Chapter 11

Molecular electronic transitions

Exercises

11.1 See the discussion of the Hund coupling cases in Section 11.1.

(i) We focus on which of the quantum numbers for orbital and spin angular momenta are good quantum numbers. For case (a) Ω, Λ, Σ; for case **(b)** Λ, S; for case **(c)** E, Ω; for case **(d)** L, S.

(ii) In each case, the degeneracy of a rotational energy level is $2J + 1$, where J is the total angular momentum.

Exercise: Describe mechanisms by which the angular momenta are decoupled.

11.2 Refer as needed to the discussion in Section 8.6. (i) A single electron (spin-1/2) gives rise to a doublet term. (ii) Since a d-orbital pertains to $l = 2$, the overlap of two d-orbitals, using the Clebsch-Gordan series (eqn 4.42), gives rise to terms with values of the orbital angular momenta of 0, 1, 2, 3, and 4, pertaining to Σ, Π, Δ, Φ, and Γ terms, respectively. (iii) The Σ term requires a label to describe its behaviour under reflection in a plane containing the internuclear axis. The molecular orbital constructed from face-to-face overlap of d_{xy} orbitals has the character of −1 under this operation so the term is Σ^{-}. (iv) For the parity classification of the terms, the molecular orbital does not change upon inversion through the center of the diatomic molecule so it has gerade symmetry.

The following terms therefore arise: $^2\Sigma_g^-$, $^2\Pi_g$, $^2\Delta_g$, $^2\Phi_g$, $^2\Gamma_g$

11.3 Refer to the specification of the selection rules in Section 11.3.

(a) $^2\Pi \rightarrow {}^2\Pi$ *allowed* by $\Delta\Lambda = 0$

(b) $^1\Sigma \rightarrow {}^1\Sigma$ *allowed* by $\Delta\Lambda = 0$

(c) $\Sigma \rightarrow \Delta$ *forbidden* ($\Delta\Lambda = \pm 2$ not allowed)

(d) $\Sigma^+ \rightarrow \Sigma^-$ *forbidden* by $\Sigma^+ \not\leftrightarrow \Sigma^-$

(e) $\Sigma^+ \rightarrow \Sigma^+$ *allowed* by $\Delta\Lambda = 0$ and $\Sigma^+ \leftrightarrow \Sigma^+$

(f) $^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ *allowed* by $\Delta\Lambda = 0$, $\Sigma^+ \leftrightarrow \Sigma^+$, and $g \leftrightarrow u$

(g) $^3\Sigma_g^+ \rightarrow {}^3\Sigma_u^-$ *forbidden* by $\Sigma^- \not\leftrightarrow \Sigma^+$

Exercise: Which of $^2\Pi \rightarrow {}^2\Sigma$, $^3\Pi_g \rightarrow {}^3\Sigma_u^+$, and $^3\Delta_g \rightarrow {}^1\Pi_u$ are allowed?

11.4 When a diatomic molecule with $S = 3/2$ dissociates, the two atoms that form may have spins S_1 and S_2, respectively, such that the Clebsch-Gordan series (eqn 4.42) for the resultant of S_1 and S_2 contains $S = 3/2$. For example, ($S_1 = 2$, $S_2 = 1/2$) results in $S = 5/2$, 3/2 so this combination of spins is allowed. The spin states, (S_1, S_2), of the atoms that may form are

(0, 3/2), (3/2, 0), (1/2, 1), (1, 1/2), (1/2, 2), (2, 1/2), (1, 3/2), (3/2, 1) and so on.

11.5 A Φ state pertains to $\Lambda = 3$. Therefore, the two atoms that form when the diatomic molecule dissociates may have may have orbital angular momenta L_1 and L_2, respectively, such that the Clebsch-Gordan series (eqn 4.42) for the resultant of L_1 and L_2

contains a value of 3. For example, the atomic terms (F, D) pertain to $L_1 = 3$ and $L_2 = 2$ with resultant values of 5, 4, 3, 2, 1, 0; therefore, since a value of 3 is possible, the atomic terms (F, D) are possible. The list of possible terms includes

(F, S), (S, F), (D, P), (P, D), (D, D), (F, D), (D, F) and so on.

