Chapter 13

The magnetic properties of molecules

Exercises

13.1 $\mathcal{B} = \mu_0 \mathcal{H}$ [eqn 13.1a]

In terms of magnitudes: (Note: 1 T = 1 V s m^{-2} and 1 J = 1 V A s = 1 N m)

$$\mathcal{B} = \mu_0 \mathcal{H}$$

$$\mathcal{H} = \mathcal{B}/\mu_0 = 1.0\ \text{T}/(4\pi \times 10^{-7}\ \text{N A}^{-2}) = \underline{8.0 \times 10^5\ \text{A m}^{-1}}$$

13.2 **(a)** $\mathcal{M} = \chi\mathcal{H}$ [eqn 13.3b]

$$\mathcal{M} = \chi\mathcal{H} = (-9.02 \times 10^{-6}) \times (80 \times 10^3\ \text{A m}^{-1}) = \underline{-0.72\ \text{A m}^{-1}}$$

(b) $\mathcal{M} = \frac{1}{\mu_0}\left(\frac{\chi}{1+\chi}\right)\mathcal{B}$ [eqn 13.3c]

$$\mathcal{B} = (1 + \chi)\mu_0 \mathcal{M}/\chi$$

$$= (1 - 9.02 \times 10^{-6}) \times (4\pi \times 10^{-7}\ \text{N A}^{-2}) \times (-0.72\ \text{A m}^{-1}) / (-9.02 \times 10^{-6})$$

$$= \underline{0.10\ \text{T}}$$

13.3 Follow the first *brief illustration* of Section 13.2. For a mass density of 5.0 g cm^{-3} and a molar mass of 210 g mol^{-1}, the number density is

$$\mathcal{N} = \frac{\rho N_\text{A}}{M} = \frac{5.0\times10^6\ \text{g m}^{-3}}{210\ \text{g mol}^{-1}} \times \left(6.022 \times 10^{23}\ \text{mol}^{-1}\right) = 1.43 \times 10^{28}\ \text{m}^{-3}$$

The magnetic susceptibility at 293 K due to complexes with $S = 1$

(so $m_0 = 2\mu_B\{S(S+1)\}^{1/2} = 8^{1/2}\mu_B$) is

$$\chi = \frac{(4\pi \times 10^{-7}\ \mathrm{T^2\ J^{-1}\ m^3}) \times 8 \times (9.274 \times 10^{-24}\ \mathrm{J\ T^{-1}})^2 \times (1.43 \times 10^{28}\ \mathrm{m^{-3}})}{3 \times (1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}) \times (293\ \mathrm{K})}$$

$$= \underline{1.0 \times 10^{-3}}$$

Note that the final answer is consistent with the assumption that $\chi \ll 1$ (as required in the derivation of eqn 13.7); all the units cancel.

13.4 The molar magnetic susceptibility is given by eqn 13.10.

$$\chi_m = \frac{\mu_0 m_0^2 N_A}{3kT}$$

$$= \frac{(4\pi \times 10^{-7}\ \mathrm{T^2\ J^{-1}\ m^3}) \times 8 \times (9.274 \times 10^{-24}\ \mathrm{J\ T^{-1}})^2 \times (6.022 \times 10^{23}\ \mathrm{mol^{-1}})}{3 \times (1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}) \times (293\ \mathrm{K})}$$

$$= \underline{4.3 \times 10^{-8}\ \mathrm{m^3\ mol^{-1}}}$$

13.5 The Curie constant C is given by eqn 13.11:

$$C = \frac{\mu_0 m_0^2 N_A}{3k}$$

$$= \frac{(4\pi \times 10^{-7}\ \mathrm{T^2\ J^{-1}\ m^3}) \times 8 \times (9.274 \times 10^{-24}\ \mathrm{J\ T^{-1}})^2 \times (6.022 \times 10^{23}\ \mathrm{mol^{-1}})}{3 \times (1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}})}$$

$$= \underline{1.3 \times 10^{-5}\ \mathrm{m^3\ K\ mol^{-1}}}$$

13.6 $\chi_m = C/T$ [eqn 13.11]. For hydrogen atoms at 298 K, $C = 4.7 \times 10^{-6}\ \mathrm{m^3\ K\ mol^{-1}}$, and $T/K = 298$; then $\chi_m = \underline{1.6 \times 10^{-8}\ \mathrm{m^3\ mol^{-1}}}$.

Exercise: Calculate the spin contribution to χ_m for the ground state of a nitrogen atom at 298 K.

13.7 Because $\langle S_x^2 \rangle = \langle S_y^2 \rangle = \langle S_z^2 \rangle$, it follows that

$$\langle S_z^2 \rangle = \tfrac{1}{3}\langle S_x^2 + S_y^2 + S_z^2 \rangle = \tfrac{1}{3}\langle S^2 \rangle$$

But $\langle S^2 \rangle = \hbar^2 S(S+1)$ for each state. Therefore, $\langle S_z^2 \rangle = \underline{\tfrac{1}{3}S(S+1)\hbar^2}$.

Exercise: Evaluate $\langle S_z^4 \rangle$ in this way.

13.8 See Fig. 13.1.

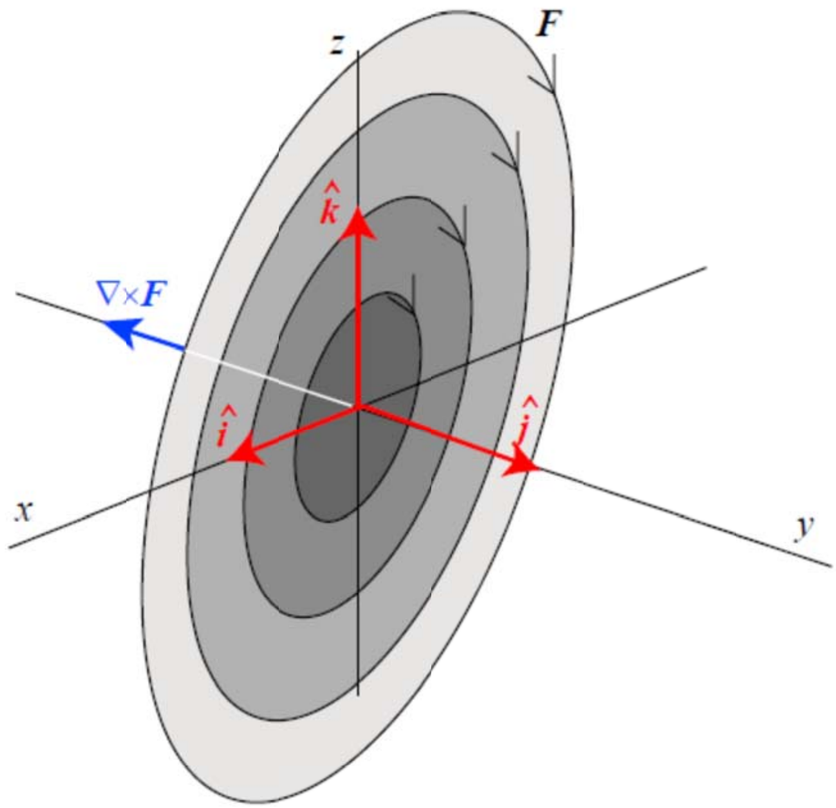

Figure 13.1: The vector function used in Exercise 13.8.

Because $F_x = -z$, $F_y = 0$, and $F_z = x$, we have

$$\nabla \cdot \boldsymbol{F} = (\partial/\partial x)(-z) + (\partial/\partial y)0 + (\partial/\partial z)x = \underline{0}$$

$$\nabla \times \boldsymbol{F} = \begin{vmatrix} \hat{\boldsymbol{i}} & \hat{\boldsymbol{j}} & \hat{\boldsymbol{k}} \\ (\partial/\partial x) & (\partial/\partial y) & (\partial/\partial z) \\ -z & 0 & x \end{vmatrix} = \hat{\boldsymbol{\imath}}\,[(\partial x/\partial y) - (\partial 0/\partial z)]$$

$$-\hat{\boldsymbol{j}}\,[(\partial x/\partial x) + (\partial z/\partial z)] + \hat{\boldsymbol{k}}\,[(\partial 0/\partial x) + (\partial z/\partial y)]$$

$$= -2\,\hat{\boldsymbol{j}}$$

Exercise: Sketch the form of $\boldsymbol{F} = x^2\hat{\boldsymbol{k}} - z^2\hat{\boldsymbol{\imath}}$, and calculate its divergence and curl.

