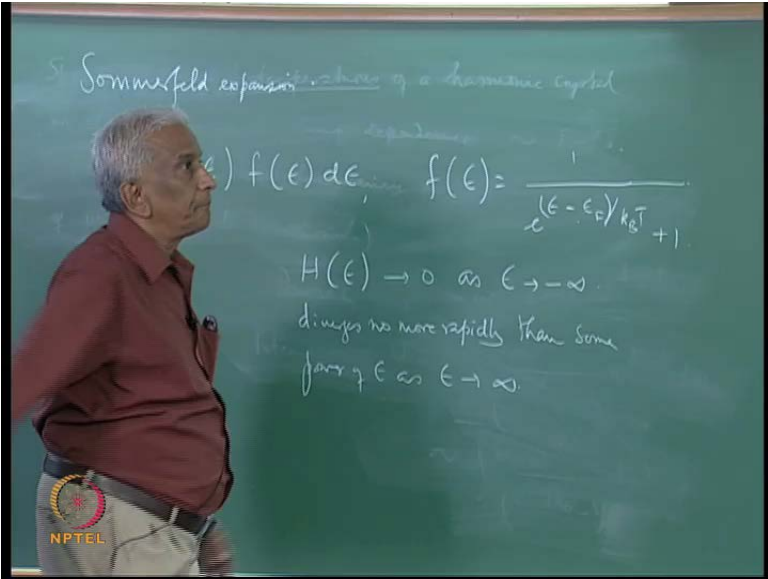
$$K(\varepsilon) = \int_{-\infty}^{\varepsilon} H(\varepsilon') d\varepsilon', \quad \text{(Prob 25.2)}$$

so that

$$H(\varepsilon) = \frac{dK(\varepsilon)}{d\varepsilon}, \quad \text{(Prob 25.3)}$$


So, what is the Sommerfeld expansion?

(Refer Slide Time: 09:18)




Sommerfeld expansion: - how of a characteristic crystal

$f(\varepsilon) d\varepsilon$, $f(\varepsilon) = \frac{1}{e^{(\varepsilon - \varepsilon_f) / k_B T} + 1}$

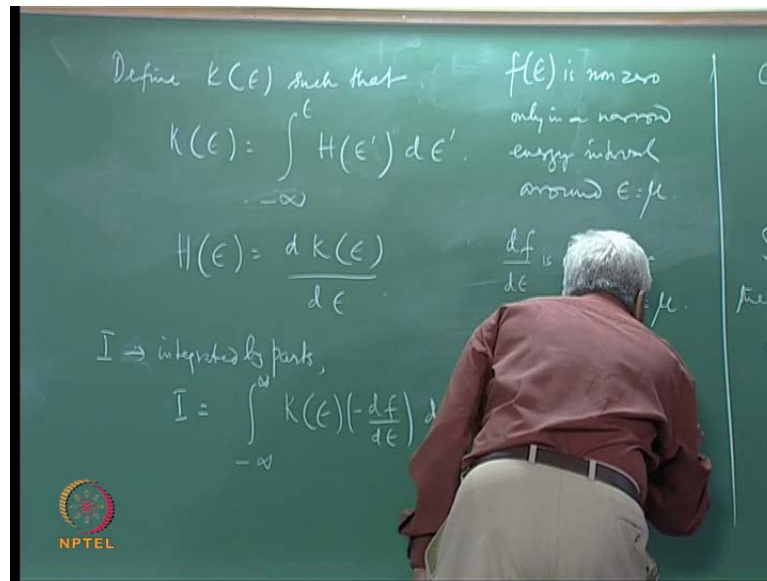
$H(\varepsilon) \rightarrow 0$ as $\varepsilon \rightarrow -\infty$.

diverges no more rapidly than some power of ε as $\varepsilon \rightarrow \infty$.



