Chapter 12

The electric properties of molecules

Exercises

12.1 **(a)** $\langle\mu_z\rangle = \alpha\mathcal{E}$ [eqn 12.9, $\mu_{0z} = 0$; $\alpha_{zz} = \alpha$]

$= 4\pi\varepsilon_0\alpha'\mathcal{E}$ [eqn 12.19, $\alpha = 4\pi\varepsilon_0\alpha'$]

$= (1.112\ 65 \times 10^{-10}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^{-1}) \times (10.5 \times 10^{-30}\ \text{m}^3) \times (1.0 \times 10^4\ \text{V m}^{-1})$

$= (1.17 \times 10^{-39}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^2) \times (1.0 \times 10^4\ \text{V m}^{-1})$

$= 1.17 \times 10^{-35}$ C m ($\underline{3.5 \times 10^{-6}\ \text{D}}$) [$1\ \text{D} = 3.336 \times 10^{-30}$ C m]

(b) $E(\mathcal{E}) - E(0) = -\frac{1}{2}\alpha\mathcal{E}^2 = -5.85 \times 10^{-32}$ J ($\underline{-3.52 \times 10^{-11}\ \text{kJ mol}^{-1}}$)

Exercise: Calculate the dipole moment induced by a singly charged ion at a distance of (a) 0.1 nm, (b) 1.0 nm from a tetrachloromethane molecule.

12.2 Use eqn 12.27 to estimate the polarizibility for the hydrogen atom. The number of valence electrons, N_V, is one; take ΔE to be the ionization energy of hydrogen, 13.6 eV or 2.18×10^{-18} J.

$$\alpha = \frac{\hbar^2 e^2 N_V}{m_e \Delta E^2}$$

$$= \frac{(1.055\times10^{-34}\ \mathrm{Js})^2 \times (1.602\times10^{-19}\ \mathrm{C})^2 \times 1}{(9.109\times10^{-31}\ \mathrm{kg}) \times (2.18\times10^{-18}\ \mathrm{J})^2}$$

$$= \underline{6.60 \times 10^{-41}\ \mathrm{J^{-1}\ C^2\ m^2}}$$

This answer gives $\underline{\alpha' = 5.93 \times 10^{-31}\ \mathrm{m^3}}$ which differs by 10.% from the experimental value.

Exercise: Suggest why the agreement between the computed and eperimental values for the polarizibilty volume is reasonably good.

12.3 $$\alpha = (\hbar^2 e^2/m_e) \sum_{n\neq 0} \left\{ f_{n0} / \Delta E_{n0}^2 \right\} \text{ [eqn 12.25]}$$

$$\approx (\hbar^2 e^2/m_e)(f/\Delta E^2) \quad \text{[one transition dominating]}$$

$$\approx (e^2/4\pi^2 m_e c^2)\lambda^2 f \quad [\Delta E = hc/\lambda]$$

$$\alpha' = \alpha/4\pi\varepsilon_0 = (e^2/16\pi^3 \varepsilon_0 m_e c^2)\lambda^2 f$$

$$= (7.138 \times 10^{-17}\ \mathrm{m})\lambda^2 f = (7.138 \times 10^{-29}\ \mathrm{cm^3})(\lambda/\mathrm{nm})^2 f$$

For $\lambda = 160$ nm and $f = 0.3$, $\alpha' \approx \underline{5 \times 10^{-31}\ \mathrm{m^3}}$, which is an order of magnitude smaller than the experimental value.

Exercise: Find a expression for α' in terms of the integrated absorption coefficient of a band.

12.4 $E^{(2)} \approx -\frac{3}{2}[I_A I_B/(I_A + I_B)](\alpha'_A \alpha'_B / R^6)$ [eqn 12.40]

$I = I_A = I_B \approx 13.6$ eV $= 1312$ kJ mol^{-1}; $\alpha'_A = \alpha'_B = 6.6 \times 10^{-31}$ m^3 [Exercise 12.2]

Consequently,

$E^{(2)} \approx -\frac{3}{4} I\alpha'^2/R^6 = \underline{-(4.29 \times 10^{-4}\ \text{kJ mol}^{-1}) \times \{1/(R/\text{nm})^6\} = -4.29 \times 10^{-10}\ \text{kJ mol}^{-1}}$

Exercise: Evaluate the dispersion energy directly on the basis of eqn 12.17 and the matrix elements listed in the solution to Problem 12.3.