13.9 (a)

$$\mathcal{B} = \mathcal{B}\hat{\boldsymbol{\imath}};$$

$$\boldsymbol{A} = \tfrac{1}{2}\mathcal{B}\hat{\boldsymbol{\imath}} \times \boldsymbol{r} = \tfrac{1}{2}\begin{vmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} & \hat{\boldsymbol{k}} \\ \mathcal{B} & 0 & 0 \\ x & y & z \end{vmatrix} = \underline{\tfrac{1}{2}\mathcal{B}(-z\hat{\boldsymbol{\jmath}} + y\hat{\boldsymbol{k}})}$$

(b)

$$\mathcal{B} = \mathcal{B}(\hat{\boldsymbol{\imath}} + \hat{\boldsymbol{\jmath}})/\sqrt{2}$$

$$\boldsymbol{A} = (\mathcal{B}/2\sqrt{2})(\hat{\boldsymbol{\imath}} + \hat{\boldsymbol{\jmath}}) \times \boldsymbol{r}$$

$$= (\mathcal{B}/2\sqrt{2})\begin{vmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} & \hat{\boldsymbol{k}} \\ 1 & 1 & 0 \\ x & y & z \end{vmatrix} = (\mathcal{B}/2\sqrt{2})\{(z\hat{\boldsymbol{\imath}} - z\hat{\boldsymbol{\jmath}} + (y - x)\,\hat{\boldsymbol{k}}\}$$

For a uniform field,

$$A^2 = \{\tfrac{1}{2}(\mathcal{B} \times \boldsymbol{r})\} \cdot \{\tfrac{1}{2}(\mathcal{B} \times \boldsymbol{r})\}$$

$$= \tfrac{1}{4}\{(\mathcal{B} \cdot \mathcal{B})(\boldsymbol{r} \cdot \boldsymbol{r}) - (\mathcal{B} \cdot \boldsymbol{r})(\boldsymbol{r} \cdot \mathcal{B})\} = \underline{\tfrac{1}{4}\{\mathcal{B}^2 r^2 - (\mathcal{B} \cdot \boldsymbol{r})^2\}}$$

(a) $\mathcal{B} \cdot \boldsymbol{r} = \mathcal{B}x;\quad A^2 = \tfrac{1}{4}\mathcal{B}^2(r^2 - x^2) = \underline{\tfrac{1}{4}\mathcal{B}^2(z^2 + y^2)}$

(b) $\mathcal{B} \cdot \boldsymbol{r} = (\mathcal{B}/\sqrt{2})(x + y);\ A^2 = \tfrac{1}{4}\mathcal{B}^2\{r^2 - \tfrac{1}{2}(x^2 + y^2)^2\}$

Exercise: Find the expressions for the vector potentials representing uniform fields directed towards the corners of a regular tetrahedron. Evaluate $\mathcal{B}$ for $\boldsymbol{A} = \mathcal{B}(x^2\hat{\boldsymbol{k}} - z^2\hat{\boldsymbol{\imath}})$.

13.10 Streamlines representing the vector function $\boldsymbol{C} + \lambda\boldsymbol{D}$ are shown in Fig. 13.2 for various values of λ.

$\boldsymbol{C} = -y\hat{\boldsymbol{\imath}} + x\hat{\boldsymbol{\jmath}}$ $\quad$ $\boldsymbol{D} = x\hat{\boldsymbol{\imath}} + y\,\hat{\boldsymbol{\jmath}}$ $\quad$ $\boldsymbol{C} + \lambda\boldsymbol{D} = (-y + \lambda x)\hat{\boldsymbol{\imath}} + (x + \lambda y)\,\hat{\boldsymbol{\jmath}}$

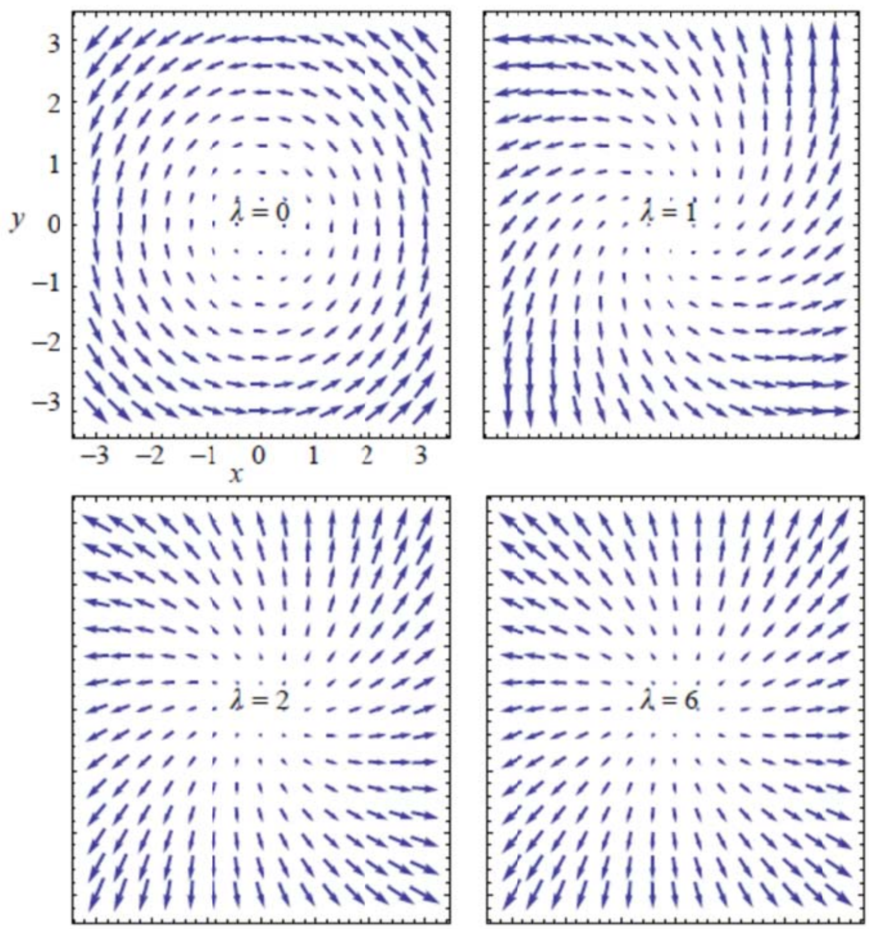

Fig. 13.2 Streamlines of $\boldsymbol{C} + \lambda\boldsymbol{D}$ for indicated values of λ.

13.11 $\boldsymbol{C} = -y\,\hat{\boldsymbol{\imath}} + x\hat{\boldsymbol{\jmath}}$

$\boldsymbol{A} = \boldsymbol{C}\,\mathrm{e}^{-\boldsymbol{k}\cdot\boldsymbol{r}} = (-y\hat{\boldsymbol{\imath}} + x\hat{\boldsymbol{\jmath}})\,\mathrm{e}^{-kz}$

$\mathcal{B} = \nabla \times \boldsymbol{A}$ [eqn 13.14]

$$= \begin{vmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} & \hat{\boldsymbol{k}} \\ \partial/\partial x & \partial/\partial y & \partial/\partial z \\ -y\mathrm{e}^{-kz} & x\mathrm{e}^{-kz} & 0 \end{vmatrix} \quad \text{[Section MB6.2]}$$

$$= -\hat{\boldsymbol{\imath}}\frac{\partial}{\partial z}(x\mathrm{e}^{-kz}) - \hat{\boldsymbol{\jmath}}\frac{\partial}{\partial z}(y\mathrm{e}^{-kz}) + \hat{\boldsymbol{k}}\left\{\frac{\partial}{\partial x}(x\mathrm{e}^{-kz}) + \frac{\partial}{\partial y}(y\mathrm{e}^{-kz})\right\}$$

$$= \mathrm{e}^{-kz}\{kx\hat{\boldsymbol{\imath}} + ky\hat{\boldsymbol{\jmath}} + 2\hat{\boldsymbol{k}}\}$$

$$\boldsymbol{\nabla}\cdot\mathcal{B} = \frac{\partial}{\partial x}(kx\mathrm{e}^{-kz}) + \frac{\partial}{\partial y}(ky\mathrm{e}^{-kz}) + \frac{\partial}{\partial z}(2\mathrm{e}^{-kz}) = 2k\mathrm{e}^{-kz} - 2k\mathrm{e}^{-kz}$$

$$= 0$$

Therefore, the magnetic field does not have non-zero divergence.