Let us consider this before answering the question. So, let us discuss the Sommerfeld expansion. In order to use this the concerned integrals of the form $\int_{-\infty}^{\infty} H(\epsilon) F(\epsilon) d\epsilon$ from minus infinity to plus infinity, where $F(\epsilon)$ is the Fermi derived distribution function and the function $H(\epsilon)$ tends to zero or vanishes as ϵ tends to minus infinity, and diverges no more rapidly than some power of ϵ as ϵ tends to infinity.

(Refer Slide Time: 11:01)




So, if it is so then let us define another function k of function ϵ define function k of ϵ such that k of ϵ equals integral zero to ϵ H of ϵ' $d\epsilon'$. In other words, H of ϵ is just $d k$ of ϵ by $d\epsilon$. With this definition, now let us go back to let us call this integral I , then this integral maybe integrated by parts, and get we get I equal to the first term will go to zero. So, we will have integral minus infinity two plus infinity k of ϵ into minus $d f$ by $d\epsilon$ times $d\epsilon$. Therefore, the $d f$ by $d\epsilon$ is large only around ϵ equal to μ .

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then one can integrate by parts in (Prob 25.1) to get

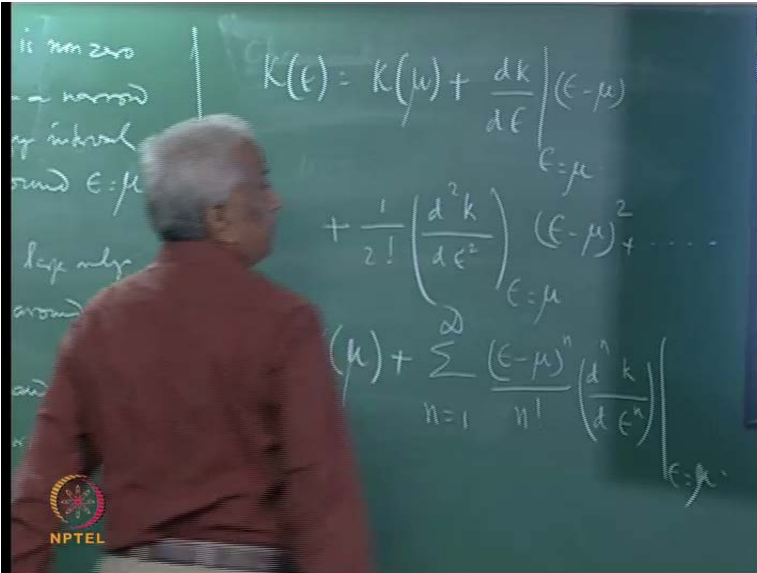
$$\int_{-\infty}^{\infty} H(\epsilon) f(\epsilon) d\epsilon = \int_{-\infty}^{\infty} K(\epsilon) \left(-\frac{df}{d\epsilon} \right) d\epsilon. \quad \text{(Prob 25.4)}$$

Since f is indistinguishable from zero when ϵ is more than a few $k_B T$ greater than μ , and indistinguishable from unity when ϵ is more than a few $k_B T$ less than μ , its ϵ -derivative will be appreciable only within a few $k_B T$ of μ . Provided that H is nonsingular and not too rapidly varying in the neighborhood of $\epsilon = \mu$, it is very reasonable to evaluate (Prob 25.4) by expanding $K(\epsilon)$ in a Taylor series about $\epsilon = \mu$, with the expectation that only the first few term will be importance:

$$K(\epsilon) = K(\mu) + \sum_{n=1}^{\infty} \left[\frac{(\epsilon - \mu)^n}{n!} \right] \left[\frac{d^n K(\epsilon)}{d\epsilon^n} \right]_{\epsilon=\mu} \quad \text{(Prob 25.5)}$$



Therefore what do we do, we expand therefore, expand k of e as in a Taylor series at ϵ equal to μ in this integral I .

