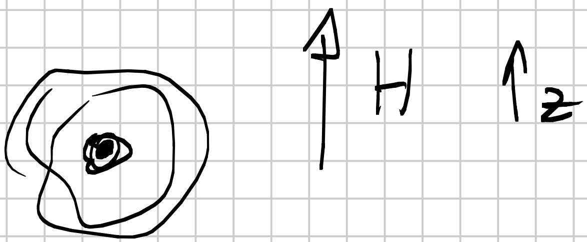
LECTURE #6

Note Title 9/19/2007

Last time: Magnetic properties atoms / ions in solids

Ashcroft-Mermin Ch 31 (644-659)

Atom n electrons



$o(H)$ $\quad$ $o(H^2)$ $\quad$ All e^- in atom

$$\mathcal{H} = \mathcal{H}^0 + \mu_B\left(\vec{L} + g\vec{S}\right)\cdot\vec{H} + \frac{m}{2}\left(\frac{eH}{mc}\right)^2 \sum_i \left(\frac{x_i}{2}\right)^2 + \left(\frac{y_i}{2}\right)^2$$

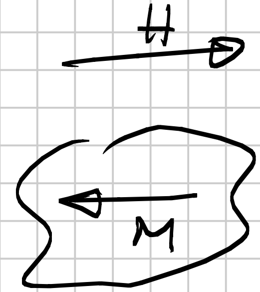
CASE #1 $\quad$ Filled shell $\Rightarrow \vec{L} = 0 \quad \vec{S} = 0$

Only $o(H^2)$ term is present

$$E_0 = \langle 0 | \mathcal{H} | 0 \rangle$$

$$M = -\frac{N}{V}\frac{\partial E_0}{\partial H} \qquad \chi = -\frac{N}{V}\frac{\partial^2 E_0}{\partial H^2}$$

$\chi < 0$ [Larmor Diamagnetism]



$$\chi^{MOLAR} = -N_A \frac{\partial^2 E_0}{\partial H^2} \qquad N_A = 6 \cdot 10^{23} \text{ atoms}$$

Case 2 Partially filled shell $L \neq 0$, $S \neq 0$

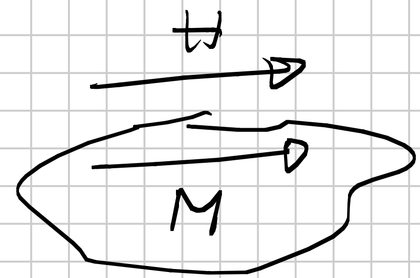
$$Mn^{2+} \Rightarrow S = \frac{5}{2} \quad L = 0$$

$$\langle G | \mu_B g \vec{S} | G \rangle \cdot \vec{H} \qquad |G\rangle = |S_z = -\frac{5}{2}\rangle$$

$$\Delta \mathcal{H}^{linear} = -\overbrace{\frac{5}{2} g \mu_B}^{\mu} H \qquad -\vec{\mu}\,\vec{H}$$

μ = MAGNETIC MOMENT OF Mn^{2+} $\quad 5\mu_B$

$$M = \frac{N}{V} 5\mu_B \longrightarrow$$



Langevin Paramagnetism

$+5/2$

$3/2$

$1/2$

$-1/2 \qquad -\mu_B H \rightarrow E_2$

$-3/2 \qquad -3\mu_B H \rightarrow E_1$

$2\mu_B H \qquad -\frac{5}{2} \qquad -5\mu_B H \rightarrow E_0$

$E_0 \longrightarrow$

Finite T

$$\frac{\sum_m E_m e^{-\beta E_m}}{\sum_m e^{-\beta E_m}} = F(T,H) \qquad \beta = \frac{1}{k_B T}$$

$$M = -\frac{N}{V}\frac{\partial F(T,H)}{\partial H} \Rightarrow \chi = -\frac{N}{V}\frac{\partial^2 F}{\partial H^2}$$

Interesting limit $k_B T \gg E_1 - E_0 = 2\mu_B H$

$$\chi = \frac{(g\mu_B)^2}{3} \frac{\overset{\frac{5}{2}\left(\frac{5}{2}+1\right) =}{S(S+1)}}{k_B T}$$