13.12

$$\chi_\mathrm{m} = -(e^2\mu_0 N_\mathrm{A}/6m_\mathrm{e})\langle r^2\rangle \quad \text{[eqn 13.40]}$$

$$\psi_{1\mathrm{s}} = (Z^{*3}/\pi a_0^3)^{1/2}\,\mathrm{e}^{-Z^*r/a_0}$$

$$\psi_{2\mathrm{s}} = (Z^{*5}/96\pi a_0^5)^{1/2}\,r\mathrm{e}^{-Z^*r/2a_0}$$

$$\langle r^2\rangle_{1\mathrm{s}} = (Z^{*3}/\pi a_0^3)\int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}\sin\theta\,\mathrm{d}\theta\int_0^{\infty}r^2\{r^2\mathrm{e}^{-2Z^*r/a_0}\}\mathrm{d}r$$

$$= (Z^{*3}/\pi a_0^3)(2\pi)(2)\{4!/(2Z^*/a_0)^5\} = 3a_0^2/Z^{*2}$$

$$\langle r^2\rangle_{2\mathrm{s}} = (Z^{*5}/96\pi a_0^5)(2\pi)(2)\int_0^{\infty}r^6\mathrm{e}^{-Z^*r/a_0}\mathrm{d}r$$

$$= (Z^{*5}/96\pi a_0^5)(4\pi)\{6!/(Z^*/a_0)^7\} = 30a_0^2/Z^{*2}$$

Therefore, in each case we write

$$\chi_m = -(e^2\mu_0 N_A/6m_e)\,Ka_0^2/Z^{*2}, \quad \textbf{(a)}\ K = 3 \text{ for 1s, } \textbf{(b)}\ K = 30 \text{ for 2s}$$

$$= \underline{-(9.95 \times 10^{-12})K/Z^{*2}}$$

(i) For the hydrogen atom, take $Z^* = 1$, $K = 3$;

$$\underline{\chi_m(\text{H}) = -2.99 \times 10^{-11}\,\text{m}^3\ \text{mol}^{-1}}$$

(ii) For the carbon atom, take $Z^*(1s) = 5.67$, $Z^*(2s) = 3.22$ [Table 7.3];

$$\chi_m(\text{C, 1s}) = \underline{-9.28 \times 10^{-13}\ \text{m}^3\ \text{mol}^{-1}};\ \chi(\text{C, 2s}) = \underline{-2.88 \times 10^{-11}\ \text{m}^3\ \text{mol}^{-1}}$$

Exercise: Use the true hydrogenic 2s-orbitals to calculate χ(H, 2s) and compare it with the Slater orbital result. Does the orthogonalization of the Slater H1s and H2s improve the agreement?

13.13 $\chi = \mu_0 \mathcal{N}\xi$ [eqn 13.33]. Using eqns 13.8 and 13.9, we obtain

$$\chi_m = \chi V_m = \mu_0 \mathcal{N}\xi\, V_m = \mu_0 \xi N_A$$

and therefore

$$\xi = \chi_m/(\mu_0 N_A).$$

(a)(i) $\xi(\text{H, 1s}) = -2.99 \times 10^{-11}\ \text{m}^3\,\text{mol}^{-1}/\{(4\pi \times 10^{-7}\ \text{T}^2\ \text{J}^{-1}\ \text{m}^3) \times (6.022 \times 10^{23}\ \text{mol}^{-1})\}$

$$= \underline{-3.95 \times 10^{-29}\ \text{N}^{-1}\ \text{A}^2\ \text{m}^3}$$

(a)(ii) $\xi(\text{C, 1s}) = -9.28 \times 10^{-13}\ \text{m}^3\,\text{mol}^{-1}/\{(4\pi \times 10^{-7}\ \text{T}^2\ \text{J}^{-1}\ \text{m}^3) \times (6.022 \times 10^{23}\ \text{mol}^{-1})\}$

$$= \underline{-1.23 \times 10^{-30}\ \text{N}^{-1}\ \text{A}^2\ \text{m}^3}$$

(b)(ii) $\xi(\text{C, 2s}) = -2.88 \times 10^{-11}\ \text{m}^3\,\text{mol}^{-1}/\{(4\pi \times 10^{-7}\ \text{T}^2\ \text{J}^{-1}\ \text{m}^3) \times (6.022 \times 10^{23}\ \text{mol}^{-1})\}$

$$= \underline{-3.81 \times 10^{-29}\ \text{N}^{-1}\ \text{A}^2\ \text{m}^3}$$

13.14 We desire contour diagrams of the type shown in Fig. 13.9 in the text.

$$\boldsymbol{j}^{\mathrm{d}} = -(e^2\mathcal{B}/2\pi m_e a_0^3)(-y\hat{\boldsymbol{\imath}} + x\hat{\boldsymbol{\jmath}})\mathrm{e}^{-2r/a_0} \text{ [eqn 13.54b]}$$

$$= -(e^2\mathcal{B}/2\pi m_e a_0^3)(-\hat{\boldsymbol{\imath}} \sin \phi + \hat{\boldsymbol{\jmath}} \cos \phi) \sin \theta\, r\mathrm{e}^{-2r/a_0}$$

$$= -(e^2\mathcal{B}/2\pi m_e a_0^2)(-\hat{\boldsymbol{\imath}}\sin \phi + \hat{\boldsymbol{\jmath}} \cos \phi) \sin \theta\, s\mathrm{e}^{-2s},\ s = r/a_0$$

The heights 0, a_0, $2a_0$ correspond to the following values of r, θ for horizontal distances σa_0 from the nucleus (Fig. 13.3):

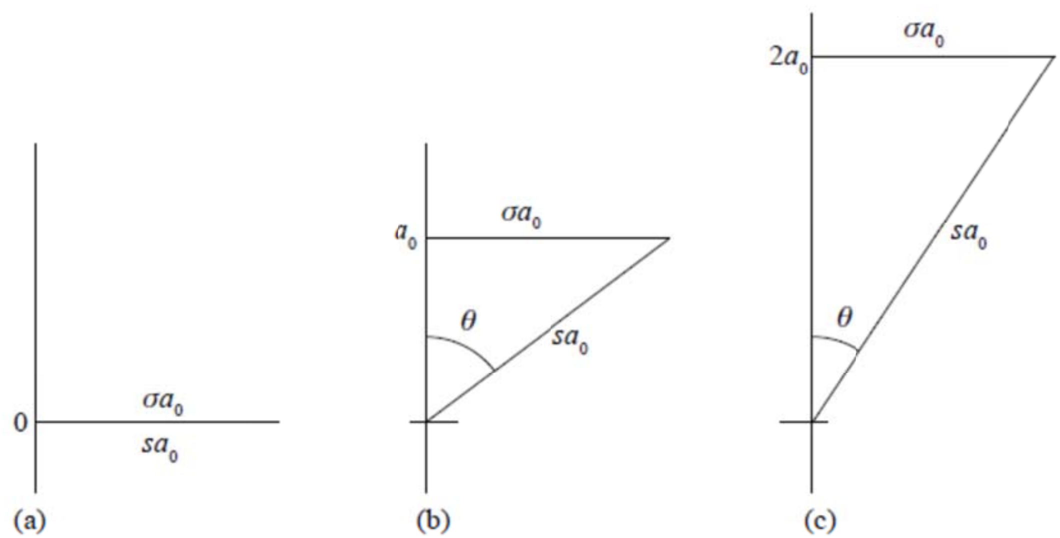

Figure 13.3: The geometry of the arrangement treated in Exercise 13.14.

(a) $0 : s = \sigma,\ \theta = 90°$,

(b) $a_0 : s \sin \theta = \sigma, \quad s = (1 + \sigma^2)^{1/2}$,

(c) $2a_0 : s \sin \theta = \sigma, \quad s = (4 + \sigma^2)^{1/2}$.

Write $j^{\ominus} = -(e^2\mathcal{B}/2\pi m_e a_0^2)$

then

$$\boldsymbol{j}^{\mathrm{d}}/j^{\ominus} = (-\hat{\boldsymbol{\imath}}\sin\phi + \hat{\boldsymbol{\jmath}}\cos\phi)\sin\theta\, s\mathrm{e}^{-2s}$$

which correspond to circles denoting magnitudes

(a) $j^{\mathrm{d}}/j^{\ominus} = \underline{\sigma \mathrm{e}^{-2\sigma}}$

(b) $j^{\mathrm{d}}/j^{\ominus} = \underline{\sigma \exp\{-2(1+\sigma^2)^{1/2}\}}$

(c) $j^{\mathrm{d}}/j^{\ominus} = \underline{\sigma \exp\{-2(4+\sigma^2)^{1/2}\}}$

These functions are plotted in Fig. 13.4.

