PHYS 460 - LECTURE 20

WHEN WE ENDED THE LAST LECTURE, WE WERE DISCUSSING THE "EXCHANGE ENERGY" OF A TWO ELECTRON WAVEFUNCTION, WHICH IS DEFINED AS THE DIFFERENCE BETWEEN STATES WITH SPIN PARALLEL AND ANTI-PARALLEL. THE ORIGIN OF THE NAME WILL BECOME APPARENT IN A MOMENT.

RECALL THE BASIC ARGUMENT. THE OVERALL MANY BODY WAVEFUNCTION MUST BE ANTISYMMETRIC FOR FERMIONS

$$\Psi(\vec{r}_1,\vec{r}_2;s_1 s_2) = \psi(\vec{r}_1,\vec{r}_2)\chi(s_1,s_2) = -\Psi(\vec{r}_2,\vec{r}_1;s_2,s_1)$$

THUS IF YOU HAVE TWO ELECTRONS WITH ORBITAL WAVEFUNCTIONS $|A(\vec{r}_1)\rangle$ AND $|B(\vec{r}_2)\rangle$, YOU CAN EITHER HAVE SPINS PARALLEL

$\chi(s_1,s_2) = |\uparrow\uparrow\rangle$, WHICH IS SYMMETRIC

$$\Rightarrow \quad \psi_{\uparrow\uparrow}(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}}\left(|A\rangle|B\rangle - |B\rangle|A\rangle\right)$$

OR YOU CAN HAVE THEM ANTIPARALLEL (AND ANTISYMMETRIC)

$$\chi(s_1,s_2) = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

$$\Rightarrow \quad \psi_{\uparrow\downarrow}(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}}\left(|A\rangle|B\rangle + |B\rangle|A\rangle\right)$$

NOTE THAT THIS JUST ANOTHER FORM OF PAULI EXCLUSION: IF $|A\rangle = |B\rangle$, THEN $\Psi = 0$ IF $s_1 = s_2$.

SINCE $\psi_{\uparrow\downarrow}$ HAS MORE ELECTRON OVERLAP, IT WILL BE THE HIGHER ENERGY STATE DUE TO COULOMB REPULSION. WE CAN CALCULATE THE DIFFERENCE.

LET $|AB\rangle \equiv |A\rangle|B\rangle$, AND ADD A COULOMB POTENTIAL $V(\vec{r}_1, \vec{r}_2)$

"triplet" $\longrightarrow$ $E_{\uparrow\uparrow} = \frac{1}{2}\left(\langle AB| - \langle BA|\right) V \left(|AB\rangle - |BA\rangle\right)$

"singlet" $\longrightarrow$ $E_{\uparrow\downarrow} = \frac{1}{2}\left(\langle AB| + \langle BA|\right) V \left(|AB\rangle + |BA\rangle\right)$

$$\Rightarrow \Delta E = E_{\uparrow\uparrow} - E_{\uparrow\downarrow} = \frac{1}{2}\left(-\langle BA|V|AB\rangle - \langle AB|V|BA\rangle - \langle BA|V|AB\rangle - \langle AB|V|BA\rangle\right)$$

$$= -\langle BA|V|AB\rangle - \langle AB|V|BA\rangle$$

$$= -2\,\mathrm{Re}\left(\langle AB|V|BA\rangle\right)$$

SINCE $\langle BA|V|AB\rangle = \left(\langle AB|V|BA\rangle\right)^*$

THUS PARALLEL SPINS HAVE LOWER COULOMB ENERGY, AND THE SIZE OF THE GAIN IS ASSOCIATED WITH THE ENERGY TO SWAP OR "EXCHANGE" ELECTRONS $A \leftrightarrows B$ $\longrightarrow$ "EXCHANGE ENERGY"

YOU MIGHT RECALL THAT A SIMILAR CALCULATION WAS DONE WHEN WE WERE CONSIDERING THE COVALENT BOND, AND IN THAT CASE SPINS WANTED TO BE ANTIPARALLEL. IN GENERAL, EITHER CASE IS POSSIBLE, BUT $\uparrow\uparrow$ IS ALWAYS PREFERRED FOR ELECTRONS ON SAME ATOM.

