Solution #8

2. $\vec{\mu}_2 \parallel \hat{x}$ Energy of a dipole of magnetic moment $\vec{\mu}_2$ when placed in the field created by another dipole $\vec{\mu}_1$.

(a) $\vec{\mu}_1 \parallel \hat{x}$

$\vec{r} = a(\pm 1, \pm 1, \pm 1)$ all in the equivalent
$|\vec{r}| = \sqrt{3}\, a$ (111) directions.

(1,1,1) (-1,-1,-1)
(-1,1,1) (1,-1,-1)
(1,-1,1) (-1,1,-1)
(1,1,-1) (-1,-1,1)

$$E_1 = -\vec{\mu}_2 \cdot \frac{3(\vec{\mu}_1 \cdot \vec{r})\vec{r} - r^2 \vec{\mu}_1}{r^5}$$

$$E_{tot} = -\vec{\mu}_2 \cdot \frac{\mu_1}{r^5}\left[3\left(\sum_i \hat{x}\cdot\vec{r}_i\right)\vec{r}_i - 8r^2\hat{x}\right]$$

$$E_{tot} = -\vec{\mu}_2 \cdot \frac{a^2\mu_1}{r^5}\Big\{3\big[(1,1,1)+(1,-1,1)+(1,1,-1)+(1,-1,-1)-(-1,1,1)-(-1,-1,-1)-(-1,1,-1)-(-1,-1,1)\big]$$
$$-8\times 3(1,0,0)\Big\}$$

$$E_{tot} = -\vec{\mu}_2 \cdot \frac{a^2\mu_1}{r^5}\left[(24,0,0)-(24,0,0)\right]$$

$$E_{tot} = 0$$

b) $\vec{\mu}_1 \parallel \hat{y}$

$$E_{tot} = -\vec{\mu}_2 \cdot \frac{\mu_1}{r^5}\left[3\left(\sum_i \hat{y}\cdot\vec{r}_i\right)\vec{r}_i - 8r^2\hat{y}\right]$$

$$E_{tot} = -\vec{\mu}_2 \cdot \frac{a^2\mu_1}{r^5}\Big\{3\big[(1,1,1)+(-1,1,1)+(1,1,-1)+(-1,1,-1)-(1,-1,1)-(-1,-1,-1)-(1,-1,-1)-(-1,-1,+1)\big]$$
$$-8\times 3(0,1,0)\Big\}$$

$$E_{tot} = 0$$

c) $\vec{\mu}_1 \parallel \hat{z}$

$E_{tot} = 0$ similar to $\hat{x}$ & $\hat{y}$.

d) μ_1 radial inwards

$\vec{r}_1 = (1,1,1)$ $\quad \vec{\mu}_1 = \mu_1(-1,-1,-1)\frac{1}{\sqrt{3}}$ $\quad \vec{r}_5 = (-1,-1,-1)$ $\quad \vec{\mu}_1 = \mu_1(1,1,1)\frac{1}{\sqrt{3}}$

$\vec{r}_2 = (-1,1,1)$ $\quad \vec{\mu}_1 = \mu_1(1,-1,-1)\frac{1}{\sqrt{3}}$ $\quad \vec{r}_6 = (1,-1,-1)$ $\quad \vec{\mu}_1 = \mu_1(-1,1,1)\frac{1}{\sqrt{3}}$

$\vec{r}_3 = (1,+1,-1)$ $\quad \vec{\mu}_1 = \mu_1(-1,-1,+1)\frac{1}{\sqrt{3}}$ $\quad \vec{r}_7 = (-1,-1,1)$ $\quad \vec{\mu}_1 = \mu_1(1,1,-1)\frac{1}{\sqrt{3}}$

$\vec{r}_4 = (-1,+1,-1)$ $\quad \vec{\mu}_1 = \mu_1(1,-1,1)\frac{1}{\sqrt{3}}$ $\quad \vec{r}_8 = (1,-1,1)$ $\quad \vec{\mu}_1 = \mu_1(-1,1,-1)\frac{1}{\sqrt{3}}$

$$E_{tot} = -\vec{\mu}_2 \cdot \frac{a^2\mu_1}{\sqrt{3}\,r^5}\Big\{3(-3)\big[(1,1,1)+(-1,1,1)+(1,1,-1)+(-1,1,-1)+(-1,-1,-1)+(1,-1,-1)+(1,-1,1)+(-1,-1,1)\big]$$

$$-3\big[(1,1,1)+(-1,1,1)+(1,1,-1)+(-1,1,-1)+(-1,-1,-1)+(1,-1,-1)+(1,-1,1)+(-1,-1,1)\big]$$

$E_{tot} = 0$

e) All of them are low energy configurations.