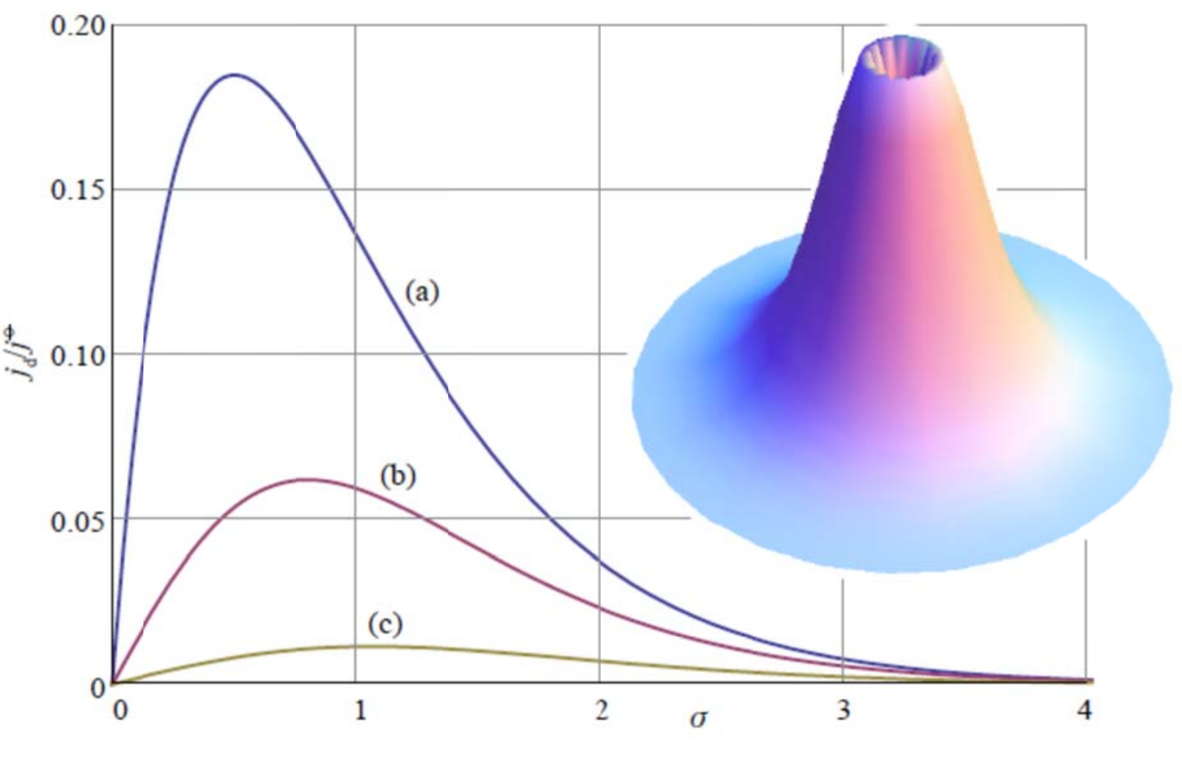

Figure 13.4: The diamagnetic current density at heights of 0, a_0, and $2a_0$ above the

xy-plane for a ground-state hydrogen atom in a magnetic field.

Exercise: Calculate and plot the current densities in the same three planes for an electron in a hydrogenic 2s-orbital.

13.15 Take the following hydrogenic orbitals [$s = r/a_0$]:

$$\psi_{2s} = R_{20}Y_{00} = (Z^3/8\pi a_0^3)^{1/2}(1 - \tfrac{1}{2}Zs)e^{-Zs/2}$$

$$\psi_{3p} = R_{31}Y_{10} = (1/27)(2Z^5/\pi a_0^3)^{1/2}s(2 - \tfrac{1}{3}Zs)e^{-Zs/3}\cos\theta$$

When the field is along z there is no paramagnetic contribution. The diamagnetic current densities are given by

$$\boldsymbol{j}^{d} = -(e^2\mathcal{B}/2m_e)\psi_0^2\boldsymbol{C} \quad \text{[eqn 13.54a]}$$

(a) $\boldsymbol{j}^{d}(2s) = -(Z^3e^2\mathcal{B}/16\pi m_e a_0^3)(1 - \tfrac{1}{2}Zs)^2\boldsymbol{C}e^{-Zs}$

$$= -(Z^3e^2\mathcal{B}/16\pi m_e a_0^2)s(1 - \tfrac{1}{2}Zs)^2(-\hat{\boldsymbol{\imath}}\sin\phi + \hat{\boldsymbol{\jmath}}\cos\phi)e^{-Zs}\sin\theta$$

which correspond to circular contours denoting magnitudes

$$j^{d}(2s)/j^* = s(1 - \tfrac{1}{2}Zs)^2e^{-Zs}\sin\theta, \quad j^* = Z^3e^2\mathcal{B}/16\pi m_e a_0^2$$

When $\theta = 90°$ and $Z = 1$,

$$j^{d}(2s)/j^* = \underline{s(1-\tfrac{1}{2}s)^2e^{-s}}$$

which is sketched in Fig. 13.5.

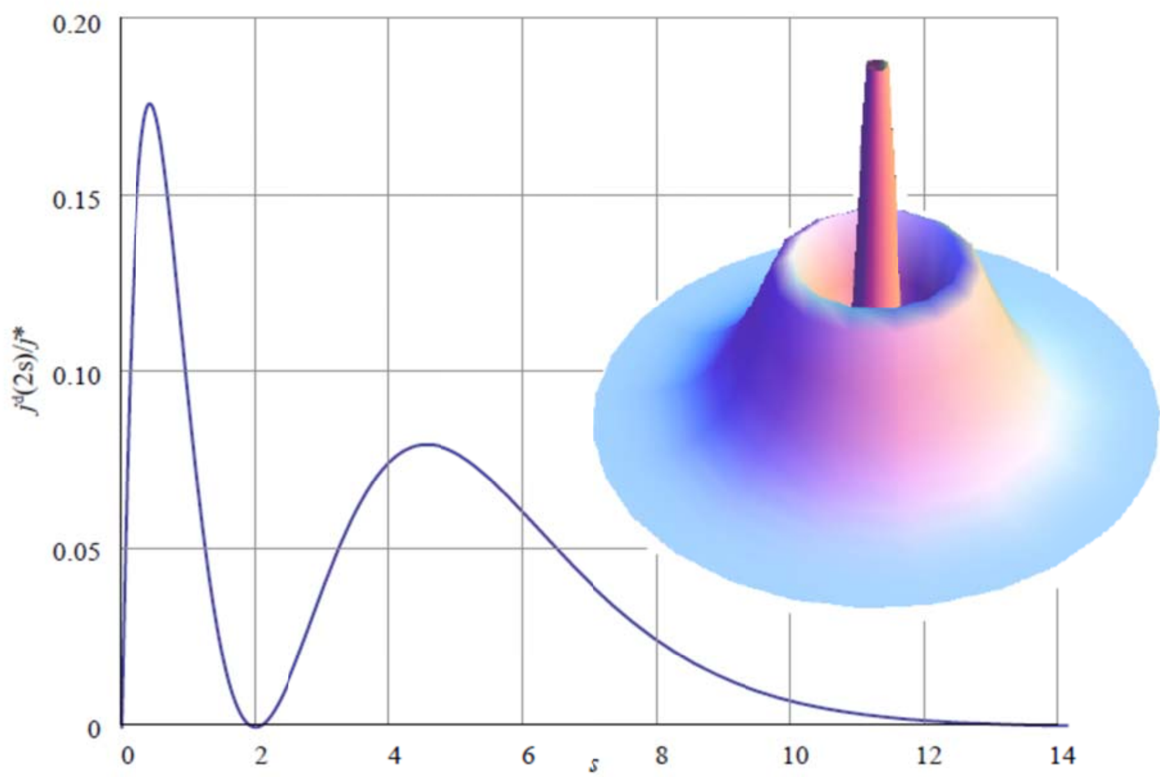

Figure 13.5: The diamagnetic current density in a 2s-orbital in a plane through the nucleus.

(b)

$$\boldsymbol{j}^{\mathrm{d}}(3\mathrm{p}_z) = -(Z^5e^2\mathcal{B}/729m_{\mathrm{e}}\pi a_0^2)s^3(2-\tfrac{1}{3}Zs)^2\mathrm{e}^{-2Zs/3}\cos^2\theta\sin\theta$$

$$\times(-\hat{\boldsymbol{\imath}}\sin\phi+\hat{\boldsymbol{\jmath}}\cos\phi)$$

This expression also corresponds to circular contours denoting magnitudes

$$j^{\mathrm{d}}(3p_z)/j^{**} = s^3(2-\tfrac{1}{3}Zs)^2\cos^2\theta\sin\theta\,\mathrm{e}^{-2Zs/3},\ j^{**} = Z^5e^2\mathcal{B}/729m_{\mathrm{e}}\pi a_0^2$$

The magnitudes are zero in the equatorial plane ($\sin\theta = 0$). For a plane parallel to the equatorial plane but at a height ha_0 above it, we have $s \sin\theta = \sigma$, as in Fig. 13.3 (Exercise 13.14), $\cos\theta = h/s$, and $s^2 = \sigma^2 + h^2$. Then, with $Z = 1$,

$$j^{\mathrm{d}}(3\mathrm{p}_z)/j^{**} = \underline{h^2\sigma(2 - \tfrac{1}{3}[\sigma^2 + h^2]^{1/2})^2 \exp\{-\tfrac{2}{3}[\sigma^2 + h^2]^{1/2}\}}$$

This expression is sketched in Fig. 13.6 for $h = 1$, when

$$j^{\mathrm{d}}(3\mathrm{p}_z)/j^{**} = \sigma\{2 - \tfrac{1}{3}\sqrt{(1 + \sigma^2)}\}^2 \exp\{-\tfrac{2}{3}\sqrt{(1 + \sigma^2)}\}$$