12.5 $E^{(2)} \approx -(23\hbar c/4\pi)(\alpha'_A\alpha'_B/R^7)$ [eqn 12.41]

$= -(23\times1.055\times10^{-34}\ \text{J s}\times2.9979\times10^{8}\ \text{m s}^{-1}/4\pi)\times(6.6\times10^{-31}\ \text{m}^3)^2/(10.0\times10^{-9}\ \text{m})^7$

$= -2.52\times10^{-30}\ \text{J or } -1.52\times10^{-9}\ \text{kJ mol}^{-1}$

12.6 The relative permittivity of a non-polar molecule such as tetracholoromethane is given by eqn 12.54:

$\varepsilon_r = (1 + 2\alpha\mathcal{N}/3\varepsilon_0)/(1 - \alpha\mathcal{N}/3\varepsilon_0)$

Since $\alpha = 4\pi\varepsilon_0\alpha'$ (eqn 12.19), $\mathcal{N} = N_A\rho/M$ (Section 12.3), and for tetracholoromethane $\alpha' = 1.05 \times 10^{-29}\ \text{m}^3$, $\rho = 1594\ \text{kg m}^{-3}$, $M = 0.153822\ \text{kg mol}^{-1}$, the relative permittivity is

$\varepsilon_r = (1 + 8\pi\alpha' N_A\rho/3M)/(1 - 4\pi\alpha' N_A\rho/3M)$

$= \underline{2.135}$

12.7 The dipole-moment density is the average of $\mu_0 \cos\theta$ weighted by the Boltzmann factor and divided by the volume V, of the sample:

$$P = \frac{\int_0^\pi \mu_0 \cos\theta\, \mathrm{d}N(\theta)}{V} = \frac{Nx\mu_0 \int_0^\pi \cos\theta\, \mathrm{e}^{x\cos\theta} \sin\theta\, \mathrm{d}\theta}{V(\mathrm{e}^x - \mathrm{e}^{-x})}$$

where we have used eqn 12.56 for the Boltzmann factor. To evaluate the above integral, let $u = \cos\theta$, $\mathrm{d}u = -\sin\theta\,\mathrm{d}\theta$:

$$\int_0^\pi \cos\theta\, \mathrm{e}^{x\cos\theta} \sin\theta\, \mathrm{d}\theta = -\int_1^{-1} u\mathrm{e}^{xu}\mathrm{d}u = \int_{-1}^{1} u\mathrm{e}^{xu}\mathrm{d}u$$

Using the standard integral:

$$\int y\mathrm{e}^{ay}\mathrm{d}y = \frac{\mathrm{e}^{ay}}{a^2}(ay-1) + \text{ constant}$$

we have

$$\int_{-1}^{1} u\mathrm{e}^{xu}\mathrm{d}u = \frac{\mathrm{e}^{xu}}{x^2}(ux-1)\Big|_{-1}^{1}$$

$$= \frac{\mathrm{e}^{x}}{x^2}(x-1) - \frac{\mathrm{e}^{-x}}{x^2}(-x-1)$$

$$= \frac{\mathrm{e}^{x}+\mathrm{e}^{-x}}{x} - \frac{\mathrm{e}^{x}-\mathrm{e}^{-x}}{x^2}$$

Therefore,

$$P = \frac{Nx\mu_0\int_0^{\pi}\cos\theta\,\mathrm{e}^{x\cos\theta}\sin\theta\,\mathrm{d}\theta}{V(\mathrm{e}^{x}-\mathrm{e}^{-x})}$$

$$= \frac{Nx\mu_0}{V(\mathrm{e}^{x}-\mathrm{e}^{-x})}\left(\frac{\mathrm{e}^{x}+\mathrm{e}^{-x}}{x} - \frac{\mathrm{e}^{x}-\mathrm{e}^{-x}}{x^2}\right)$$

$$= \mu_0\left(\frac{N}{V}\right)\left(\frac{\mathrm{e}^{x}+\mathrm{e}^{-x}}{\mathrm{e}^{x}-\mathrm{e}^{-x}} - \frac{1}{x}\right)$$

which, with $\mathcal{N}=N/V$ and the definition of the Langevin function in eqn 12.58, is eqn 12.57.

12.8 The number density $\mathcal{N}= N_{\mathrm{A}}\rho/M$. Therefore, eqn 12.62b can be written as

$$\varepsilon_{\mathrm{r}} = \frac{1+2C}{1-C}$$

where

$$C = \left(\alpha + \frac{\mu_0^2}{3kT}\right)\rho N_{\mathrm{A}}/3M\varepsilon_0$$

We now confirm that the expression for C above matches that given in eqn 12.63.

$$C = \left(4\pi\varepsilon_0\alpha' + \frac{\mu_0^2}{3kT}\right)\rho N_{\mathrm{A}}/3M\varepsilon_0$$

$$= \frac{4\pi\varepsilon_0\alpha'\rho N_{\mathrm{A}}}{3M\varepsilon_0} + \frac{\mu_0^2\rho N_{\mathrm{A}}}{9\varepsilon_0 MkT}$$

$$= \frac{4\pi\rho N_{\mathrm{A}}}{3M}(\alpha' + \mu_0^2/12\pi\varepsilon_0 kT)$$