(Refer Slide Time: 13:23)



is non zero
- a narrow
of interval
around $\epsilon = \mu$
large only
around

$$K(\epsilon) = K(\mu) + \left. \frac{dK}{d\epsilon} \right|_{\epsilon=\mu} (\epsilon - \mu) + \frac{1}{2!} \left(\left. \frac{d^2 K}{d\epsilon^2} \right)_{\epsilon=\mu} (\epsilon - \mu)^2 + \dots$$

$$K(\mu) + \sum_{n=1}^{\infty} \frac{(\epsilon - \mu)^n}{n!} \left(\left. \frac{d^n K}{d\epsilon^n} \right)_{\epsilon=\mu} \right.$$


So if we do this, we get things like K of e equals K of μ plus dK by $d\epsilon$ ϵ equal to μ times ϵ minus μ plus 1 by 2 factorial $d^2 k$ like $d\epsilon$ square at ϵ equal to μ times ϵ minus μ hole square plus terms like this. So, in general, we can write this as k of μ plus the sum from over n equal to one to infinity of

epsilon mu minus mu to the power l by n factorial into d n k by d epsilon n evaluated at epsilon equal to mu.

(Refer Slide Time: 14:33)


When we substitute (Prob 25.5) in (Prob 25.4), the leading term gives just $K(\mu)$, since

$$\int_{-\infty}^{\infty} \left(-\frac{\partial f}{\partial \epsilon} \right) d\epsilon = 1.$$

Furthermore, since $\partial f / \partial \epsilon$ is an even function of $\epsilon - \mu$, only terms with even n in (Prob 25.5) contribute to (Prob 25.4), and if we reexpress K in terms of the original function H through (Prob 25.2), we find that:

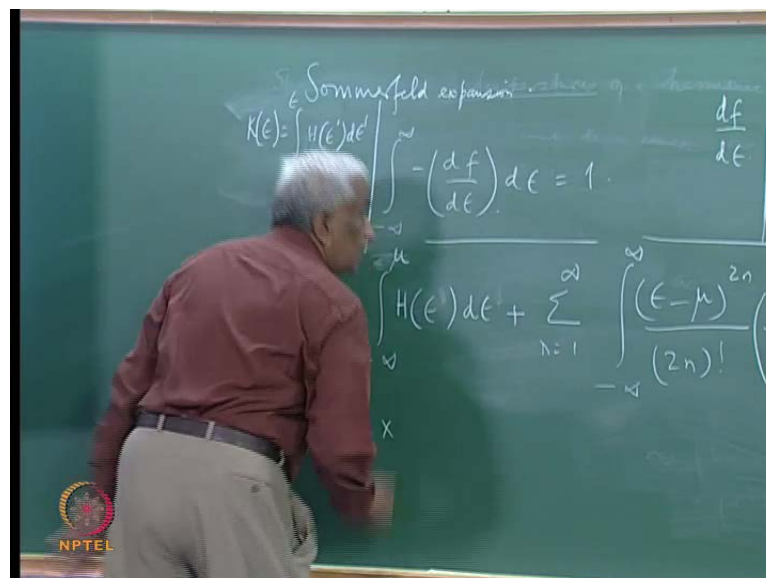
$$\int_{-\infty}^{\infty} d\epsilon H(\epsilon) f(\epsilon) = \int_{-\infty}^{\mu} H(\epsilon) d\epsilon + \sum_{n=1}^{\infty} \int_{-\infty}^{\infty} \frac{(\epsilon - \mu)^{2n}}{(2n)!} \left(-\frac{\partial f}{\partial \epsilon} \right) d\epsilon \frac{d^{2n-1}}{d\epsilon^{2n-1}} H(\epsilon) \Big|_{\epsilon=\mu}.$$

(Prob 25.6)



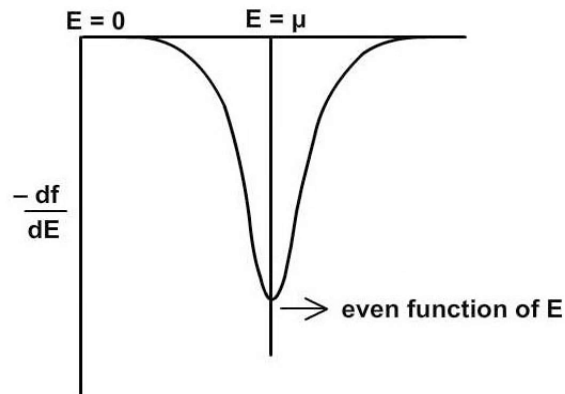
So, this is what we are going to substitute here.