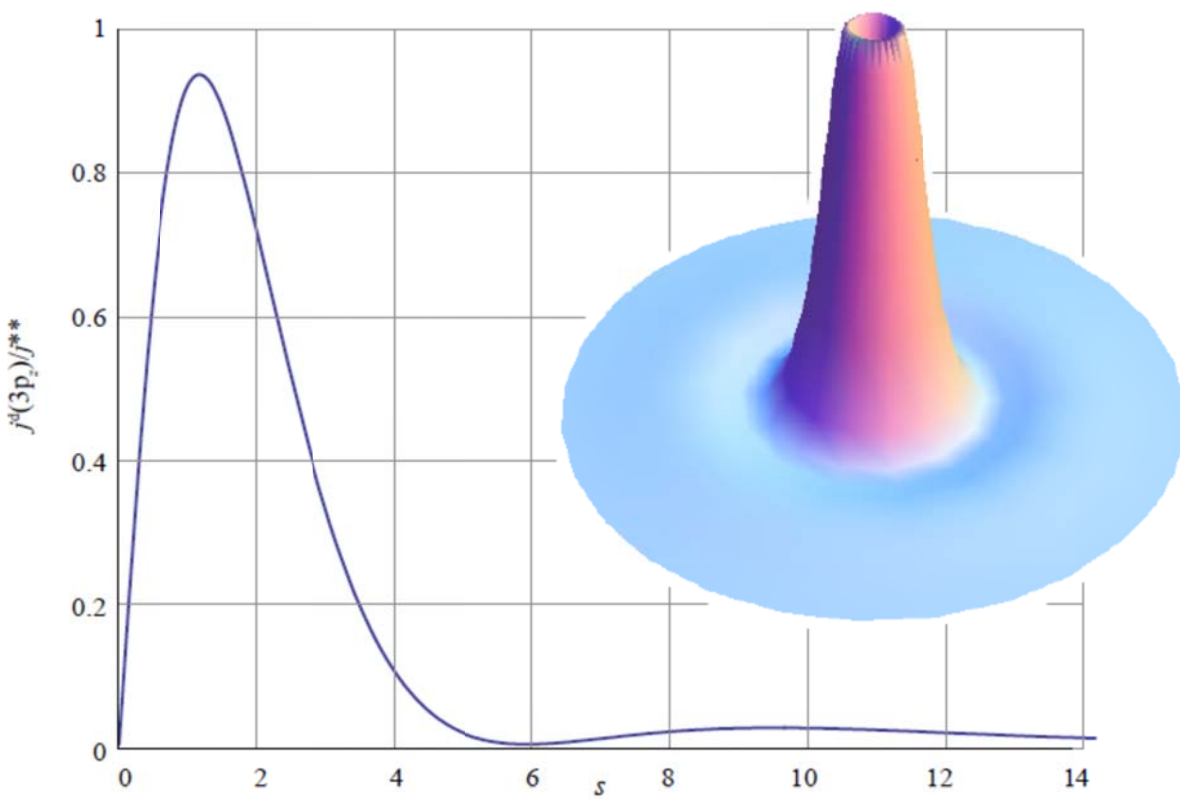

Figure 13.6: The diamagnetic current density in a $3\mathrm{p}_z$-orbital in a plane at a height a_0 above the xy-plane.

Exercise: Evaluate $\boldsymbol{j}(4\mathrm{p}_z)$ and $\boldsymbol{j}(3\mathrm{s})$ for hydrogenic orbitals, the magnetic field being applied in the z-direction.

13.16 We need to show that the vector potential given in eqn 13.62b has zero divergence. If the spin angular momentum $\boldsymbol{I}$ and the position vector $\boldsymbol{r}$ are written in terms of their components

$$\boldsymbol{I} = I_x\,\hat{\boldsymbol{\imath}} + I_y\hat{\boldsymbol{\jmath}} + I_z\hat{\boldsymbol{k}} \qquad \boldsymbol{r} = x\hat{\boldsymbol{\imath}} + y\hat{\boldsymbol{\jmath}} + z\hat{\boldsymbol{k}}$$

then, using the definition of the vector product (eqn MB3.4e), we find

$$\boldsymbol{A}_{\text{nuc}} = \left(\frac{\gamma_{\text{N}}\mu_0}{4\pi r^3}\right)\{\hat{\boldsymbol{\imath}}(I_yz - yI_z) + \hat{\boldsymbol{\jmath}}\,(I_zx - zI_x) + \hat{\boldsymbol{k}}\,(I_xy - xI_y)\}$$

Using the definition of the divergence (eqn MB6.3), we obtain

$$\nabla\cdot\boldsymbol{A}_{\text{nuc}} = \left(\frac{\gamma_{\text{N}}\mu_0}{4\pi r^3}\right)\left[\frac{\partial}{\partial x}(I_yz - yI_z) + \frac{\partial}{\partial y}(I_zx - zI_x) + \frac{\partial}{\partial z}(I_xy - xI_y)\right]$$

$$= 0$$

because I_y and z are independent of x and so forth.

Exercise: Evaluate the curl of the vector potential given in eqn 13.62b.

13.17 A magnetic dipole that has only a z-component can be written $\boldsymbol{m} = m_z\,\boldsymbol{k}$. The vector potential $\boldsymbol{A}$ then takes the form (see eqn 13.62a):

$$\boldsymbol{A} = \left(\frac{\mu_0}{4\pi r^3}\right)\boldsymbol{m}\times\boldsymbol{r}$$

$$= \left(\frac{\mu_0}{4\pi r^3}\right)\begin{vmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} & \hat{\boldsymbol{k}} \\ 0 & 0 & m_z \\ x & y & z \end{vmatrix}$$

$$= \left(\frac{\mu_0 m_z}{4\pi r^3}\right)(-y\hat{\boldsymbol{\imath}} + x\hat{\boldsymbol{\jmath}})$$

13.18

$\sigma^{\rm d} = (e^2\mu_0/12\pi m_{\rm e})\langle(1/r)\rangle$ [eqn 13.74]

$\psi(2{\rm s}) = (Z^{*5}/96\pi a_0^5)^{1/2}\, r{\rm e}^{-Z^*r/2a_0}$ [Exercise 13.12]

$\psi(2{\rm p}_z) = (Z^{*5}/32\pi a_0^5)^{1/2}\, r\cos\theta\, {\rm e}^{-Z^*r/2a_0}$ [Problem 13.4]

$$\langle(1/r)\rangle_{2{\rm s}} = (Z^{*5}/96\pi a_0^5)\int_0^{2\pi}{\rm d}\phi\int_0^{\pi}\sin\theta{\rm d}\theta\int_0^{\infty}r^2\,\{r^2(1/r){\rm e}^{-Z^*r/a_0}\}{\rm d}r$$

$$= (Z^{*5}/96\pi a_0^5)(2\pi)(2)\{3!/(Z^*/a_0)^4\} = \tfrac{1}{4}(Z^*/a_0)$$

$$\langle(1/r)\rangle_{2{\rm p}_z} = (Z^{*5}/32\pi a_0^5)\int_0^{2\pi}{\rm d}\phi\int_0^{\pi}\sin\theta{\rm d}\theta\int_0^{\infty}r^2\,\{r^2(1/r)\cos^2\theta\,{\rm e}^{-Z^*r/a_0}\}{\rm d}r$$

$$= (Z^{*5}/32\pi a_0^5)(2\pi)(2/3)\{3!/(Z^*/a_0)^4\} = \tfrac{1}{4}(Z^*/a_0)$$

Therefore, for each type of orbital,

$$\sigma^{\rm d} = (e^2\mu_0/12\pi m_{\rm e})(Z^*/4a_0) = e^2\mu_0 Z^*/48\pi m_{\rm e}a_0$$

$$= 4.44\times10^{-6}\,Z^*$$

For an electron in a carbon atom, for which $Z^*(2{\rm s}) = 3.22$ and $Z^*(2{\rm p}) = 3.14$ [Table 7.3],

(a) $\underline{2{\rm s}:\sigma^{\rm d} = 1.43\times10^{-5}}$ **(b)** $\underline{2{\rm p}:\sigma^{\rm d} = 1.39\times10^{-5}}$

Exercise: Calculate the contribution to σ^{d} of an electron in (a) a hydrogenic 2s-orbital, (b) Slater 3s- and 3p-orbitals.