12.9 Begin with the equation following eqn 12.70:

$$\langle\mu_z\rangle = \mu_{0z} + \sum_{n\neq 0}\{\mu_{z,0n}a_n(t)\mathrm{e}^{-\mathrm{i}\omega_{n0}t} + \mu_{z,n0}a_n^*(t)\mathrm{e}^{\mathrm{i}\omega_{n0}t}\}$$

We need to substitute into the above equation the expressions for $a_n(t)$ and its complex conjugate obtained from eqn 12.72:

$$a_n(t) = \frac{\mu_{z,n0}\,\mathcal{E}}{\hbar}\left\{\frac{e^{i(\omega+\omega_{n0})t}}{\omega+\omega_{n0}} - \frac{e^{-i(\omega-\omega_{n0})t}}{\omega-\omega_{n0}}\right\}$$

$$a_n^*(t) = \frac{\mu_{z,n0}^*\,\mathcal{E}}{\hbar}\left\{\frac{\mathrm{e}^{-\mathrm{i}(\omega+\omega_{n0})t}}{\omega+\omega_{n0}} - \frac{\mathrm{e}^{\mathrm{i}(\omega-\omega_{n0})t}}{\omega-\omega_{n0}}\right\}$$

Proceed piecewise and use $\mathrm{e}^{\mathrm{i}x} = \cos x + \mathrm{i}\sin x$:

$$\mu_{z,0n}a_n(t)\mathrm{e}^{-\mathrm{i}\omega_{n0}t} = \frac{|\mu_{z,n0}|^2\,\mathcal{E}}{\hbar}\left\{\frac{\mathrm{e}^{\mathrm{i}\omega t}}{\omega+\omega_{n0}} - \frac{\mathrm{e}^{-\mathrm{i}\omega t}}{\omega-\omega_{n0}}\right\}$$

$$= \frac{|\mu_{z,n0}|^2\,\mathcal{E}}{\hbar}\left\{\frac{\omega(\mathrm{e}^{\mathrm{i}\omega t} - \mathrm{e}^{-\mathrm{i}\omega t}) - \omega_{n0}(\mathrm{e}^{\mathrm{i}\omega t} + \mathrm{e}^{-\mathrm{i}\omega t})}{\omega^2 - \omega_{n0}^2}\right\}$$

$$= \frac{2|\mu_{z,n0}|^2\,\mathcal{E}}{\hbar}\left\{\frac{\mathrm{i}\omega\sin\omega t - \omega_{n0}\cos\omega t}{\omega^2 - \omega_{n0}^2}\right\}$$

$$\mu_{z,n0}a_n^*(t)e^{i\omega_{n0}t} = \frac{|\mu_{z,n0}|^2\,\mathcal{E}}{\hbar}\left\{\frac{e^{-i\omega t}}{\omega+\omega_{n0}} - \frac{e^{i\omega t}}{\omega-\omega_{n0}}\right\}$$

$$= \frac{|\mu_{z,n0}|^2\,\mathcal{E}}{\hbar}\left\{\frac{\omega(e^{-i\omega t}-e^{i\omega t})-\omega_{n0}(e^{i\omega t}+e^{-i\omega t})}{\omega^2-\omega_{n0}^2}\right\}$$

$$= \frac{2|\mu_{z,n0}|^2\,\mathcal{E}}{\hbar}\left\{\frac{-i\omega\sin\omega t-\omega_{n0}\cos\omega t}{\omega^2-\omega_{n0}^2}\right\}$$

$$\mu_{z,0n}a_n(t)\mathrm{e}^{-\mathrm{i}\omega_{n0}t} + \mu_{z,n0}a_n^*(t)\mathrm{e}^{\mathrm{i}\omega_{n0}t}$$

$$= \frac{2|\mu_{z,n0}|^2\,\mathcal{E}}{\hbar}\left\{\frac{\mathrm{i}\omega\sin\omega t-\omega_{n0}\cos\omega t-\mathrm{i}\omega\sin\omega t-\omega_{n0}\cos\omega t}{\omega^2-\omega_{n0}^2}\right\}$$

$$= \frac{2|\mu_{z,n0}|^2\,\mathcal{E}}{\hbar}\left\{\frac{2\omega_{n0}\cos\omega t}{\omega_{n0}^2-\omega^2}\right\}$$

Therefore,

$$\langle\mu_z\rangle = \mu_{0z} + \sum_{n\neq 0}\frac{2|\mu_{z,n0}|^2\,\mathcal{E}}{\hbar}\left\{\frac{2\omega_{n0}\cos\omega t}{\omega_{n0}^2-\omega^2}\right\}$$

$$= \mu_{0z} + \left\{\frac{2}{\hbar}\sum_{n\neq 0}\left\{\frac{\omega_{n0}\,|\mu_{z,n0}|^2}{\omega_{n0}^2-\omega^2}\right\}\right\}\times 2\,\mathcal{E}\cos\omega t$$

which is eqn 12.73.