2.

a) The bound state diamagnetism comes from the term proportional to B^2 in the perturbation H' where

$$\mathcal{H}' = \mu_0(\vec{L}+2\vec{S})\cdot\vec{B} + \frac{e^2B^2}{8mc^2}\sum_i (x_i^2+y_i^2) \qquad (\vec{B}=B\hat{z}).$$

Ground state, so use wave function

$$\psi_{100}(r,\theta,\varphi) = \frac{2}{a_0^{3/2}} e^{-r/a_0}\, Y_0^0(\theta,\varphi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

$$\Delta E_{dia} = \frac{e^2B^2}{8mc^2}\langle 0|\sum_i (x_i^2+y_i^2)|0\rangle = \frac{e^2B^2}{8mc^2}\langle 0|x^2+y^2|0\rangle \qquad i=1 \text{ for H atom}$$

$$\langle x^2+y^2\rangle_0 = \frac{2}{3}\langle r^2\rangle_0 =$$

$$= \frac{2}{3}\int \psi^* r^2 \psi \, r^2 \sin\theta \, dr\, d\theta\, d\varphi$$

$$= \frac{2}{3}\cdot\frac{4\pi}{\pi a_0^3}\int_0^\infty r^4 e^{-2r/a_0}\, dr$$

$$= \frac{8}{3a_0^3}\cdot\frac{3a_0^5}{4} = 2a_0^2$$

$$\Delta E_{dia} = \frac{e^2B^2}{8mc^2}\, 2a_0^2 = \frac{e^2B^2a_0^2}{4mc^2}$$

$$\mu_{dia} = -\frac{\partial E}{\partial B} = \frac{-e^2a_0^2B}{2mc^2}$$

$M_{dia} = N\mu_{dia}$ where N is the density

$$\chi_{dia} = \left.\frac{\partial M}{\partial B}\right)_{dia} = -\frac{Ne^2 a_0^2}{2mc^2}$$

Assuming ideal gas : $\frac{N}{V} = \frac{P}{kT} = \frac{1.013\times10^5\ N/m^2}{\frac{1}{40}\times1.6\times10^{-19}\ J} = 2.53\times10^{19}/cm^3$

$$\chi_{dia} = -9.99\times10^{-11}$$

b) For the 2s state, the wavefunction $\psi_{200}(r,\theta,\varphi) = \frac{2}{(2a_0)^{3/2}}(1-r/2a_0)e^{-r/2a_0}\cdot\frac{1}{2\sqrt{\pi}}$

$$\langle x^2+y^2\rangle_{2s} = \frac{2}{3}\langle r^2\rangle = \frac{2}{3}\int \psi_{200}^* r^2 \psi_{200}\, r^2\sin\theta\, dr\, d\theta\, d\varphi$$

$$= \frac{2}{3}\cdot\frac{1}{2a_0^3}\int_0^\infty r^4\left(1-\frac{r}{2a_0}\right)^2 e^{-r/a_0}\,dr$$

$$= 28a_0^2$$

Since $\chi_{dia} \propto \langle r^2\rangle$

$$\frac{\chi_{dia}(2s)}{\chi_{dia}(1s)} = \frac{28a_0^2}{2a_0^2} = 14$$

c) Ground state (1s) so $l=0$, $s=1/2$, $j=1/2$ i.e. $g=2$

$$\langle E\rangle_{para} = -g\mu_0 Bj\,\frac{\sum_{m_j}(m_j/j)\,e^{-m_j x/j}}{\sum_{m_j} e^{-m_j x/j}} \qquad x = g\mu_0 Bj/k_BT$$