13.19 The 2s-orbital gives zero paramagnetic contribution. The 2p-electron contributes

$$\sigma^{\mathrm{p}} = -(e^2\mu_0/12\pi\, m_{\mathrm{e}}^2)\sum_{n\neq 0}\frac{\boldsymbol{l}_{0n}\cdot(r^{-3}\boldsymbol{l})_{n0}}{\Delta E_{n0}}\} \quad \text{[eqn 13.75]}$$

$$= -(e^2\mu_0/12\pi\, m_{\mathrm{e}}^2)\langle \mathrm{p}_z|l_x|\mathrm{p}_y\rangle\langle \mathrm{p}_y|r^{-3}l_x|\mathrm{p}_z\rangle/\Delta E$$

[We are assuming that the orbital mixed in is p_y, so only l_x contributes; another p_x-orbital nearby would give an additional contribution through l_y.] Because $l_x\mathrm{p}_z = -\mathrm{i}\hbar\mathrm{p}_y$ this expression becomes

$$\sigma^{\mathrm{p}} = -(e^2\mu_0\hbar^2/12\pi\, m_{\mathrm{e}}^2)\langle \mathrm{p}_y|(1/r^3)|\mathrm{p}_y\rangle/\Delta E$$

$$\langle(1/r^3)\rangle_{2\mathrm{p}_y} = \langle(1/r^3)\rangle_{2\mathrm{p}_z}$$

$$= (Z^{*5}/32\pi\, a_0^5)\int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}\sin\theta\mathrm{d}\theta\int_0^{\infty} r^2\ \{r^2(1/r^3)\cos^2\theta\,\mathrm{e}^{-Z^*r/a_0}\}\mathrm{d}r$$

$$= (Z^{*5}/32\pi\, a_0^5)(2\pi)(2/3)\{1/(Z^*/a_0)^2\} = Z^{*3}/24a_0^3$$

Consequently,

$$\sigma^{\mathrm{p}} = -(e^2\mu_0\hbar^2/12\pi\, m_{\mathrm{e}}^2)\ (Z^{*3}/24a_0^3)(1/\Delta E)$$

$$= -(e^2\mu_0\hbar^2/288\pi\, m_{\mathrm{e}}^2a_0^3)(Z^{*3}/\Delta E)$$

$$= \underline{-2.013\times 10^{-5}\, Z^{*3}/(\Delta E/\mathrm{eV})}$$

For carbon, $Z^* = 3.14$ [Table 7.3], so

$$\sigma^{\mathrm{p}} = -6.23 \times 10^{-4}/(\Delta E/\mathrm{eV}) = -1.2 \times 10^{-4} \text{ when } \Delta E/\mathrm{eV} = 5.0$$

Exercise: Calculate the paramagnetic contribution to the shielding of an electron in a 3p$_z$-orbital.

13.20 The magnetic perturbation transforms as a rotation. In C_{2v}, R_x, R_y, R_z transform as $\underline{\mathrm{B}_2, \mathrm{B}_1, \mathrm{A}_2}$ respectively. Therefore, because

$$\mathrm{A}_1 \times \{\mathrm{B}_2, \mathrm{B}_1, \mathrm{A}_2\} = \{\mathrm{B}_2, \mathrm{B}_1, \mathrm{A}_2\}$$

it follows that for NO_2 the components g_{xx}, g_{yy}, g_{zz} depend on the admixture of $\underline{{}^2\mathrm{B}_2, {}^2\mathrm{B}_1, {}^2\mathrm{A}_2}$ terms respectively. Because

$$\mathrm{B}_1 \times \{\mathrm{B}_2, \mathrm{B}_1, \mathrm{A}_2\} = \{\mathrm{A}_2, \mathrm{A}_1, \mathrm{B}_2\}$$

it follows that for ClO_2, g_{xx}, g_{yy}, g_{zz} depend on the admixture of ${}^2\mathrm{A}_2$, ${}^2\mathrm{A}_1$, ${}^2\mathrm{B}_2$ respectively.

Exercise: What states contribute to g_{xx}, g_{yy}, g_{zz} in the ${}^2\mathrm{E}_1'$ state of a D_{5h} molecule?

13.21 $\psi(\mathrm{d}_{z_2}) = \left(\frac{5}{16\pi}\right)^{\frac{1}{2}} R_{n2}(r)(3\cos^2\theta - 1)$ [eqn 3.74a]

$$\langle 1 - 3\cos^2\theta\rangle = \int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}\int_{r=0}^{\infty} \psi(\mathrm{d}_{z_2})(1 - 3\cos^2\theta)\psi(\mathrm{d}_{z_2}) r^2 \sin\theta \mathrm{d}\theta \mathrm{d}\varphi \mathrm{d}r$$

$$= \frac{5}{16\pi}\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}\int_{r=0}^{\infty} R_{n2}^2(r)(3\cos^2\theta - 1)^2(1 - 3\cos^2\theta) r^2 \sin\theta \mathrm{d}\theta \mathrm{d}\varphi \mathrm{d}r$$

Since the radial function R_{n2} is normalized, integration over r contributes unity; integration over φ contributes 2π. Therefore,

$$\langle 1-3\cos^2\theta\rangle = \frac{5}{8}\int_{\theta=0}^{\pi}(3\cos^2\theta-1)^2(1-3\cos^2\theta)\sin\theta\mathrm{d}\theta$$

$$=\frac{5}{8}\int_{\theta=0}^{\pi}(-27\cos^6\theta+27\cos^4\theta-9\cos^2\theta+1)\sin\theta\mathrm{d}\,\theta$$

$$=\frac{5}{8}\left\{\frac{-2\times 27}{7}+\frac{2\times 27}{5}-2\times 3+2\right\}$$

$$=-4/7$$

13.22 The spherical average of $(1-3\cos^2\theta)^2$ is given by the integral

$$\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}(1-3\cos^2\theta)^2\sin\theta\mathrm{d}\theta\mathrm{d}\varphi = 2\pi\int_{\theta=0}^{\pi}(1-3\cos^2\theta)^2\sin\theta\mathrm{d}\theta$$

$$=2\pi\int_{\theta=0}^{\pi}(9\cos^4\theta-6\cos^2\theta+1)\sin\theta\mathrm{d}\theta$$

$$=2\pi\left\{\frac{9}{5}\times 2+2\times(-2)+2\right\}$$

$$=16\pi/5$$

Problems

13.1 Under the influence of the perturbation $H^{(1)}=-\gamma_e l_z\mathcal{B}$ the non-degenerate, real, ground state ψ_0 changes to $\psi=\psi_0+c\psi_1$, with $c=-\langle\psi_1|H^{(1)}|\psi_0\rangle/\Delta E$ [eqn 6.26]. In this case $c=\gamma_e\mathcal{B}l_{z,10}/\Delta E$; which is imaginary. Therefore ψ is complex. It follows that

$$\langle\psi|l_q|\psi\rangle=\langle\psi|l_q|\psi\rangle^* \quad \text{[hermiticity]}$$

$$\langle\psi|l_q|\psi\rangle = \langle\psi_0|l_q|\psi_0\rangle + \langle\psi_0|l_q|\psi_1\rangle c + c^*\langle\psi_1|l_q|\psi_0\rangle + \mathrm{O}(c)^2$$

$$\langle\psi|l_q|\psi\rangle^* = \langle\psi_0|l_q|\psi_0\rangle^* + \langle\psi_0|l_q|\psi_1\rangle^* c^* + c\langle\psi_1|l_q|\psi_0\rangle^* + \mathrm{O}(c^2)$$

$$= -\langle\psi_0|l_q|\psi_0\rangle - \langle\psi_0|l_q|\psi_1\rangle c^* - c\langle\psi_1|l_q|\psi_0\rangle + \mathrm{O}(c^2)$$

On comparing the two expressions, noting that $\langle\psi_0|l_q|\psi_0\rangle = 0$, we are left with

$$\langle\psi_0|l_q|\psi_1\rangle c + c^*\langle\psi_1|l_q|\psi_0\rangle = \langle\psi_0|l_q|\psi_1\rangle c + c^*\langle\psi_1|l_q|\psi_0\rangle$$

which does not require a value of zero. Hence $\langle\psi|l_q|\psi\rangle$ need not disappear.

Exercise: Show that the expectation value of linear momentum is zero when the state is real but may be nonzero in the presence of an appropriate perturbation.

13.4. $\psi = (\psi_\mathrm{N} - \psi_\mathrm{O})/\sqrt{2}$

$$\psi_{2\mathrm{p}} = (Z^{*5}/32\pi a_0^5)^{1/2} r \cos\theta\, \mathrm{e}^{-Z^* r/2a_0}, \quad Z^*_\mathrm{N} = 3.83,\ Z^*_\mathrm{O} = 4.45 \text{ [Table 7.3]}$$

Let the vector potential be centred on a point a fraction λ of the bond (of length R) from N, Fig. 13.7.