THIS CALCULATION IS THE MAIN JUSTIFICATION FOR THE FIRST HUND'S RULE

HUND'S RULE (1): ELECTRONS ON AN ATOM WILL ALWAYS MAXIMIZE TOTAL S (BY ALIGNING THEIR SPINS)

THE OTHER TWO ARE

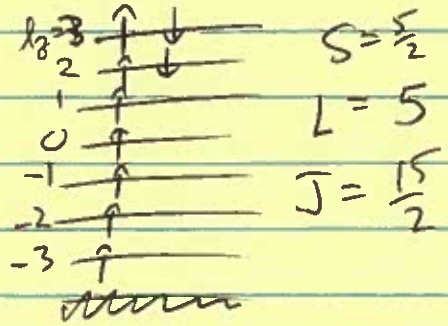
HUND'S RULE (2): WHILE SATISFYING (1), ELECTRONS WILL THEN MAXIMIZE L

HUND'S RULE (3): WHILE SATISFYING (1) & (2), TOTAL ANGULAR MOMENTUM $J = L-S$ FOR SHELLS LESS THAN HALF FULL AND $J = L+S$ FOR SHELLS MORE THAN HALF FULL

THE RESULT OF RULE (2) IS A SIMILAR ARGUMENT ABOUT ELECTRON AVOIDANCE AND IS COULOMBIC IN NATURE, RULE (3) IS ASSOCIATED WITH SPIN-ORBIT (RUSSEL-SAUNDERS) COUPLING $\mathcal{H}_{S\text{-}O} = \lambda \vec{L}_i \cdot \vec{S}_i$, WHICH SAYS THAT EACH ELECTRON WILL WANT ITS SPIN AND ORBITAL ANG MOM TO ANTI-ALIGN.

e.g. Dy^{3+} $[Xe]\,4f^9$

$l = 3$

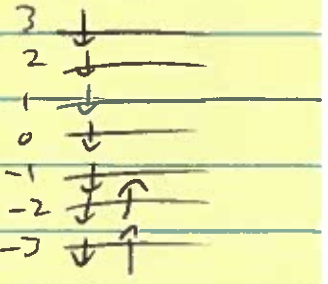


$S = \frac{5}{2}$

$L = 5$

$J = \frac{15}{2}$

COULD HAVE DRAWN IT



$\vec{L}_i$ ANTI PARALLEL TO $\vec{S}_i$

MAGNETIZATION OF LONE ATOMS

HUND'S RULES ALLOW ONE TO WORK OUT THE TOTAL ANGULAR MOMENTUM

$$\vec{J} = \vec{L} + \vec{S}$$

WHICH IS GREAT, BUT RECALL THE HAMILTONIAN FOR THE LONE ATOM WAS

$$\mathcal{H} = \mathcal{H}_0 + \mu_B \vec{B} \cdot (\vec{L} + g\vec{S}) + \frac{e^2}{8 m_e} \sum_i^Z |\vec{B} \times \vec{r}_i|^2$$

THE PARAMAGNETIC TERM DOESN'T INVOKE $\vec{J}$, BUT $\vec{L} + g\vec{S}$, WHICH HAS AN EXTRA g-FACTOR IN FRONT OF THE $\vec{S}$

I'M NOT GOING TO SHOW IT HERE (BUT YOU MAY ON YOUR HOMEWORK), BUT IT TURNS OUT THAT IT REDUCES TO

$$\mathcal{H}_{PARA} = \tilde{g} \mu_B \vec{B} \cdot \vec{J}$$

IF WE DEFINE THE LANDÉ g-FACTOR

$$\tilde{g} = \frac{1}{2}(g+1) + \frac{1}{2}(g-1)\left[\frac{S(S+1) - L(L+1)}{J(J+1)}\right]$$

NOTE THAT THIS WOULD IMPLY THAT THE TOTAL MOMENT IS BEST THOUGHT OF AS

$$\mu_J = \tilde{g} \mu_B \vec{J}$$

OFTEN INFORMALLY (AND INCORRECTLY) REFERRED TO AS "SPIN"

WITH THIS INFORMATION, WE ARE NOW IN A POSITION TO CALCULATE MAGNETIZATION, LET'S CONSIDER THE TWO TERMS SEPARATELY. SIMPLE CASE FIRST

LARMOR DIAMAGNETISM

CONSIDER THE SPECIAL CASE $J=0$.