Curie's law of solids

$\vec{L} \neq 0$ & $\vec{S} \neq 0$

LANDÉ COEFFICIENT

Show that $\vec{L} + g\vec{S} = g^L \vec{J}$

Then REPACE $\begin{cases} S \to J \\ g \to g^L \end{cases}$

(3) case

Carbon

$l_z=+1$	$l_z=0$	
$\uparrow$	$\uparrow$	

$$L = 1$$
$$S = 1$$

half-filling minus one electron

$$J = |L - S| = 0$$

$$J = 0 \quad \Rightarrow \quad \vec{L} + g\vec{S} \propto \vec{J}$$

$$\vec{L} + g\vec{S} = 0$$

$\boxed{\text{No Langevin paramagnetism}}$

$$\langle G | \vec{L} + g\vec{S} | G \rangle = 0$$

Use second order perturbation

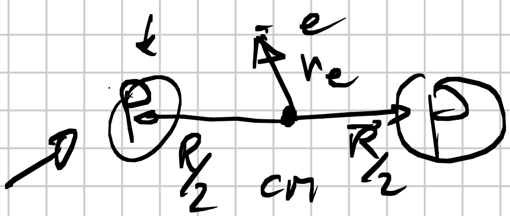
theory

$$\sum_{n} \frac{|\langle G|(\vec{L} + g\vec{S})\cdot \vec{H}|n\rangle|^2}{E_G - E_n} < 0$$

$\Rightarrow$ Paramagnetic effect

Van Vleck Paramagnetism

MOLECULES



H_2^+ molecule

Still get rid of center of mass motion

We are left with 2 coordinates

$\vec{r}_e$ position electron

$\vec{R}$ relative position of 2 protons

$\vec{R} = \vec{r}_{p_1} - \vec{r}_{p_2}$

2 Body problem

$\psi(\vec{r}_e, \vec{R})$

$$\left(-\underset{\substack{\downarrow \\ \text{proton reduced mass}}}{\frac{\hbar^2}{2\mu_p}} \vec{\nabla}_R^2 - \frac{\hbar^2}{2m} \vec{\nabla}_r + \underbrace{\frac{e^2}{|\vec{R}|}}_{V_{pp}} \underbrace{- \frac{e^2}{\left|\vec{r}_e + \frac{\vec{R}}{2}\right|} - \frac{e^2}{\left|\vec{r}_e - \frac{\vec{R}}{2}\right|}}_{V_{pe}} \right) \psi(r_e, R)$$

$$= E\,\psi(r_e, R)$$

$\boxed{\mu_p \gg m_e}$ $\Rightarrow$ BORN-OPPENHEIMER APPROXIMATION

$$\psi(r_e, R) = \psi_p(\vec{R})\, \psi_e^R(\vec{r}_e)$$

Depends on R in a parametric way

(1) Fix the positions of the protons

$\Rightarrow$ Protons have no kinetic energy

$$\left(-\frac{\hbar^2}{2m_e}\vec{\nabla}_e^2 + V_{pp}(R) + V_{pe}(R)\right)\psi_e^R(r_e)\,\cancel{\psi_p(R)} = E(R)\,\psi_e^R(r)\,\cancel{\psi_p(R)}$$

$\downarrow$ single electron problem

$$\psi_n^R(r) \qquad E_n(R)$$

$$\frac{d^2}{dx^2} f g \qquad f g'' \quad g' f' \quad g f''$$

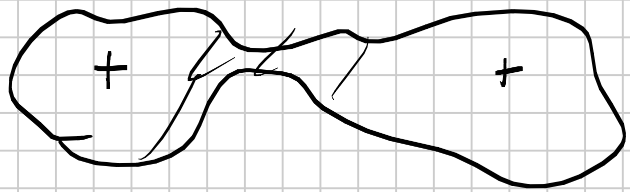
What about protons?

$$\vec{\nabla}_R^2\, \psi_e^R(\vec{r}_e)\, \psi_p(\vec{R})$$

$\rightarrow$ $\boxed{\psi_e^R\, \vec{\nabla}_R^2\, \psi_p(R)}$ Keep this

$\rightarrow$ $\boxed{\vec{\nabla}_R \psi^R(r_e)} \cdot \vec{\nabla}_R \psi_p(R)$ $\leftarrow$ small

