PHYS 460 - LECTURE 19

LAST LECTURE I BEGAN DISCUSSING MAGNETISM IN MATERIALS, MOSTLY RESTRICTING MYSELF TO DEFINITIONS AND DISCUSSIONS OF THE ORIGIN OF MAGNETIC MOMENTS. WE SAW THAT MOMENTS AROSE NATURALLY FROM NON-ZERO ANGULAR MOMENTUM OF CHARGED ELECTRONS (PLUS A NEGLIGIBLE CONTRIBUTION FROM ATOMIC NUCLEI).

IN PARTICULAR, AN ATOM WITH QUANTUM NUMBERS l, m_l, s, m_s (IN ORBIT) HAS ANGULAR MOMENTUM

$$L = \sqrt{l(l+1)}\,\hbar \qquad S = \sqrt{s(s+1)}\,\hbar$$

$$L_z = m_l \hbar \qquad S_z = m_s \hbar$$

LEADING TO MAGNETIC MOMENTS

$$\mu_L = \sqrt{l(l+1)}\,\mu_B \qquad \mu_S = \sqrt{s(s+1)}\,g\mu_B$$

NOTE NEGATIVES →

$$\mu_{L_z} = -m_l \mu_B \qquad \mu_{S_z} = -m_s g \mu_B$$

WHERE "g-FACTOR" IS ≈ 2 FOR ELECTRONS

AND $$\mu_B = \frac{e\hbar}{2m_e}$$

WHAT I DIDN'T EMPHASIZE YESTERDAY, BUT WILL BE IMPORTANT IS THE NEGATIVE SIGN IN THE Z-COMPONENT OF L_z, S_z. THIS IS DUE TO THE NEGATIVE CHARGE OF THE ELECTRON

WE ALSO CONSIDERED THE MAGNETIC SUSCEPTIBILITY OF METAL BY INCLUDING A TERM

$$\Delta E = g\mu_B \vec{B}\cdot\vec{S}$$

IN THE HAMILTONIAN AND FOUND THAT THE APPLICATION OF FIELDS INDUCED A SMALL TEMPERATURE INDEPENDENT PARAMAGNETIC MOMENT (PAULI PARAMAGNETISM)

(FIELDS ENCOURAGE SPINS TO ANTI-ALIGN, WHICH MEANS MOMENT ALIGNS → PARAMAGNETISM!)

THE -VE SIGN! →

IN GENERAL, ELECTRONS CAN BE LOCALIZED TO AN ATOM (MOST ARE) AND WE HAVE TO CONSIDER BOTH ORBITAL AND SPIN CONTRIBUTIONS. WE ALSO HAVE TO CONSIDER THE EFFECT OF ALL THE ELECTRONS, NOT JUST VALENCE ELECTRONS

LET'S START BY CONSIDERING A SINGLE ATOM IN ISOLATION

ATOM IN A MAGNETIC FIELD

CONSIDER AN ATOM WITH Z ELECTRONS, WHERE EACH OF THE ELECTRONS HAS SPIN $m_{s_i} = \pm\frac{1}{2}$. WE APPLY A FIELD $\vec{B}=B_z\hat{z}$

THUS, JUST LIKE THE PAULI CASE, THIS FORCES US TO ADD A SPIN TERM TO THE HAMILTONIAN

$$\mathcal{H}_{SPIN} = \sum_{i=1}^{Z} g\mu_B \vec{B}\cdot\vec{S}_i$$

$$= g\mu_B \vec{B}\cdot\vec{S} \quad \text{WHERE } \vec{S} = \sum_{i=1}^{Z}\vec{S}_i$$

WE ALSO NEED TO ACCOUNT FOR MODIFICATION OF ELECTRON ORBITALS, WHICH WE CAN DO THROUGH USE OF THE CANONICAL MOMENTUM

$$\vec{p} \rightarrow \vec{p} + e\vec{A}$$

WHERE $\vec{\nabla} \times \vec{A} = \vec{B}$

WE HAVE SOME FREEDOM IN CHOOSING $\vec{A}$. IT IS CONVENIENT IN THIS CASE TO PICK

$$\vec{A} = \frac{1}{2}\vec{B} \times \vec{r}$$

WHICH YOU CAN CONFIRM REDUCES TO THE CORRECT FIELD IF $\vec{B}$ = CONSTANT.