11.6 Dissocation of O_2^+ produces $O + O^+$. (i) The $^4\Pi_u$ state has a spin multiplicity of $(2S + 1) = 4$; that is, $S = 3/2$. Therefore, if S_1 is the total spin for the O atom (an integer since the atom has an even number of electrons) and S_2 is the total spin for the O^+ ion (a half-integer since the ion has an odd number of electrons), then possible values for S_1 and S_2 are those for which the Clebsch-Gordan series (eqn 4.42) for the coupling of S_1 and S_2 includes a value of 3/2. For example, the combination of $S_1 = 0$ (a singlet term) and $S_2 = 3/2$ (a quartet term) is possible. (ii) The $^4\Pi_u$ pertains to $\Lambda = 1$. Therefore, the states that form when the diatomic molecule dissociates may have orbital angular momenta L_1 and L_2 such that the Clebsch-Gordan series (eqn 4.42) for the resultant of L_1 and L_2 contains a value of 1. For example, the terms (P, D) pertain to $L_1 = 2$ and $L_2 = 3$ with resultant values of 5, 4, 3, 2, 1, 0; therefore, since a value of 1 is possible, the terms (P, D) are possible.

The list of possible terms includes

$O(^1P) + O^+(^4S)$, $O(^3P) + O^+(^4S)$, $O(^3P) + O^+(^2S)$, $O(^1D) + O^+(^4S)$, $O(^3D) + O^+(^4S)$, $O(^1P) + O^+(^2D)$, $O(^1S) + O^+(^2P)$, and so on.

11.7 The transition element $\langle ^1A_2|\mu_q|^1A_1\rangle$ transforms as

$$A_2 \times \Gamma(\mu_q) \times A_1 = A_2 \times \Gamma(\mu_q);$$

but as $\Gamma(\mu_q) = A_1, B_1, B_2$, it must vanish.

The normal coordinates of H_2O are of symmetry species $2A_1 + B_2$. Since $B_2 \times A_2 = B_1$, the vibronic transition matrix element

$$\langle {}^1A_2, {}^1B_2|\mu_q|{}^1A_1, {}^0B_2\rangle$$

is of symmetry species $A_2 \times B_2 \times \Gamma(\mu_q) \times A_1 \times A_1 = B_1 \times \Gamma(\mu_q)$. It is A_1 when $\Gamma(\mu_q) = B_1$, which is so where $q = x$. Therefore, an x-polarized vibronic transition may occur.

Exercise: Show that the transition ${}^2B_2 \leftarrow {}^2B_1$ is forbidden in ClO_2 (a C_{2v} molecule), but may be vibronically allowed.

11.8 Determine which states are mixed by rotations. In D_{6h} rotations transform as A_{2g} and E_{1g}. Therefore, $B_{1u} \times \{A_{2g}, E_{1g}\} = \{B_{2u}, E_{2u}\}$ and $B_{2u} \times \{A_{2g}, E_{1g}\} = \{B_{1u}, E_{2u}\}$. Therefore $\underline{{}^1B_{2u} \text{ and } {}^1E_{2u}}$ may be mixed into ${}^3B_{1u}$ and $\underline{{}^1B_{1u} \text{ and } {}^1E_{2u}}$ may be mixed into ${}^3B_{2u}$.

Exercise: What triplet states may be mixed into the ${}^1E$ state of NH_3? What states would be mixed if the molecule were planar in the ${}^1E$ excited state?

Problems

11.1 $\psi_{2s} = (Z/a_0)^{3/2}(1/2\sqrt{2})(2 - \rho)e^{-\rho/2}Y$ [Table 3.4] with $\rho = Zr/a_0$

(a)

$$\langle r\rangle = \int_0^\infty rR^2r^2\mathrm{d}r = \int_0^\infty \rho^3R^2(\rho)\mathrm{d}\rho(a_0/Z)^4$$

$$= (a_0/Z)(1/8)\int_0^\infty \rho^3(2-\rho)^2e^{-\rho}\mathrm{d}\rho \quad [Z = 2]$$

$$= \underline{12a_0/Z\ (318\ \text{pm})} \quad \left[\int_0^\infty x^3(2-x)^2e^{-x}\mathrm{d}x = 96\right]$$

(b)

$$P(R) = (Z/a_0)^3(1/8)\int_0^R (2-\rho)^2 r^2 e^{-\rho} dr$$

$$= \tfrac{1}{8}\int_0^A (2-\rho)^2 \rho^2 e^{-\rho} d\rho = 0.90 \quad [A = ZR/a_0]$$

That is, we need to solve

$$\text{Integral}(A) = \int_0^A (2-\rho)^2 \rho^2 e^{-\rho} d\rho = 7.20 \quad \text{for } A$$