$\rightarrow$ $\psi_p(R)\, \boxed{\vec{\nabla}_R^2\, \psi_e^R(\vec{r}_e)}$ $\leftarrow$ small



$\nabla_R \, \psi_e^R$

$\psi_p(R)$ very localized  $\Rightarrow \vec{\nabla}_R \, \psi_p(\vec{R})$ $\boxed{\text{big}}$

$\psi_e^R(r)$ delocalized, weak dependence on R

$\Rightarrow \nabla_R \, \psi_e^R(r_e)$ $\boxed{\text{small}}$

$$-\frac{\hbar^2}{2\mu_p}\cancel{\psi_e^R(r)}\,\vec{\nabla}_R^2\,\psi_p(\vec{R}) \quad + \quad E_n(R)\,\cancel{\psi_n^R(r_e)}$$

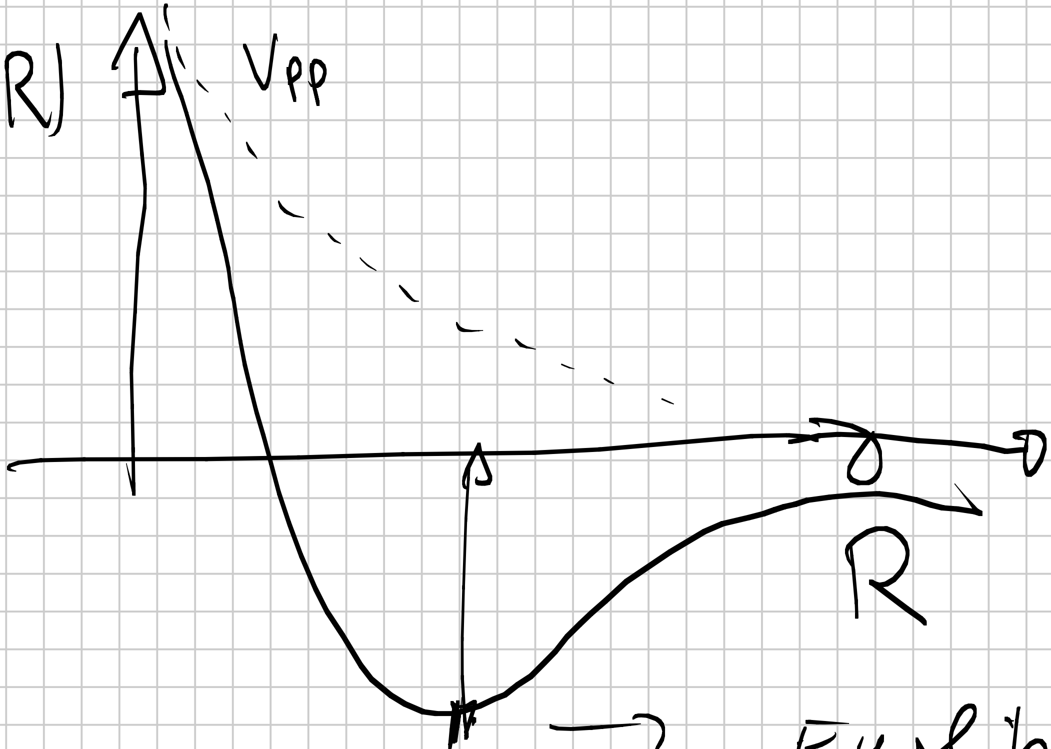
$$\boxed{\left[-\frac{\hbar^2}{2m_e}\vec{\nabla}_r^2 + V_{pp}(R) + V_{pe}(R)\right]\psi_e^R(r_e)}\;\psi_p(R) = E\,\cancel{\psi_e^R(r_e)}\,\psi_p(\vec{R})$$

Equation for the protons

Pick up Ground state for the electron problem $E_0(R)$

$$\left(-\frac{\hbar^2}{2\mu_p} \vec{\nabla}_R^2 + \underbrace{E_0(R)} \right) \psi_p(R) = E\, \psi_p(R)$$

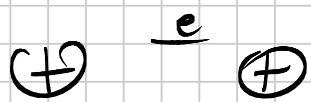
Effective potential for the 2 protons coming from the electron



Equilibrium position for 2 protons

$\boxed{\text{Covalent bonding}}$

More stable



then