WITH THESE TWO MODIFICATIONS

$$\mathcal{H} = \sum_{i=1}^{Z} \left(\frac{[\vec{p}_i + e\vec{A}]^2}{2m_e} + V_i \right) + g\mu_B \vec{B} \cdot \vec{S}$$

WHERE V_i IS THE ELECTRIC POTENTIAL FELT BY ELECTRON i

$$= \sum_{i=1}^{Z} \left(\frac{p_i^2}{2m_e} + V_i \right) + \sum_{i=1}^{Z} \left(\frac{eA^2}{2m_e} + \frac{e}{m_e}\vec{p}_i \cdot \vec{A} \right) + g\mu_B \vec{B} \cdot \vec{S}$$

BUT THE FIRST TERM IS JUST $\mathcal{H}_0$, THE HAMILTONIAN IN ZERO FIELD.

ALSO

$$\vec{p}_i \cdot \vec{A} = \frac{1}{2}\vec{p}_i \cdot (\vec{B} \times \vec{r}) = \frac{1}{2}\vec{B} \cdot (\vec{r} \times \vec{p}_i)$$

$$= \frac{\hbar}{2}\vec{B} \cdot \vec{L}_i$$

So IF WE DEFINE TOTAL ANGULAR MOMENTUM

$$\hbar \vec{L} = \sum_{i=1}^{Z} \vec{r}_i \times \vec{p}_i$$

WE GET

$$\hat{H} = \hat{H}_0 + \mu_B \vec{B} \cdot (\vec{L} + g\vec{S}) + \frac{e^2}{8m_e} \sum_{i=1}^{Z} |\vec{B} \times \vec{r}_i|^2$$

PARAMAGNETIC TERM — DIAMAGNETIC TERM

THE HAMILTONIAN HAS TWO TERMS AS A RESULT OF $\vec{B} \neq 0$

THE FIRST IS THE EXACT SAME TERM WE SAW LED TO PAULI PARAMAGNETISM, AND REFLECTS THE ALIGNMENT OF THE TOTAL ANGULAR MOMENTUM PARALLEL TO FIELD. IT IS KNOWN AS THE "PARAMAGNETIC TERM" AND IS CLOSELY RELATED TO THE ZEEMAN EFFECT IN ATOMIC PHYSICS.

THE LAST TERM IS ALWAYS POSITIVE, AND WE WILL SEE IT IS RESPONSIBLE FOR DIAMAGNETIC EFFECTS → "DIAMAGNETIC TERM"

NOTE: (1) EVERY ATOM HAS A DIAMAGNETIC TERM

(2) ONLY ATOMS WITH NON-ZERO $\vec{L}$ OR $\vec{S}$ HAVE A PARAMAGNETIC TERM

(3) SINCE THE SECOND TERM IS LINEAR AND LAST TERM IS SQUARED, PARAMAGNETISM ALMOST ALWAYS DOMINATES WHEN PRESENT

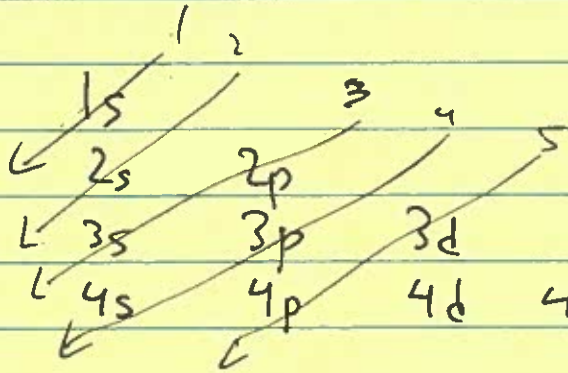
DETERMINING $\vec{L}$ & $\vec{S}$ FOR AN ATOM

ACCORDING TO THE DERIVED HAMILTONIAN, TO KNOW THE STATE OF ATOM IN A FIELD, WE NEED TO FIND $\vec{L}$ & $\vec{S}$ (WHICH IS EQUIVALENT TO SAYING WE NEED TO KNOW m_{li}, m_{si} $\forall i$, MAKING THIS A TRIVIAL STATEMENT)

FOR MOST MAGNETIC MATERIALS OF INTEREST, THERE ARE >20 ELECTRONS, ALL BOUND BY PAULI EXCLUSION PRINCIPLE AND OTHER RULES OF QUANTUM MECHANICS. OPERATING UNDER THE ASSUMPTION THAT ELECTRONS SUCCESSIVELY OCCUPY HYDROGEN-LIKE ORBITALS WITH QUANTUM NUMBERS $|n, l, m_l, s=\frac{1}{2}, m_s\rangle$ (WHICH IS HOW WE EXPLAIN THE PERIODIC TABLE), WE NEED GUIDING PRINCIPLES TO SAY WHAT GOES WHERE.

WE PARTIALLY ADDRESSED THIS IN LECTURE 3, WHEN I PRESENTED MADELUNG'S RULE (ORBITALS ARE OCCUPIED IN A WAY THAT MINIMIZES $n+l$)

OCCUPY ORBITALS AS FOLLOWS



WHAT WE DIDN'T DISCUSS WAS m_l & m_s, WHICH ARE DEGENERATE IN THE HYDROGEN PICTURE!