The graph of this integral as a function of A is shown in Fig. 11.1. We see that it has the value 7.20 at $A = 9.12539$, so

$$R = \underline{9.12539 a_0/Z} \ (241 \text{ pm})$$

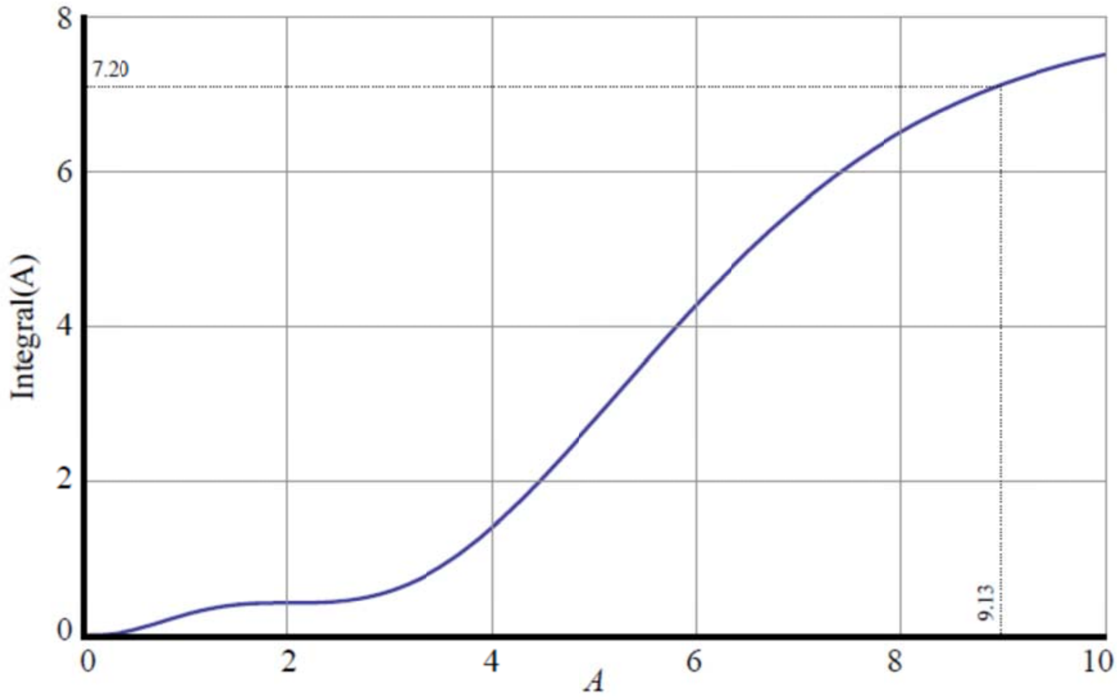

Figure 11.1: The integral in Problem 11.1 as a function of $A = ZR/a_0$.

Exercise: Repeat the calculation for a 3s-orbital.

11.4 The vibrational wavefunctions are:

$$\text{Lower: } \psi_v = N_v H_v(y) e^{-\frac{1}{2}y^2}, \quad y = (m\omega/\hbar)^{1/2} x \quad [x = R - R_e]$$

$$\text{Upper: } \psi_v = N_v H_v(y') e^{-\frac{1}{2}y'^2}, \quad y' = (m\omega/\hbar)^{1/2}(x - \Delta R)$$

Then the overlap integral is

$$S_{v0} = N_v N_0 \int_{-\infty}^{\infty} H_v(y') H_0(y) e^{-\frac{1}{2}(y^2 + y'^2)} dx$$

$$= (1/2^v v!\pi)^{1/2}\int_{-\infty}^{\infty} H_v(y')\mathrm{e}^{-\frac{1}{2}(y^2+y'^2)}\mathrm{d}y$$

$$S_{10} = (2/\pi)^{1/2}\int_{-\infty}^{\infty} y'\mathrm{e}^{-\frac{1}{2}(y^2+y'^2)}\mathrm{d}y$$

$$= (2/\pi)^{1/2}\mathrm{e}^{-\frac{1}{4}z^2}\int_{-\infty}^{\infty} y'\mathrm{e}^{-(y'+\frac{1}{2}z)^2}\mathrm{d}y'$$

$$= (2/\pi)^{1/2}\mathrm{e}^{-\frac{1}{4}z^2}\int_{-\infty}^{\infty}(w-\tfrac{1}{2}z)\mathrm{e}^{-w^2}\mathrm{d}w \quad [w = y' + \tfrac{1}{2}z]$$

$$= (2/\pi)^{1/2}\mathrm{e}^{-\frac{1}{4}z^2}(-\tfrac{1}{2}z)\int_{-\infty}^{\infty}\mathrm{e}^{-w^2}\mathrm{d}w = -(z/\sqrt{2})\mathrm{e}^{-\frac{1}{4}z^2}$$

$$S_{10}^2 = \tfrac{1}{2}z^2\mathrm{e}^{-\frac{1}{2}z^2} = \underline{(m\omega/2\hbar)\Delta R^2\exp\{-(m\omega/2\hbar)\Delta R^2\}}$$