12.10 Let $D = \alpha(\omega)\mathcal{N}/\varepsilon_0$. Then, from eqn 12.78,

$$n_{\mathrm{r}}^2 = \frac{1+2D/3}{1-D/3}$$

which, upon substitution into the left-hand side of eqn 12.79, yields

$$\frac{n_{\mathrm{r}}^2-1}{n_{\mathrm{r}}^2+2} = \frac{\dfrac{1+2D/3}{1-D/3}-\dfrac{1-D/3}{1-D/3}}{\dfrac{1+2D/3}{1-D/3}+\dfrac{2-2D/3}{1-D/3}} = \frac{\dfrac{D}{1-D/3}}{\dfrac{3}{1-D/3}} = \frac{D}{3}$$

With $D = \alpha(\omega)\mathcal{N}/\varepsilon_0$, the expression $D/3$ matches the right-hand side of eqn 12.79.

12.11 $\varphi_\pm = \omega t - 2\pi z n_\pm \nu/c = \omega t - z n_\pm \omega/c$ [eqn 12.84, $\omega = 2\pi\nu$]

Letting $n = \frac{1}{2}(n_+ + n_-)$ and $\Delta n = n_+ - n_-$, we obtain $n_+ = n + \Delta n/2, n_- = n - \Delta n/2$ or $n_\pm = n \pm \Delta n/2$. Therefore

$$\varphi_\pm = \omega t - \frac{zn_\pm\omega}{c} = \omega t - \frac{z\left(n \pm \frac{\Delta n}{2}\right)\omega}{c} = \omega t - \frac{zn\omega}{c} \mp \frac{\omega z\Delta n}{2c}$$

which is eqn 12.85.

Problems

12.1 $\alpha_{xx} = 2\sum_{n\neq 0} \{\mu_{x,0n}\mu_{x,n0}/\Delta E_{n0}\}$ [eqn 12.16 with $z \to x$]

$$\mu_{x,0n} = \langle 0| - ex + \tfrac{1}{2}eL|n\rangle = -e\langle 0|x|n\rangle \quad [\langle 0|L|n\rangle = \langle 0|n\rangle L = 0,\ n \neq 0]$$

$$\langle 0|x|n\rangle = \begin{cases} -(8/\pi^2)Ln/(n^2-1)^2, & n \text{ even} \\ 0 & n \text{ odd} \end{cases} \quad \text{[Problem 6.8]}$$

$$\Delta E_{n0} = (n^2 - 1)(h^2/8mL^2)$$

$$\alpha_{xx} = 2e^2(8L/\pi^2)^2(8mL^2/h^2)\sum_n^{\text{even}} \{n^2/(n^2-1)^5$$

$$= 2(8/\pi^2)^2 a\sum_n^{\text{even}} \{n^2/(n^2-1)^5 \quad a = (eL)^2/(h^2/8mL^2)$$

$$\sum_n^{\text{even}} \{n^2/(n^2-1)^5 = 0.016\,48 \quad \text{[Problem 6.8]}$$

Therefore, $\alpha_{xx} = 0.021\,66a = \dfrac{0.021\,66e^2L^2}{h^2/8mL^2}$.

For $m = m_e$, $\alpha_{xx} = 9.229\ (L/\text{pm})^4 \times 10^{-51}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^2$

$$\alpha'_{xx} = \alpha_{xx}/4\pi\varepsilon_0 = 8.295 \times 10^{-35}\ (L/\text{pm})^4\ \text{cm}^3$$

With L = 150 pm, $\alpha'_{xx} = \underline{4.199 \times 10^{-26}\ \text{cm}^3}$.

Exercise: Calculate the polarizability volume of a rectangular, three-dimensional box of sides X, Y, Z, and the mean polarizability volume, and relate α' to $V = XYZ$.