TO FIND WHICH l_z AND S_z STATES ARE OCCUPIED FOR A PARTIALLY FILLED BAND (ONLY SOME OF AVAILABLE l_z, S_z STATES OCCUPIED FOR GIVEN l), A USEFUL SET OF PRINCIPLES IS HUND'S RULES, FIRST WRITTEN DOWN BY FRIEDRICH HUND IN 1925, IN ORDER OF DECREASING IMPORTANCE:

RULE ①: ELECTRONS IN A GIVEN ATOM WILL ALWAYS TRY TO MAXIMIZE S.

→ YOU SHOULD FILL ALL $S_z = \frac{1}{2}$ ORBITALS BEFORE FILLING ANY $S_z = -\frac{1}{2}$ ORBITALS

THIS, WE WILL SEE, SIMPLY REFLECTS THE FACT THAT ELECTRONS IN THE SAME SPIN STATE ARE LESS LIKELY TO BE IN THE SAME PLACE

RULE ②: ELECTRONS WILL ALSO TRY TO MAXIMIZE L, CONSISTENT WITH RULE ①

→ START WITH HIGHEST (OR LOWEST) l_z AND FILL IN ORDER

AGAIN, RELEVANT ENERGY IS COULOMB ENERGY, AS ELECTRONS OVERLAP LESS WHEN ORBITING NUCLEI IN SAME DIRECTION

RULE (3): GIVEN RULES (1) & (2), L & S EITHER ALIGN OR ANTI-ALIGN. TOTAL ANGULAR MOMENTUM $J = |L - S|$ IF SHELL IS LESS THAN HALF FULL, AND $J = |L+S|$ IF MORE THAN HALF FULL

- RESULT OF RELATIVISTIC SPIN ORBIT COUPLING $\mathcal{H}_{S\text{-}O} = \lambda \vec{S}\cdot\vec{L}$ AND IS MORE IMPORTANT FOR HEAVIER ATOMS

EXAMPLE 1 (FROM SIMON): Pr $[Xe]\,4f^3 6s^2$ (59 e^-)

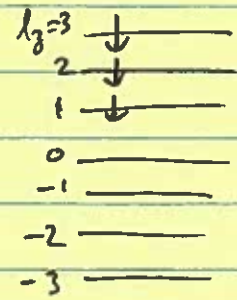
WHERE $[Xe] \equiv 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 4p^6$

$f \rightarrow l = 3$

RULE (1) → ALL S PARALLEL

RULE (2) → HIGHEST l_z STATES

RULE (3) → OPPOSITE DIR



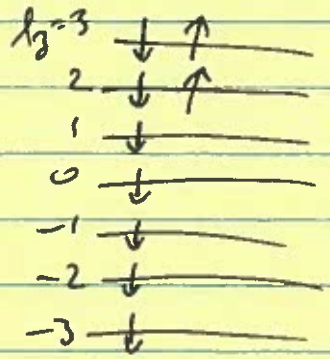
$S = 3 \cdot \frac{1}{2} = \frac{3}{2}$

$L = 1+2+3 = 6$

$J = 6 - \frac{3}{2} = \frac{9}{2}$

EXAMPLE 2: Dy^{3+} $[Xe]\,4f^9$

AGAIN $l = 3$



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

$L = 3+2 = 5$

$J = 5 + \frac{5}{2} = \frac{15}{2}$

NOTE THAT ELECTRONS WILL CONTINUE TO WORK TOGETHER AND ATOM ACTS AS $J = \frac{9}{2}$ OR $\frac{15}{2}$ MOMENT

EXCHANGE INTERACTIONS

HOW DO WE UNDERSTAND THE ORIGIN OF HUND'S RULES. IN PARTICULAR, WHY DO MOMENTS ASSOCIATED WITH ELECTRONS ON THE SAME ATOM TEND TO ALIGN?

FIRST, WE SHOULD NOTE THE MAGNETIC DIPOLE FORCES HAVE NOTHING TO DO WITH IT. THE ENERGY SCALE IS SIMPLY TOO SMALL TO HAVE MUCH EFFECT

$$\mathcal{U} = -\vec{M}\cdot\vec{B}$$

$$\vec{B} = \frac{\mu_0}{4\pi}\left(\frac{3\vec{r}(\vec{m}\cdot\vec{r})}{r^5} - \frac{\vec{m}}{r^3}\right)$$

$$\rightarrow \mathcal{U} \sim \frac{\mu_0}{4\pi}\frac{\mu_B^2}{r^3} = \frac{\left(1.257\times10^{-6}\,\frac{kg\,m}{s^2A^2}\right)\left(9.274\times10^{-24}\,Am^2\right)^2}{4\pi\left(1\times10^{-10}\,m\right)^3}$$

$$\sim 5\times10^{-5}\ eV$$

$$\sim k_B\,(0.6\ K)$$

THE ALIGNMENT IS THE RESULT PRIMARILY COMES FROM COULOMB ENERGY AND PAULI EXCLUSION

CONSIDER THE GENERAL, TWO PARTICLE WAVEFUNCTION

$$\underline{\mathcal{F}}(\vec{r}_1, s_1; \vec{r}_2, s_2) = \underset{\text{orbital}}{\mathcal{H}}(\vec{r}_1, \vec{r}_2)\,\underset{\text{spin}}{\chi}(s_1, s_2)$$