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In integral has we also take into account, in fact, this is the delta function with a value one from minus infinity to plus infinity, this is an even function.

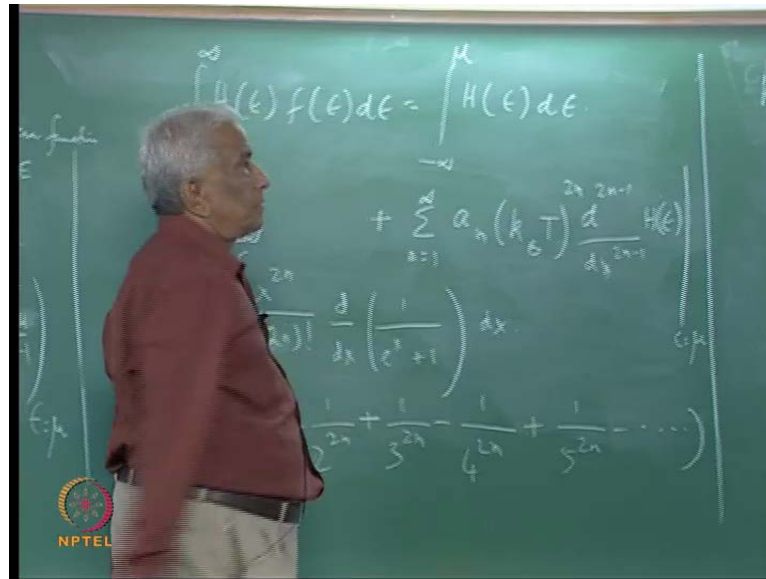
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So it is look like this, so that would be df by strictly it becomes in the related becomes delta function. So, we use this property therefore, it is a even function of epsilon. Therefore, in this integration over E , we have only left with terms, which are even n . So, taking only those terms we can write the integral required integral as we have the definition that k of E is integral using that. So, the first term will be k of μ . So, this will be a minus infinity to μ that will be the first term plus sigma n equal to 1 to infinity of the integral minus infinity to plus infinity epsilon minus μ , we considered only even terms. So, with the power $2n$ and $2n$ factorial here into minus df by dE into d^{2n-1} by $d\epsilon$ $2n-1$ of k evaluated at epsilon equal to μ , times and this is H because I have written $2n-1$ here. So, this is the final result which we can now integrate.

(Refer Slide Time: 17:42)



So, we finally, make the substitution epsilon minus mu by k b t as x because that is what is occurring in the derivative of the Fermi Dirac function.

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Finally making the substitution $(\epsilon - \mu) / k_B T = x$, we find that

$$\int_{-\infty}^{\infty} H(\epsilon) f(\epsilon) d\epsilon = \int_{-\infty}^{\infty} H(\epsilon) d\epsilon + \sum_{n=1}^{\infty} a_n (k_B T)^{2n} \frac{d^{2n-1}}{d\epsilon^{2n-1}} H(\epsilon) \Big|_{\epsilon=\mu} \quad \text{(Prob 25.7)}$$

where the a_n are dimensionless numbers given by

$$a_n = \int_{-\infty}^{\infty} \frac{x^{2n}}{(2n)!} \left(-\frac{d}{dx} \frac{1}{e^x + 1} \right) dx. \quad \text{(Prob 25.8)}$$