12.4. We continue with Problem 12.3, including the contribution from all p-orbitals:

$$\alpha_{zz} = (2^9 e^2 a_0^2/3hc\mathrm{R_H}) \sum_{n=2}^{\infty} \left\{ \frac{n^9 (n-1)^{2n-5}}{(n+1)^{2n+5}(n^2-1)} \right\}$$

$$= (2^9 e^2 a_0^2/3hc\mathrm{R_H}) \sum_{n=2}^{\infty} \left\{ \frac{n^9 (n-1)^{2n-6}}{(n+1)^{2n+6}} \right\}$$

$$= (2^9 e^2 a_0^2/3hc\mathrm{R_H})\{0.0087 + 0.0012 + 0.0004 + \ldots\}$$

$$= (2^9 e^2 a_0^2/3hc\mathrm{R_H}) \times 0.0106 = 5.97 \times 10^{-41}\ \mathrm{J^{-1}\ C^2\ m^2}$$

$$\alpha'_{zz} = \alpha_{zz}/4\pi\varepsilon_0 = \underline{5.37 \times 10^{-25}\ \text{cm}^3}$$

Exercise: Calculate the polarizability of one-electron ions with atomic number Z.

12.7 To derive the expression for the third-order correction to the energy, which we denote $E_0^{(3)}$, we follow the procedure set out in Section 6.2. We include the term $\lambda^3 H^{(3)}$ in eqn 6.20a, $\lambda^3 \psi_0^{(3)}$ in eqn 6.20b, and $\lambda^3 E_0^{(3)}$ in eqn 6.20c. We then obtain in addition to the equations shown in eqn 6.21 the following equation by collecting λ^3 coefficients:

$$\{H^{(0)} - E_0^{(0)}\}\,\psi_0^{(3)} = \{E_0^{(3)} - H^{(3)}\}\,\psi_0^{(0)} + \{E_0^{(2)} - H^{(2)}\}\,\psi_0^{(1)} + \{E_0^{(1)} - H^{(1)}\}\,\psi_0^{(2)}$$

The first- and second-order corrections to the energy are given in eqns 6.24 and 6.30, respectively; the first-order correction to the wavefunction is given in eqn 6.27. For later use, the second- and third-order corrections to the wavefunction are written as

$$\Psi_0^{(2)} = \sum_{n\neq 0} b_n \Psi_n^{(0)}$$

$$\Psi_0^{(3)} = \sum_{n\neq 0} c_n \Psi_n^{(0)}$$

The equation above obtained by collection of λ^3 coefficients is written in ket notation as

$$\{H^{(0)} - E_0^{(0)}\}\sum_{n\neq 0} c_n|n\rangle = \{E_0^{(3)} - H^{(3)}\}|0\rangle + \{E_0^{(2)} - H^{(2)}\}\sum_{n\neq 0} a_n|n\rangle$$

$$+ \ \{E_0^{(1)} - H^{(1)}\}\sum_{n\neq 0} b_n|n\rangle$$

where the coefficients a_n for the first-order correction to the wavefunction are given by eqn 6.26. We now multiply this equation through from the left by $\langle 0|$, which gives (recognizing that $H^{(0)}|n\rangle = E_n^{(0)}|n\rangle$)

$$0 = E_0^{(3)} - H_{00}^{(3)} - \sum_{n\neq 0} a_n H_{0n}^{(2)} - \sum_{n\neq 0} b_n H_{0n}^{(1)}$$

If the matrix elements of the second- and third-order perturbations $H^{(2)}$ and $H^{(3)}$ vanish, then the above expression simplies to

$$E_0^{(3)} = \sum_{n\neq 0} b_n H_{0n}^{(1)}$$

To find the third-order correction to the energy, we need the coefficients b_n. To find them, we start with eqn 6.29a and multiply through from the left by $\langle k|$ (setting matrix elements of $H^{(2)}$ to zero):

$$b_k\{E_k^{(0)} - E_0^{(0)}\} = a_k E_0^{(1)} - \sum_{n\neq 0} a_n H_{kn}^{(1)}$$

Therefore, using eqns 6.24 and 6.26, we find

$$b_k = -\frac{H_{00}^{(1)}H_{k0}^{(1)}}{(E_0^{(0)} - E_k^{(0)})^2} - \sum_{n\neq 0}\frac{H_{n0}^{(1)}H_{kn}^{(1)}}{(E_0^{(0)} - E_n^{(0)})(E_k^{(0)} - E_0^{(0)})}$$

When we replace in the above equation the indices n by m, and k by n and substitute the resulting expression for b_n into $E_0^{(3)} = \sum_n b_n H_{0n}^{(1)}$, we obtain

$$E_0^{(3)} = -H_{00}^{(1)}\sum_{n\neq 0}\frac{H_{n0}^{(1)}H_{0n}^{(1)}}{(E_0^{(0)} - E_n^{(0)})^2}$$

$$-\sum_{n\neq 0}\sum_{m\neq 0}\frac{H_{m0}^{(1)}H_{nm}^{(1)}H_{0n}^{(1)}}{(E_0^{(0)} - E_m^{(0)})(E_n^{(0)} - E_0^{(0)})}$$

which matches (upon interchange of the indices m and n in the double summation) the expression given in Problem 12.6.