$j = 1/2$

$m_j = \pm 1/2$

$$\langle E\rangle_{para} = -\mu_B B \frac{e^{x} - e^{-x}}{e^{-x} + e^{x}} \qquad x = \frac{\mu_B B}{k_B T}$$

$$= -\mu_B B \tanh x$$

For small B (hence small x) $\tanh x \approx x$

$$\langle E\rangle_{para} = -\frac{\mu_B^2 B^2}{k_B T} \qquad \mu_B = 9.27 \times 10^{-21} \frac{erg}{G}$$

$$M_{para} = -N \frac{\langle E\rangle_{para}}{B} = +\frac{N\mu_B^2 B}{k_B T}$$

$$\chi_{para} = \frac{N\mu_B^2}{k_B T} = 5.23 \times 10^{-8}$$

d) The binding energy of hydrogen at room temperature is ~ 4.5 eV.

Using Boltzmann factor: $P = e^{-\frac{E_B}{k_B T}} = e^{-\frac{4.5}{1/40}} \approx 10^{-79}$

We can safely say that the probability of H_2 to dissociate into 2 H atoms at room temperature is zero.

e) At room temperature Molecular hydrogen is diamagnetic. The molecular orbital has the two electrons paired in the bonding orbital. No unpaired spin results in no paramagnetism.

f) At room temperature ^4He is in the ground state due to a high energy barrier (~ 10 eV) to create first excited state. There are no unpaired spins so χ_{para} is zero.

^3He has no unpaired electrons and therefore no χ_{para} due to electrons. The magnetic moment of a nucleon is 1000 times smaller than for an electron so essentially $\chi_{para} \approx 0$.

3. neodymium ion

Nd^{3+} ion electronic configuration $4f^3$

i) S maximised

$m_\ell \rightarrow$ 3	2	1	0	-1	-2	-3
↑	↑	↑				

$f \rightarrow \ell = 3$

3 electrons $s = \frac{3}{2}$ $\quad 2s+1 = 4$

ii) L maximised highest ℓ value we can make is to take

$m_{\ell_1 max} = 3$, $m_{\ell_2 max} = 2$, $m_{\ell_3 max} = 1$

$m_{\ell_{total, max}} = 6$

$\therefore$ $L = 6 \Rightarrow I$ multiplicity

iii) less than half-full $\therefore$ $j = \ell - s = 6 - \frac{3}{2} = \frac{9}{2}$

configuration ${}^4I_{9/2}$ $\quad {}^{(2S+1)}L_J$

b) The ground state is $2j+1 = 10$ - fold degenerate,

$m_j = \frac{-9}{2}, \frac{-7}{2}, \ldots, \frac{7}{2}, \frac{9}{2}$

In low field, these states split according to the perturbation

$\langle L, S, J, M_j | J_z | L, S, J, M_J \rangle = M_j \hbar$

Zeeman pattern $\Rightarrow$ 10 states separated by $\mu_B g B \hbar$

$$g = \frac{\frac{3}{2} j(j+1) + \frac{1}{2} s(s+1) - \frac{1}{2} \ell(\ell+1)}{j(j+1)} = \frac{3}{2} + \frac{1}{2} \frac{\frac{3}{2} \cdot \frac{5}{2} - 6 \times 7}{\frac{9}{2} \times \frac{11}{2}}$$

$g = \frac{48}{66} = \frac{8}{11}$

The first excited state is found by relaxing Hund's third ru[le]
That is, $j = 9/2$ corresponds to the most energetically favourab[le]
state (ground state) but the quantum number j can take
values in the range

$|L-S| < J < |L+S|$ by unit steps.

The next most energetically favourable state is $j = 7/2$
and a weak magnetic field will produce a splitting of these
8 m_j states by $\mu_B g B_{th}$, with $g = \frac{2}{7}$

c) For the case of Nd^{2+} ion in the ground state

Nd^{2+} $(4f^4)$

$S = 2$, $L = 6$, $J = L - S = 4$ $\qquad ({}^{2}I_{4})$

The ground state is 9-fold degenerate.

Zeeman pattern $\Rightarrow$ 9 states separated by $\mu_B g B_{th}$

with $g = \frac{3}{5}$.