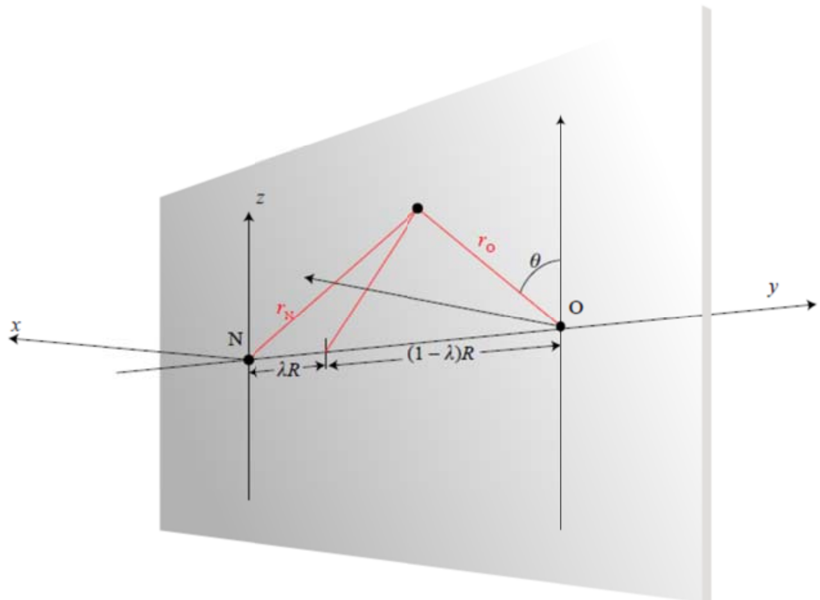

Figure 13.7: The coordinates used in Problem 13.4.

Then for a uniform field along *x*,

$$\boldsymbol{A} = \tfrac{1}{2}\boldsymbol{\mathcal{B}} \times \boldsymbol{r} = \tfrac{1}{2}\mathcal{B}(-z\hat{\boldsymbol{j}} + y\hat{\boldsymbol{k}})$$

We need to express cos θ and r (on both N and O) in terms of the same y and z coordinates. (Note in passing that there is no 'natural' origin for $\boldsymbol{A}$: different values of λ correspond to different choices of gauge. In due course we shall see that the diamagnetic current density depends on the choice of gauge. The total current density, however, is independent of gauge.)

On N:

$$r_N^2 = y_N^2 + z_N^2 = (y + \lambda R)^2 + z^2$$

$$\cos\theta_N = z_N/r_N = z/\{(y + \lambda R)^2 + z^2\}^{1/2}$$

On O:

$$r_O^2 = y_O^2 + z_O^2 = [y - (1 - \lambda)R]^2 + z^2$$

$$\cos\,\theta_O = z_O/r_O = z/\{[y - (1 - \lambda)R]^2 + z^2\}^{1/2}$$

Consequently,

$$\psi_{N2p_z} = (Z_N^{*5}/32\pi a_0^5)^{1/2}\,z\,\exp\{-Z_N^*\,[(y + \lambda R)^2 + z^2]^{1/2}/2a_0\}$$

$$\psi_{O2p_z} = (Z_O^{*5}/32\pi a_0^5)^{1/2}\,z\,\exp\{-Z_O^*\,\{[y - (1 - \lambda)R]^2 + z^2\}^{1/2}/2a_0\}$$

The diamagnetic current density in the *yz*-plane is therefore

$$\boldsymbol{j}^{d} = -(e^2\mathcal{B}/2m_e)\,\psi_0^2\boldsymbol{C} \quad [\text{eqn 13.54a, } \boldsymbol{C} = -z\hat{\boldsymbol{j}} + y\hat{\boldsymbol{k}}]$$

$$= -(e^2\mathcal{B}/4m_e)\,(\psi_N^2 + \psi_O^2 - 2\psi_N\psi_O)\,(-z\hat{\boldsymbol{j}} + y\hat{\boldsymbol{k}})$$

$$= -j^{\#}\left\{Z_N^{*5}e^{-2f_N} + Z_O^{*5}e^{-2f_O} - 2(Z_N^*Z_O^*)^{5/2}\,e^{-(f_N+f_O)}\right\}z^2(-z\hat{\boldsymbol{j}} + y\hat{\boldsymbol{k}})$$

with

$$j^{\#} = e^2\mathcal{B}/128\pi m_e\,a_0^5$$

$$f_N = (Z_N^*/2a_0)\,\{[y + \lambda R]^2 + z^2\}^{1/2}$$

$$f_O = (Z_O^*/2a_0)\,\{[y - (1 - \lambda)R]^2 + z^2\}^{1/2}$$

Now write

$$\zeta = z/a_0,\ \eta = y/a_0,\ s = R/a_0,\ \gamma = (Z_N^*/Z_O^*)^{5/2},\ j^{\dagger} = (Z_N^*/Z_O^*)^{5/2}\,j^{\#}$$

Then

$$-\boldsymbol{j}^{\mathrm{d}}/j^{\dagger} = \{\gamma\, \mathrm{e}^{-2f_{\mathrm{N}}} + (1/\gamma)\, \mathrm{e}^{-2f_{\mathrm{O}}} - 2\mathrm{e}^{-(f_{\mathrm{O}}+f_{\mathrm{N}})}\}\ \zeta^2(-\zeta\hat{\boldsymbol{j}} + \eta\hat{\boldsymbol{k}})\, a_0^3$$

$$f_{\mathrm{N}} = \tfrac{1}{2} Z_{\mathrm{N}}^{*}\, \{(\eta + \lambda s)^2 + \zeta^2\}^{1/2}$$

$$f_{\mathrm{O}} = \tfrac{1}{2} Z_{\mathrm{O}}^{*}\, \{[\eta - (1-\lambda)s]^2 + \zeta^2\}^{1/2}$$

Take $R = 115$ pm (so $s = 2.17$). The current densities should be plotted for (a) $\lambda = 0$, (b)$\lambda = \frac{1}{2}$, (c) $\lambda = 1.0$.

Exercise: Use mathematical software to plot the current densities. Calculate and plot the current density for a plane parallel to the one considered above, but offset from it by a distance a_0.

13.7 $$\chi_{\mathrm{m},\|} = -(e^2\mu_0 N_{\mathrm{A}}/4m_{\mathrm{e}})\langle x^2 + y^2\rangle \quad \text{[eqns 13.40 and 13.35]}$$

$$\chi_{\mathrm{m},\perp} = -(e^2\mu_0 N_{\mathrm{A}}/4m_{\mathrm{e}})\langle x^2 + z^2\rangle$$

$$x^2 + y^2 = r^2 \sin^2\theta\,(\cos^2\phi + \sin^2\phi) = r^2 \sin^2\theta$$

$$\psi_{2\mathrm{p}_z} = (Z^{*5}/32\pi a_0^5)^{1/2}\, r \cos\,\theta\, \mathrm{e}^{-Z^{*}r/2a_0}$$

(a)

$$\langle x^2 + y^2\rangle = (Z^{*5}/32\pi a_0^5)\int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}\sin\theta\,\mathrm{d}\theta\int_0^{\infty} r^2\ \{r^4 \sin^2\,\theta\cos^2\,\theta\,\mathrm{e}^{-Z^{*}r/a_0}\}\mathrm{d}r$$

$$= (Z^{*5}/32\pi a_0^5)\,(2\pi)(4/15)\{6!/(Z^{*}/a_0)^7\} = 12a_0^2/Z^{*2}$$

(b)

$$\langle x^2 + z^2\rangle = r^2(\sin^2\theta\cos^2\phi + \cos^2\theta)\rangle$$

$$= (Z^{*5}/32\pi a_0^5)\int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \sin\theta\, \mathrm{d}\theta \int_0^{\infty} r^2\ \{r^4(\sin^2\theta\cos^2\theta + \cos^2\theta)$$

$$\times \cos^2\theta\, \mathrm{e}^{-Z^*r/a_0}\}\mathrm{d}r$$

$$= (Z^{*5}/32\pi a_0^5)\ \{(\pi)(4/15) + (2\pi)(2/5)\}\{6!/(Z^*/a_0)^7\}$$

$$= 24a_0^2/Z^{*2}$$

(a)

$$\chi_{\|,\mathrm{m}} = -(3e^2 a_0^2 \mu_0 N_\mathrm{A}/m_\mathrm{e})(1/Z^{*2})$$

$$= \underline{-1.791 \times 10^{-10}/Z^{*2}\ \mathrm{m^3\ mol^{-1}}}$$

(b)

$$\chi_{\perp,\mathrm{m}} = -(6e^2 a_0^2 \mu_0 N_\mathrm{A}/m_\mathrm{e})(1/Z^{*2})$$

$$= \underline{-3.583 \times 10^{-10}/Z^{*2}\ \mathrm{m^3\ mol^{-1}}}$$

$$\chi_\mathrm{m} = \tfrac{1}{3}(\chi_\| + 2\chi_\perp) = \tfrac{5}{3}\chi_\| \quad [\chi_\perp = 2\chi_\|]$$

$$= \underline{-2.985 \times 10^{-10}/Z^{*2}\ \mathrm{m^3\ mol^{-1}}}$$

For the carbon atom, $Z^* = 3.14$ [Table 7.3]; consequently

$$\underline{\chi_{\|,\mathrm{m}} = -1.82\times10^{-11}};\quad \underline{\chi_{\perp,\mathrm{m}} = -3.63\times10^{-11}};$$

$$\underline{\chi_\mathrm{m} = -3.03\times10^{-11}\ \mathrm{m^3\ mol^{-1}}}$$

Exercise: Evaluate $\chi_\|$ and $\chi_\perp$ for Slater 3d$_{z^2}$ -orbitals.