Exercise: Derive the expression for the third-order correction to the wave-function.

12.10

$$[H, x^2] = -(\hbar^2/2m_e)[(d^2/dx^2), x^2] \qquad [[V, x^2] = 0]$$

$$= -(\hbar^2/2m_e)\{(d^2/dx^2)x^2 - x^2(d^2/dx^2)\}$$

$$= -(\hbar^2/2m_e)\{2 + 4x(d/dx) + x^2(d^2/dx^2) - x^2(d^2/dx^2)\}$$

$$= -(\hbar^2/m_e) - 2(\hbar^2/m_e)x(d/dx)$$

$$= -(\hbar^2/m_e) - 2i(\hbar/m_e)xp$$

$$\langle m|[H, x^2]|n\rangle = (E_m - E_n)\langle m|x^2|n\rangle = \hbar\omega_{mn}(x^2)_{mn}$$

$$= \langle m| - (\hbar^2/m_e) - 2i(\hbar/m_e)xp|n\rangle$$

$$= -(\hbar^2/m_e)\delta_{mn} - 2i(\hbar/m_e)\sum_f x_{mf}\, p_{fn}$$

$$= -(\hbar^2/m_e)\delta_{mn} - 2i(\hbar/m_e)(\mathrm{i}m_e)\sum_f x_{mf}\,\omega_{fn} x_{fn} \quad \text{[eqn 12.112 in FI 12.2]}$$

$$= -(\hbar^2/m_e)\delta_{mn} + 2\hbar\sum_f x_{mf}\, x_{fn}\,\omega_{fn}$$

Therefore

$$\sum_f x_{mf}\, x_{fn}\,\omega_{fn} = (\hbar/2m_e)\delta_{mn} + \tfrac{1}{2}\,\omega_{mn}(x^2)_{mn}$$

Exercise: Devise a sum rule based on $[H, x^3]$.

12.13

$$\left.\begin{aligned} n_r(\omega) &\approx 1 + (N_A\rho/3\hbar\varepsilon_0 M)C(\omega) \\ C(\omega) &= \sum_{n\neq 0}\frac{\omega_{n0}|\mu_{0n}|^2}{\omega_{n0}^2-\omega^2} \end{aligned}\right\} \quad \text{[eqn 12.77]}$$

Evaluate $C(\omega)$ numerically, drawing on the information in the solution of Problem 12.4.

$$C(\omega) = \sum_{n,l,m_l \neq (1,0,0)} \frac{\omega_{n,1s} \,|\, \mu_{1s,nlm_l} \,|^2}{\omega_{n,1s}^2 - \omega^2}$$

$$= 3 \sum_{n,l,m_l \neq (1,0,0)} \frac{\omega_{n,1s} \,|\, \mu_{z;1s,nlm_l} \,|^2}{\omega_{n,1s}^2 - \omega^2} \quad [\mu_x^2 = \mu_y^2 = \mu_z^2]$$

$$= 3e^2 \sum_{n \neq 1} \frac{\omega_{n,1s} \,|\, z_{np_z}, 1s \,|^2}{\omega_{n,1s}^2 - \omega^2} \quad [\text{only } n\text{p}_z\text{-orbitals contribute}]$$

$$= (3e^2 \mathrm{R_H}/2\pi c) \sum_{n \neq 1} \frac{[1-(1/n^2)] \,|\, z_{np_z}, 1s \,|^2}{[1-(1/n^2)]^2 \mathrm{R_H^2} - (1/\lambda^2)}$$

$$\left[\hbar\omega_{n,1s} = hc\mathrm{R_H}\left(1 - \frac{1}{n^2}\right)\right]$$

$$= (2^7/\pi)(e^2 a_0^2 \mathrm{R_H}/c) \sum_{n \neq 1} \frac{[1-(1/n^2)]n^7 (n-1)^{2n-5}/(n+1)^{2n+5}}{[1-(1/n^2)]^2 \mathrm{R_H^2} - (1/\lambda^2)}$$

$$= (2^7/\pi)(e^2 a_0^2 /\mathrm{R_H} c) D(\lambda),$$

$$D(\lambda) = \sum_{n \neq 1} \frac{[1-(1/n^2)]n^7 (n-1)^{2n-5}/(n+1)^{2n+5}}{[1-(1/n^2)]^2 - (1/\lambda \mathrm{R_H})^2}$$

$$= \sum_{n \neq 1} \frac{n^9 (n-1)^{2n-4}/(n+1)^{2n+4}}{(n^2-1)^2 - \gamma^2 n^4}, \quad \gamma = 1/\lambda \mathrm{R_H}$$