THIS OCCURS WHEN (1) ALL SHELLS ARE FULL

OR (2) SHELL IS ONE LESS THAN HALF FULL

THEN THE PARAMAGNETIC TERM IS ZERO, AND MAGNETIZATION IS ENTIRELY DETERMINED BY THE DIAMAGNETIC TERM FOR A SINGLE ORBITAL

$$\mathcal{H}_{DIA} = \frac{e^2}{8m_e}|\vec{B}\times\vec{r}|^2 = \frac{e^2 B_z^2}{8m_e}(x^2+y^2)$$

IF $\vec{B} = B_z\hat{z}$

SINCE THERE IS NOTHING SPECIAL ABOUT THE $\hat{z}$-DIRECTION

$$\langle x^2+y^2\rangle = \frac{2}{3}\langle x^2+y^2+z^2\rangle = \frac{2}{3}\langle r^2\rangle$$

$$\Rightarrow E_{DIA} = \frac{e^2 B_z^2}{12m_e}\langle r^2\rangle$$

$$M = -\frac{dE}{dB} = -\frac{e^2\langle r^2\rangle B_z}{6m_e}$$

$$\rightarrow \chi = \frac{-\mu_0 M}{B} = \frac{-e^2 \mu_0 \langle r^2 \rangle}{6 m_e}$$

ASSUMING THERE IS A DENSITY, ρ, OF SUCH ATOMS, YOU GET WHAT IS KNOWN AS "LARMOR DIAMAGNETISM"

$$\chi_{LARMOR} = -\frac{\rho e^2 \mu_0 \langle r^2 \rangle}{6 m_e} = -\frac{N}{V} \frac{e^2 \mu_0}{6 m_e} \sum_{i=1}^{Z} \langle r_i \rangle^2$$

FOR N ATOMS CONTAINING Z ELECTRONS

$\chi \sim -10^{-8} \frac{m^3}{kg}$

THIS IS COMPARABLE TO PAULI PARAMAGNETISM, BUT ORDER OF MAGNITUDE WEAKER THAN RESPONSE WHEN $J \neq 0$, CONSIDERED NEXT

CURIE (OR LANGEVIN) PARAMAGNETISM

RECALL $H_{PARA} = \tilde{g} \mu_B \vec{B} \cdot \vec{J}$

$= \tilde{g} \mu_B B J_z$

NOTE THAT I SWITCHED CONVENTIONS, HERE $J = \sqrt{j(j+1)}$, WITHOUT THE $\hbar$

IF $\vec{B} = B\hat{z}$. FOR TOTAL ANGULAR MOMENTUM J, WE KNOW ALLOWED VALUES FOR $J_z = -J, -J+1, \ldots, J-1, J$. TO FIND MAGNETIZATION, WE NEED TO KNOW THE RELATIVE POPULATIONS OF EACH OF THESE STATES, WHICH IS A CLASSIC PROBLEM IN STATISTICAL MECHANICS.

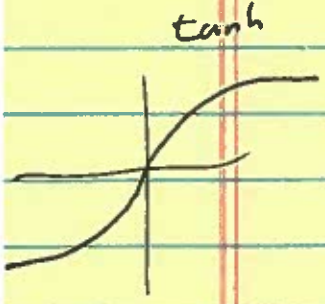
FOR THOSE UNFAMILIAR WITH SUCH CALCULATIONS, IT IS INFORMATIVE TO CONSIDER THE SIMPLEST CASE: $L=0$, $S=\frac{1}{2}$. THE PARTITION FUNCTION FOR THIS CASE IS

$$Z = e^{-\frac{\mu_B B}{k_B T}} + e^{\frac{\mu_B B}{k_B T}} \qquad \text{USING } S=\pm\tfrac{1}{2},\ g=2$$

THE AVERAGE VALUE FOR S_z IS THEN

$$\langle S_z \rangle = \frac{1}{Z} \sum_i S_i e^{-\frac{\mu_B B S_i}{k_B T}}$$

$$= \frac{-\frac{1}{2} e^{\frac{\mu_B B}{k_B T}} + \frac{1}{2} e^{-\frac{\mu_B B}{k_B T}}}{e^{\frac{\mu_B B}{k_B T}} + e^{-\frac{\mu_B B}{k_B T}}}$$