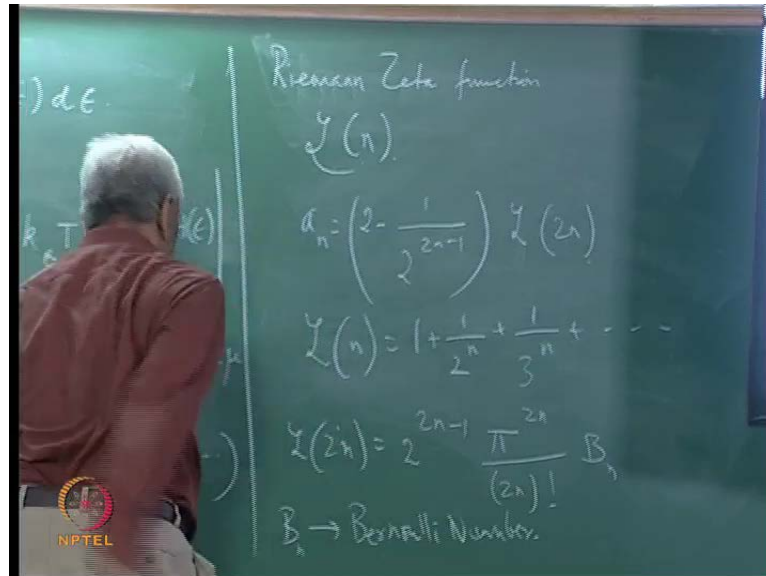
By elementary manipulations one can show that

$$a_n = 2 \left(1 - \frac{1}{2^{2n}} + \frac{1}{3^{2n}} - \frac{1}{4^{2n}} + \frac{1}{5^{2n}} - \dots \right). \quad \text{(Prob 25.9)}$$

Therefore, we get the integral finally as integral minus infinity H of e F of e d e equals plus sigma n equal to 1 to infinity of a n times k B T to the power 2 n into d to the power 2 n minus 1 by d x to the power 2 n minus 1 of H of e epsilon evaluated at epsilon equal to mu. Where a n as the integral of the form x to the power 2 n by 2 n factorial into d by d x of 1 by e to the power x plus 1 d x . So, one can show that this this integral can be

evaluated and we arrive at $2^{-1} \cdot 2^{-n} + 1 \cdot 2^{-2n} + 1 \cdot 3^{-2n} + \dots$ to the power $2n - 1$ by 4 to the power 2 plus 1 by 5 to the power $2n$ and so on. This is a standard result, which we will assume here.

(Refer Slide Time: 19:38)




So, this is written usually in terms Riemann zeta function.

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This usually written in terms of the Riemann zeta function, $\zeta(n)$, as

$$a_n = \left(2 - \frac{1}{2^{2(n-1)}}\right) \zeta(2n), \quad \text{(Prob 25.10)}$$

where

$$\zeta(n) = 1 + \frac{1}{2^n} + \frac{1}{3^n} + \frac{1}{4^n} + \dots \quad \text{(Prob 25.11)}$$



Zeta of n , so we write a_n as $2^{-1} \cdot 2^{-n} + 1 \cdot 2^{-2n} + 1 \cdot 3^{-2n} + \dots$ to the power $2n - 1$ into zeta of $2n$. Where zeta n is $1 + 1 \cdot 2^{-n} + 1 \cdot 3^{-n} + 1 \cdot 4^{-n} + \dots$ plus etcetera.

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For the first few n , $\zeta(2n)$ has the values

$$\zeta(2n) = 2^{2n-1} \frac{\pi^{2n}}{(2n)!} B_n \quad (\text{Prob 25.12})$$

where the B_n are known as Bernoulli numbers, and

$$B_1 = \frac{1}{6}, B_2 = \frac{1}{30}, B_3 = \frac{1}{42}, B_4 = \frac{1}{30}, B_5 = \frac{1}{66}. \quad (\text{Prob 25.13})$$


So, this can be evaluated, so zeta $2n$ in general as the form 2 to the power $2n$ minus 2 times π to the power $2n$ by $2n$ factorial into B_n , where B_n is known as the Bernoulli number.