Since $\gamma = 1/(590\text{ nm}) \times (1.097 \times 10^5\text{ cm}^{-1}) = 0.155$, numerical evaluation of the sum (up to $n \approx 20$) leads to D(590 nm) = 0.0112. Therefore,

$$C = (8.91 \times 10^{-73}\text{ C}^2\text{ m}^2\text{ s})D = 9.98 \times 10^{-75}\text{ C}^2\text{ m}^2\text{ s}$$

Consequently,

$$n_r \approx 1 + (\mathcal{N}/3\hbar\varepsilon_0)C \quad [\rho = Nm_{\mathrm{H}}/V,\ m_{\mathrm{H}} = M(H)/N_{\mathrm{A}}]$$

$$\approx 1 + (\mathcal{N}/\text{atoms m}^{-3}) \times (3.56 \times 10^{-30})$$

When $\mathcal{N} \approx 10^5$ atoms m^{-3}

$$n_r - 1 \approx \underline{3.6 \times 10^{-25}}$$

For a gas of atoms at 1.00 atm and 25°C,

$$\mathcal{N} = p/kT = 2.46 \times 10^{25}\ \mathrm{m}^{-3}$$

and then $n_r \approx 1.000\ 088$.

Exercise: Find an expression for the refractive index of a gas of one-electron ions of atomic number Z.

12.16 Take as a trial function $\psi = \psi_{1\mathrm{s}} + a\psi_{2\mathrm{p}_z}$ for each atom, so that the overall trial function is

$$\psi = (\psi_{\mathrm{A},1\mathrm{s}} + a_{\mathrm{A}}\psi_{\mathrm{A},2\mathrm{p}_z})(\psi_{\mathrm{B},1\mathrm{s}} + a_{\mathrm{B}}\psi_{\mathrm{B},2\mathrm{p}_z})$$

The denominator of the Rayleigh ratio is therefore

$$\int \psi^2 \mathrm{d}\tau = \int (\psi_{\mathrm{A},1\mathrm{s}} + a_{\mathrm{A}}\psi_{\mathrm{A},2\mathrm{p}_z})^2 (\psi_{\mathrm{B},1\mathrm{s}} + a_{\mathrm{B}}\psi_{\mathrm{B},2\mathrm{p}_z})^2 \mathrm{d}\tau_{\mathrm{A}}\mathrm{d}\tau_{\mathrm{B}}$$

$$= (1 + a_{\mathrm{A}}^2)(1 + a_{\mathrm{B}}^2) \quad \text{[basis functions are orthonormal]}$$

The hamiltonian is

$$H = H_{\mathrm{A}} + H_{\mathrm{B}} + H^{(1)}, \quad H_{\mathrm{A}}\psi_{\mathrm{A},nl} = E_n\psi_{\mathrm{A},nl}$$

The numerator of the Rayleigh ratio is therefore

$$\int \psi H \psi \, \mathrm{d}\tau = \int (\psi_{\mathrm{A,1s}} + a_{\mathrm{A}}\psi_{\mathrm{A,2p}_z})(\psi_{\mathrm{B,1s}} + a_{\mathrm{B}}\psi_{\mathrm{B,2p}_z})$$

$$\times \{(E_1\psi_{\mathrm{A,1s}} + a_{\mathrm{A}}E_2\psi_{\mathrm{A,2p}_z})(\psi_{\mathrm{B,1s}} + a_{\mathrm{B}}\psi_{\mathrm{B,2p}_z})$$

$$+ (\psi_{\mathrm{A,1s}} + a_{\mathrm{A}}\psi_{\mathrm{A,2p}_z})(E_1\psi_{\mathrm{B,1s}} + a_{\mathrm{B}}E_2\psi_{\mathrm{B,2p}_z})$$

$$+ H^{(1)}(\psi_{\mathrm{A,1s}} + a_{\mathrm{A}}\psi_{\mathrm{A,2p}_z})(\psi_{\mathrm{B,1s}} + a_{\mathrm{B}}\psi_{\mathrm{B,2p}_z})\}$$

$$= (E_1 + a_{\mathrm{A}}^2 E_2)(1 + a_{\mathrm{B}}^2) + (E_1 + a_{\mathrm{B}}^2 E_2)(1 + a_{\mathrm{A}}^2)$$

$$+ \int (\psi_{\mathrm{A,1s}}\psi_{\mathrm{B,1s}} + a_{\mathrm{A}}\psi_{\mathrm{A,2p}_z}\psi_{\mathrm{B,1s}}$$