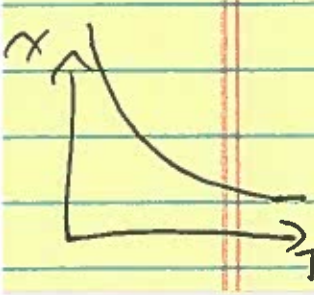


$$= -\frac{1}{2} \tanh\left(\frac{\mu_B B}{k_B T}\right)$$

$$\Rightarrow M = -g\mu_B \langle S_z \rangle = \mu_B \tanh\left(\frac{\mu_B B}{k_B T}\right)$$

TO FIND χ, WE ARE INTERESTED IN THE LOW FIELD LIMIT, $\mu_B B \ll k_B T$. WE THUS NOTE

$$\lim_{B \to 0} M(B) = \frac{\mu_B^2 B}{k_B T}$$



$$\Rightarrow \chi = \mu_0 \frac{M}{B} = \frac{n \mu_0 \mu_B^2}{k_B T}$$

FOR A DENSITY, n, OF FREE ATOMS

NOW LET'S GENERALIZE TO ANY INTEGER J

$$Z = \sum_{J_z=-J}^{J} e^{-\frac{\tilde{g}\mu_B B J_z}{k_B T}} \equiv \sum_{J_z=-J}^{J} e^{-J_z x}$$

WHERE $x = \frac{\tilde{g}\mu_B B}{k_B T}$

$$\Rightarrow Z = e^{-Jx} + e^{(-J+1)x} + e^{(-J+2)x} + \cdots + e^{Jx}$$

$$= e^{-Jx}\left(1 + e^{x} + e^{2x} + \cdots + e^{(2J+1)x}\right)$$

ARITHMETIC SERIES: $\sum_{j=1}^{n} a r^{j-1} = \frac{a(1-r^n)}{(1-r)}$

$$= e^{-Jx}\left(\frac{1 - e^{(2J+1)x}}{(1-e^{x})}\right)$$

$$= \frac{\sinh\left((2J+1)\frac{x}{2}\right)}{\sinh\left(\frac{x}{2}\right)}$$

THUS, JUST AS BEFORE

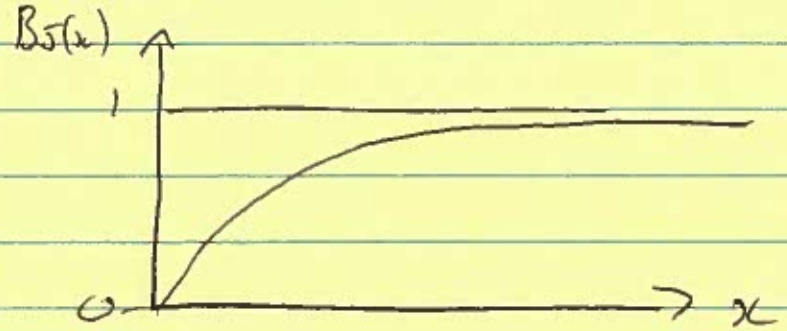
$$\langle J_z \rangle = \frac{1}{Z} \sum_{J_z=-J}^{J} J_z e^{-J_z x} = -\frac{1}{Z}\frac{\partial Z}{\partial x}$$

$$M = n\tilde{g}\mu_B \langle J_z \rangle \equiv n\tilde{g}\mu_B J B_J(x)$$

WHERE YOU CAN SHOW WITH SOME ALGEBRA

$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J}\coth\left(\frac{x}{2J}\right)$$

THIS FUNCTION IS CALLED THE "BRILLOUIN FUNCTION" AND DESCRIBES THE ENTIRE EVOLUTION OF MAGNETIZATION WITH FIELD FROM 0, TO WHERE ALL MOMENTS ARE ALIGNED



TO FIND χ, WE LOOK AT THE LOW FIELD LIMIT WHERE $M \propto B$, AND USE THE FACT THAT

$$\coth x \approx \frac{1}{x} + \frac{x}{3} \quad \text{WHEN } x \ll 1$$

IN THIS LIMIT, ONE CAN SHOW

$$\chi = \frac{\mu_0 M}{B} \approx \frac{J(J+1)\,\tilde{g}^2 \mu_B^2 \mu_0}{3 k_B T} \equiv \frac{C}{T}$$