13.10 The normalized forms of the d-orbitals are

$$d_{z^2} = (5/16\pi)^{1/2}(3\cos^2\theta - 1)r^2 f(r) = (5/16\pi)^{1/2}(3z^2 - r^2)f(r)$$

$$d_{xz} = -(15/4\pi)^{1/2}\cos\theta\sin\theta\cos\phi\, r^2 f(r) = -(15/4\pi)^{1/2}\, xzf(r)$$

$$d_{yz} = -(15/4\pi)^{1/2}\cos\theta\sin\theta\sin\phi\, r^2 f(r) = -(15/4\pi)^{1/2}\, yzf(r)$$

Consequently,

$$l_z d_{z^2} = 0$$

$$l_y d_{z^2} = (5/16\pi)^{1/2}(\hbar/\mathrm{i})\{z(\partial/\partial x) - x(\partial/\partial z)\}(3z^2 - r^2)f(r)$$

$$= 6\mathrm{i}\hbar(5/16\pi)^{1/2}\, xzf(r) = -\mathrm{i}\hbar\sqrt{3}\, d_{xz}$$

$$l_x d_{z^2} = (5/16\pi)^{1/2}(\hbar/\mathrm{i})\{y(\partial/\partial z) - z(\partial/\partial y)\}(3z^2 - r^2)f(r)$$

$$= -6\mathrm{i}\hbar(5/16\pi)^{1/2} yzf(r) = +\mathrm{i}\hbar\sqrt{3}\, d_{yz}$$

Therefore,

$$g_{zz} = \underline{g_e}$$

$$g_{yy} = g_e - 2\lambda\langle d_{xz}|l_y|d_{z^2}\rangle^2/\Delta E \text{ [eqn 13.87a]}$$

$$= g_e - 6\lambda\hbar^2/\Delta E = \underline{g_e - 6hc\zeta/\Delta E}$$

$$g_{xx} = g_e - 2\lambda\langle d_{yz}|l_x|d_{z^2}\rangle^2/\Delta E = \underline{g_e - 6hc\zeta/\Delta E}$$

Taking $\zeta = 154\ \mathrm{cm}^{-1}$ and $\Delta E/hc = 10^4\ \mathrm{cm}^{-1}$ gives

$$g_{zz} = g_e = \underline{2.002}, \quad g_{yy} = g_{xx} = g_e - 0.092 = \underline{1.910}$$

Exercise: In a similar complex the d_{xy} orbital was the lowest; calculate the g-values.

13.13 $J \approx (2\mu_0 g_e \mu_B/3)^2 \gamma_A \gamma_B |\chi_A(0)|^2 |\chi_B(0)|^2 c_A^2 c_B^2 / \Delta E^{(T)}$ [eqn 13.110]

$$c_A^2 = c_B^2 \approx \tfrac{1}{2}; \quad \chi_A^2(0) = \chi_B^2(0) = 1/\pi a_0^3$$

$$\gamma_A = \gamma(^1\mathrm{H}) = g(^1\mathrm{H})\mu_N/\hbar, \quad g(^1\mathrm{H}) = 5.5857$$

$$\gamma_B = \gamma(^2\mathrm{H}) = g(^2\mathrm{H})\mu_N/\hbar, \quad g(^2\mathrm{H}) = 0.85745$$

$$J \approx (2\mu_0 g_e \mu_B/3)^2\, g(^1\mathrm{H})g(^2\mathrm{H})\, \mu_N^2 (1/\pi a_0^3)^2\, (1/2)^2/\Delta E^{(T)}\hbar^2$$

$$\approx (g_e \mu_0 \mu_B \mu_N/3\pi a_0^3)^2 g(^1\mathrm{H})g(^2\mathrm{H})/\Delta E^{(T)}\hbar^2$$

$$\approx 7.122 \times 10^{-51}\, g(^1\mathrm{H})g(^2\mathrm{H})/\hbar^2(\Delta E^{(T)}/\mathrm{J})$$

$$\approx 4.445 \times 10^{-32}\, g(^1\mathrm{H})g(^2\mathrm{H})/\hbar^2(\Delta E^{(T)}/\mathrm{eV})$$

$$\hbar^2 J/h = (67.1\ \mathrm{Hz}) \times \frac{g(^1\mathrm{H})g(^2\mathrm{H})}{(\Delta E^{(T)}/\mathrm{eV})} = \frac{321\ \mathrm{Hz}}{\Delta E^{(T)}/\mathrm{eV}}$$

$$\approx \underline{32\ \mathrm{Hz}} \text{ when } \Delta E^{(T)} \approx 10\ \mathrm{eV}$$

Exercise: Find an expression for the spin–spin coupling involving two nuclei, one of atomic number Z_1 and the other of atomic number Z_2. Express c_A and c_B in terms of α_1, α_2, and β in a Hückel type of approximation.

13.16 Write $\psi = a\psi_{2s} + b\psi_{1s}$, and choose a and b so that

$$\int \psi_{1s}\psi\, d\tau = a\int \psi_{1s}\psi_{2s} d\tau + b = 0$$

$$\int \psi^2 d\tau = \int (a\psi_{2s} + b\psi_{1s})^2 d\tau = a^2 + b^2 + 2ab \int \psi_{2s}\psi_{1s} d\tau = 1$$

Write $S = \int \psi_{1s}\psi_{2s} d\tau$, then

$$b = -aS \text{ and } a = \frac{1}{(1-S^2)^{1/2}}$$

Consequently, the orthogonalized 2s-orbital is

$$\psi = \frac{\psi_{2s} - S\psi_{1s}}{(1-S^2)^{1/2}}, \quad S = \int \psi_{1s}\psi_{2s}\mathrm{d}\tau$$

Then, since $\psi_{2s}(0) = 0$,

$$\psi^2(0) = S^2\psi_{1s}^2(0)/(1-S^2)$$

$$\psi_{1s} = (Z_{1s}^{*3}/\pi a_0^3)^{1/2}\mathrm{e}^{-Z_{1s}^{*}r/a_0} \qquad \text{[Exercise 13.12]}$$

$$\psi_{1s}^2(0) = Z_{1s}^{*3}/\pi a_0^3$$

$$\psi_{2s} = (Z_{2s}^{*5}/96\pi a_0^5)^{1/2} r\mathrm{e}^{-Z_{2s}^{*}r/2a_0}$$

$$S = 4\pi(Z_{1s}^{*3}Z_{2s}^{*5}/96\pi^2 a_0^8)^{1/2}\int_0^\infty r^2\{r\mathrm{e}^{-Z_{2s}^{*}r/2a_0}\}\{\mathrm{e}^{-Z_{1s}^{*}r/a_0}\}\mathrm{d}r$$

$$= 4\pi\left(\frac{Z_{1s}^{*3}Z_{2s}^{*5}}{96\pi^2 a_0^8}\right)^{1/2}\left\{\frac{3!a_0^4}{(Z_{1s}^{*} + \frac{1}{2}Z_{2s}^{*})^4}\right\}$$

$$= \frac{(6Z_{1s}^{*3}Z_{2s}^{*5})^{1/2}}{(Z_{1s}^{*} + \frac{1}{2}Z_{2s}^{*})^4}$$

Consequently,

$$\psi^2(0) = \frac{(6/\pi a_0^3)Z_{1s}^{*6}Z_{2s}^{*5}/(Z_{1s}^{*} + \frac{1}{2}Z_{2s}^{*})^8}{1 - 6Z_{1s}^{*3}Z_{2s}^{*5}/(Z_{1s}^{*} + \frac{1}{2}Z_{2s}^{*})^8}$$

$$= \frac{(6/\pi a_0^3) Z_{1s}^{*6} Z_{2s}^{*5}}{(Z_{1s}^* + \frac{1}{2} Z_{2s}^*)^8 - 6 Z_{1s}^{*3} Z_{2s}^{*5}}$$

In the case of ^{14}N, $Z_{1s}^* = 6.67$, $Z_{2s}^* = 3.85$ [Table 7.3], and $\psi^2(0) = 15.8/\pi a_0^3$. Therefore, with

$$H^{(\text{spin})} = CI_z s_z \quad C = (2 g_e g_N \mu_B \mu_N \mu_0 / 3\hbar^2)\psi^2(0) \quad \text{[eqn 13.97b]}$$

$$\hbar^2 C = 10.5(g_e g_N \mu_B \mu_N \mu_0 / \pi a_0^3)$$

Since $g_N(^{14}\text{N}) = 0.40356$

$$\hbar^2 C = 1.1 \times 10^{-24}\ \text{J}; \quad \underline{\hbar^2 C/h = 1.7\ \text{GHz}}$$

(The experimental value is 1.5 GHz.)

Exercise: Find an expression for the contact interaction involving an electron in an orthogonalized Slater 3s-orbital (i.e. one orthogonalized to both ψ_{1s} and the orthogonalized ψ_{2s}).