$$+ a_{\mathrm{B}}\psi_{\mathrm{A,1s}}\psi_{\mathrm{B,2p}_z} + a_{\mathrm{A}}a_{\mathrm{B}}\psi_{\mathrm{A,2p}_z}\psi_{\mathrm{B,2p}_z})$$

$$\times H^{(1)}(\psi_{\mathrm{A,1s}}\psi_{\mathrm{B,1s}} + a_{\mathrm{A}}\psi_{\mathrm{A,2p}_z}\psi_{\mathrm{B,1s}} + a_{\mathrm{B}}\psi_{\mathrm{A,1s}}\psi_{\mathrm{B,2p}_z}$$

$$+ a_{\mathrm{A}}a_{\mathrm{B}}\psi_{\mathrm{A,2p}_z}\psi_{\mathrm{B,2p}_z})\mathrm{d}\tau_{\mathrm{A}}\mathrm{d}\tau_{\mathrm{B}}$$

Only the $z_{\mathrm{A}}z_{\mathrm{B}}$ components of $H^{(1)}$ contribute to the integral (because only it has nonvanishing matrix elements between 1s and $2\mathrm{p}_z$), so we take

$$H^{(1)} = -2(1/4\pi\varepsilon_0 R^3)\mu_{\mathrm{A}z}\mu_{\mathrm{B}z}$$

Then the only surviving terms are

$$2a_{\mathrm{A}}a_{\mathrm{B}}\left\{\int \psi_{\mathrm{A,1s}}\psi_{\mathrm{B,1s}}H^{(1)}\psi_{\mathrm{A,2p}_z}\psi_{\mathrm{B,2p}_z}\mathrm{d}\tau_{\mathrm{A}}\mathrm{d}\tau_{\mathrm{B}}\right.$$

$$\left.+\int \psi_{\mathrm{A,2p}_z}\psi_{\mathrm{B,2p}_z}H^{(1)}\psi_{\mathrm{A,1s}}\psi_{\mathrm{B,1s}}\mathrm{d}\tau_{\mathrm{A}}\mathrm{d}\tau_{\mathrm{B}}\right\}$$

$$= -(e^2/\pi\varepsilon_0 R^3)a_{\mathrm{A}}a_{\mathrm{B}}z_{\mathrm{A;1s,2p}_z}z_{\mathrm{B;1s,2p}_z}$$

$$= -a_{\mathrm{A}}a_{\mathrm{B}}KZ, \quad K = e^2/\pi\varepsilon_0 R^3, \quad Z = z_{\mathrm{A;1s,2p}_z}z_{\mathrm{B;1s,2p}_z}$$

The Rayleigh ratio is then

$$\epsilon = \frac{E_1 + a_A^2 E_2}{(1+a_A^2)+(E_1+a_B^2 E_2)/(1+a_B^2)}$$

$$-\frac{a_A a_B KZ}{(1+a_A^2)+(1+a_B^2)}$$

The optimum values of $a_A a_B$ are those for which $\partial\epsilon/\partial a_A = \partial\epsilon/\partial a_B = 0$.

$$\partial\epsilon/\partial a_A = 2a_A E_2/(1+a_A^2) - 2a_A(E_1 + a_A^2 E_2)/(1+a_A^2)^2$$

$$- a_B KZ/(1+a_A^2)(1+a_B^2) + 2a_A^2 a_B KZ/(1+a_A^2)^2(1+a_B^2) = 0$$

Likewise for $\partial\epsilon/\partial a_B$. Therefore we must solve

$$2(E_2 - E_1)a_A + 2(E_2 - E_1)a_B^2 a_A - a_B KZ + a_B a_A^2 KZ = 0$$

$$2(E_2 - E_1)a_B + 2(E_2 - E_1)a_A^2 a_B - a_A KZ + a_A a_B^2 KZ = 0$$

Let $\Delta E = E_2 - E_1 = \frac{3}{4}hc\mathrm{R}_H$. Then, since $a_A^2 = a_B^2$ by symmetry, we have

$$a_A = \pm\left(\frac{KZ - 2\Delta E}{KZ + 2\Delta E}\right)^{1/2} \qquad a_B = \pm\left(\frac{KZ - 2\Delta E}{KZ + 2\Delta E}\right)^{1/2}$$

It follows that, setting $\gamma = (KZ - 2\Delta E)/(KZ + 2\Delta E)$,

$$\epsilon = \left\{\frac{2E_1 + 2\gamma E_2}{1+\gamma}\right\} - \left\{\frac{\gamma KZ}{(1+\gamma)^2}\right\}$$

Exercise: Calculate the dispersion energy on the basis that the trial function (a) also includes a 3p-orbital component, (b) includes a ‘1p-orbital’ component.