THIS IS KNOWN AS CURIE PARAMAGNETISM, NAMED AFTER PIERRE CURIE, WHO FIRST WORKED IT OUT WITH HIS STUDENT PAUL LANGEVIN. "C" IS CALLED CURIE'S CONSTANT, AND IS SOMETIMES WRITTEN

$$C \equiv \frac{n\, p_{eff}^2\, \mu_B^2 \mu_0}{3 k_B}$$

WHERE $p_{eff} \equiv \tilde{g}[J(J+1)]^{\frac{1}{2}}$ IS CALLED THE "EFFECTIVE MOMENT"

NOTE: p_{eff} IS AN EXPERIMENTAL DEFINITION, AND SHOULD BE USED ONLY IN THE CONTEXT OF THE CURIE'S LAW

WE THUS HAVE TWO CONVIENT WAYS TO EXRACT TOTAL MOMENT μ_S FROM MEASURMENT OF MAGNETIZATION

(1) - FIELD DEPENDENCE (AND SATURATION) OF M

(2) TEMPERATURE DEPENDENCE AT LOW FIELD

THIS IS EXACTLY WHAT IS DONE IN REAL MAGNETIC MATERIALS, WHERE THE FORMULA FOR χ_{CURIE} IS MODIFIED IN SOME IMPORTANT WAYS. WE WILL DO THAT SOON, BUT FIRST IT IS WORTH ASKING: DO YOU EVER GET LOCAL MOMENTS IN A REAL MATERIAL?

THIS IS NOT A STUPID QUESTION. ACCORDING TO BAND THEORY, ELECTRON ORBITALS ARE GIVE METALLIC BEHAVIOR IF PARTIALLY FULL

$\rightarrow \chi = \chi_{PAULI}$

AND ARE ONLY INSULATORS IF ALL SHELLS ARE COMPLETELY FILLED

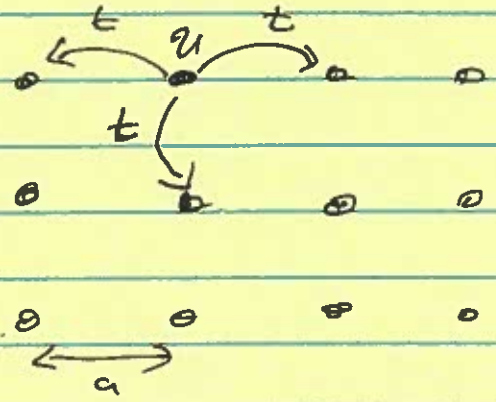
$\rightarrow \chi = \chi_{LARMOR}$

SHELLS ↔ BANDS

FROM WHENCE COME THESE INSULATORS WITH PARTIALLY FILLED BANDS?

THE ANSWER IS THAT MAGNETISM INVOLVING LOCAL MOMENTS REPRESENTS A BREAKDOWN OF BAND THEORY, AND IN FACT IS CLOSELY RELATED TO WHAT I CALLED A "MOTT INSULATOR".

THINK TIGHT BINDING MODEL. YOU HAVE A SERIES OF ORBITALS ON INDIVIDUAL ATOMS. WHEN ATOMS ARE FAR APART, THEY FORM MOMENTS μ ACCORDING TO HUND'S RULES, AS WE DISCUSSED.



HOWEVER IT IS THESE SAME ORBITALS WHICH LEAD TO BANDS IN THE TIGHT BINDING MODEL. IN PARTICULAR, WE FOUND THAT WHEN ATOMS ARE BROUGHT CLOSE TOGETHER, ELECTRONS "HOP" BETWEEN ATOMS. BANDWIDTH IS PROPORTIONAL TO THE OVERLAP ("HOPPING") INTEGRAL. BUT BAND THEORY NEGLECTS COULOMB REPULSION! SOMETIMES THE ENERGY COST OF HAVING TWO ELECTRONS ON THE SAME SITE (U) IS SO GREAT THAT $t \to 0$.

NO HOPPING → GRIDLOCK
→ IMMOBILE ELECTRONS
→ "LOCAL MOMENTS"