(Refer Slide Time: 21:07)


Sommerfeld expansion

$$B_1 = \frac{1}{6}, B_2 = \frac{1}{30}, \dots$$

$$\zeta(2) = \frac{\pi^2}{6}$$

$$E_F = \frac{\pi^2}{6} (k_B T)^2 \frac{D'(E_F)}{D(E_F)}$$

$$D(E) = \text{const.} \quad D'(E_F) = 0.$$


$$\mu(T) = E_F$$


So, this Bernoulli number as the following values B_1 for n equal to 1 is just $1/6$; B_2 is $1/30$ and so on. So, these are known standard results. So, in most practical calculations in metal physics, we need to know rarely more than zeta two the Riemann's zeta function is just $\pi^2/6$.

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Solution


The chemical potential at any temperature T is given by the Sommerfeld expansion as $E_F^0 - \frac{\pi^2}{6} (k_B T)^2 D'(E_F) / D(E_F)$.



So, using this result we get the chemical potential μ at any temperature T as E_F^0 , the chemical potential or the Fermi energy and absolute zero minus using the expansion Sommerfeld expansion and truncating it in the first term π^2 by $6 k_B T$ whole square into D of E_F where D of E_F is the density of states D dash by D E_F . Where D dash E_F is derivative with respect to the energy.

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In 2 dimensions $D(E_F) = \text{constant}$ and so $D'(E_F) = 0$. Hence the chemical potential $= E_F^0$.



So, we arrive at this result for the chemical potential in two dimensions, the question was about chemical potential in two dimensions, for D equal to 2, we know that the density


of states d of e is constant this is the reason which we have considered already. Therefore, $D \propto E^0$ is zero. Therefore, μ of T the chemical potential at any temperature T above zero k is just the Fermi energy at T equal to zero k , because this term vanishes, so that is the result that we are required to prove.

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Problem 26

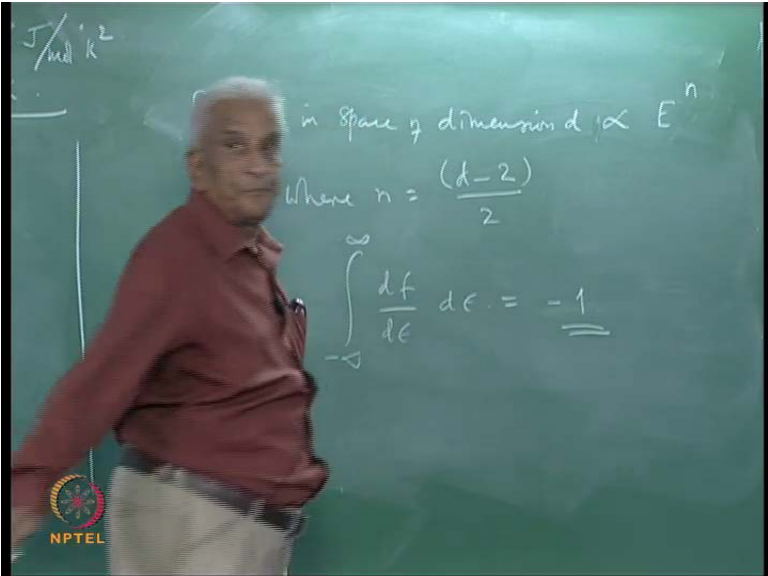
Fill in the blanks in the following:

- i. The density of states $D(E)$ for free electrons in a space of dimension ' d ' is proportional to E^n where $n = \text{-----}$.
- ii. If $f(E)$ is the Fermi-Dirac distribution function,

$$\int_{-\infty}^{\infty} \frac{df}{dE} dE = \text{-----}$$


The next question is given in the form of a fill in the blanks, fill in the blanks are straightforward.

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The density of states d of e for free electrons in the space of dimension d in space of dimension d is proportional to the energy to the power n where n is the answer; obviously, we have considered this already the answer is; obviously, d minus 2 by 2. And the next question is about Fermi Dirac distribution function, if the f of e is the Fermi Dirac distribution function integral $d f$ by $d e$ time $d e$ over minus infinity to plus infinity is the answer obviously, minus 1.