WHERE $\psi_{ORBITAL}(\vec{r}_1, \vec{r}_2)$ IS WHAT WE HAVE BEEN DISCUSSING SO FAR AND DESCRIBES THE LOCATION OF CHARGE DENSITY, AND $\chi_{SPIN}(S_1, S_2)$ DESCRIBES THE VARIATION OF SPINS IN SPACE

ONE WAY OF STATING THE PAULI EXCLUSION PRINCIPLE IS TO SAY THAT THE TOTAL WAVEFUNCTION HAS TO BE ANTISYMMETRIC

i.e IF $\psi(\vec{r}_1, \vec{r}_2)$ IS ANTISYMMETRIC $\left(\psi(\vec{r}_2, \vec{r}_1) = -\psi(\vec{r}_1, \vec{r}_2)\right)$ THEN THE $\chi(S_1, S_2)$ MUST BE SYMMETRIC, AND VICE VERSA

THUS, A SITUATION WHERE $S_1 = S_2$ EVERYWHERE $(\uparrow\uparrow)$, WHICH IS SYMMETRIC, MUST BE ASSOCIATED WITH AN ANTISYMMETRIC ORBITAL PART

THE CONDITION $\psi(\vec{r}_2, \vec{r}_1) = -\psi(\vec{r}_1, \vec{r}_2)$ REQUIRES $\psi(\vec{r}_1, \vec{r}_2) \to 0$ AS $\vec{r}_1 \to \vec{r}_2$.

i.e THE TWO ELECTRONS ARE NOT IN THE SAME PLACE

$\longrightarrow$ COULOMB ENERGY SAVINGS!

LET'S DO THE CALCULATION (SEE PG 213 OF SIMON)

NOTE SIMILARITY TO HYDROGEN ATOM PROBLEM

CONSIDER TWO ELECTRONS WITH ORBITAL WAVEFUNCTIONS $A(\vec{r})$ AND $B(\vec{r})$. WE WANT TO COMBINE THEM IN AN ANTISYMMETRIC WAY. IF SPINS ARE ALIGNED

$|\uparrow\uparrow\rangle$ OR $|\downarrow\downarrow\rangle$ OR $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$

THIS IS A SPIN TRIPLET, AND THE ORBITAL PART MUST BE $\frac{1}{\sqrt{2}}(|AB\rangle - |BA\rangle)$

THERE IS ONLY ONE WAY TO COMBINE SPINS IN AN ANTISYMMETRIC WAY

$$\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

THIS IS A SPIN SINGLET AND MUST HAVE ORBITAL PART $\frac{1}{\sqrt{2}}(|AB\rangle + |BA\rangle)$

THE INTERACTION BETWEEN THE ELECTRONS IS A SIMPLE COULOMB INTERACTION, $V(\vec{r}_1, \vec{r}_2)$

$$E_{\text{spin triplet}} = \frac{1}{2}(\langle AB| - \langle BA|)V(|AB\rangle - |BA\rangle)$$

$$E_{\text{spin singlet}} = \frac{1}{2}(\langle AB| + \langle BA|)V(|AB\rangle + |BA\rangle)$$

$$\Rightarrow \quad \Delta E = E_s - E_t = \frac{1}{2}(-\langle BA|V|AB\rangle - \langle AB|V|BA\rangle - \langle BA|V|AB\rangle - \langle AB|V|BA\rangle)$$

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

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

SO THE ENERGY DIFFERENCE BETWEEN ALIGNED AND ANTI-ALIGNED SPINS IS THE ENERGY TO SWITCH THE ATOM POSITIONS

→ "EXCHANGE ENERGY"

NOTE THAT THE SPIN TRIPLET IS ALWAYS LOWER ENERGY HERE, BUT WHEN WE CONSIDERED SPATIALLY SEPARATED ATOMS IN THE TIGHT BINDING MODEL, WE FOUND THE OPPOSITE

→ IN GENERAL, EITHER IS POSSIBLE. THE NAME STICKS

BUT FOR (SINGLE ATOM) HUND'S RULE WINS.