11.7 H_2CO belongs to C_{2v}, and μ_q transforms as B_1, B_2, A_1 for x, y, z, respectively. The transition ${}^1A_2 \leftarrow {}^1A_1$ is therefore allowed only if it is vibronic [$\langle A_2|\mu_q|A_1\rangle$ does not span A_1]. Since the six vibrations of H_2CO span $3A_1 + B_1 + 2B_2$, possible singly excited vibronic states of the A_2 electronic state are of symmetry species $A_1 \times A_2 = A_2$, $B_1 \times A_2 = B_2$, and $B_2 \times A_2 = B_1$. These vibronic states may be stimulated from the A_1 state by y-polarized (B_2) or x-polarized (B_1) radiation.

Ethene belongs to D_{2h}, and μ_q transforms as B_{3u}, B_{2u}, B_{1u} for x, y, z, respectively. Therefore $B_{2u} \leftarrow A_g$ is allowed for y-polarized radiation. The vibrations of ethene span

$$3A_g + 2B_{1g} + B_{2g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u}$$

[Problem 10.23], and so the possible vibronic states of the B_{2u} electronic state are

$$B_{2u} \times (A_g, B_{1g}, B_{2g}, A_u, B_{1u}, B_{2u}, B_{3u}) = B_{2u}, B_{3u}, A_u, B_{2g}, B_{3g}, A_g, B_{1g}$$

[Refer to the character table, form $\chi(R)\chi'(R)$ for $\Gamma \times \Gamma'$, and identify the set of characters so produced]. Of these, B_{2u} and B_{3u} may be reached by an electric dipole transition from the A_g ground state.

Exercise: Assess the polarization of the $^1B_2 \leftarrow {}^1B_1$ transition in H_2CO and the $B_{1g} \leftarrow A_g$ transition in ethene.

11.10

$P_2(t) = (2V/\Omega)^2 \sin^2(\frac{1}{2}\Omega t)$, $\Omega^2 = \omega_{21}^2 + 4V^2$ [eqn 6.63].

$\hbar\omega_{21} = \hbar J$. For state 2 taken as T_0, $\hbar V = \hbar\xi/\sqrt{2}$ [Problem 11.9];

for state 2 corresponding to $T_\pm$, $\hbar V = \hbar\xi/2$. Therefore,

$$P(T_0) = \underline{\{2\xi^2/(J^2+2\xi^2)\}\sin^2\left\{\tfrac{1}{2}(J^2+2\xi^2)^{1/2}t\right\}}$$

$$P(T_\pm) = \underline{\{\xi^2/(J^2+\xi^2)\}\sin^2\left\{\tfrac{1}{2}(J^2+\xi^2)^{1/2}t\right\}}$$

$$P(T) = \underline{P(T_0)+P(T_+)+P(T_-)}$$

For a range of initial times, $0 \le t_0 \le T$; the time t then corresponds to the duration since initiation, which is $t - t_0$ for a given member of the system. Therefore, since t_0 ranges from 0 to T, the average population is:

$$\mathcal{P}(T_0) = \{2\xi^2/(J^2+2\xi^2)\}(1/T)\int_0^T \sin^2\left\{\tfrac{1}{2}(J^2+2\xi^2)^{1/2}(t-t_0)\right\}\mathrm{d}t_0$$

$$= \{2\xi^2/(J^2+2\xi^2)\}(1/T)\int_{t-T}^{t} \sin^2(a\tau)\mathrm{d}\tau \quad [\tau = t-t_0, a = \tfrac{1}{2}(J^2+2\xi^2)^{1/2}]$$

$$= \{\xi^2/(J^2+2\xi^2)\}\{1 - \gamma/2aT\}$$

$$\gamma = [1 - \cos(2aT)]\sin(2at) + \sin(2aT)\cos(2at)$$

If T is long in the sense that $2aT >> 1$,

$$\mathcal{P}(T_0) \approx \xi^2/(J^2 + 2\xi^2)$$

Likewise

$$\mathcal{P}(T_\pm) \approx \tfrac{1}{2}\xi^2/(J^2 + \xi^2)$$

Overall, therefore,

$$\mathcal{P}(T) \approx \xi^2/(J^2 + 2\xi^2) + \xi^2/(J^2 + \xi^2) = \underline{\frac{(2J^2 + 3\xi^2)\xi^2}{(J^2 + \xi^2)(J^2 + 2\xi^2)}}$$

When $J^2 >> \xi^2$, $\mathcal{P}(T) \approx 2\xi^2/J^2$.

Exercise: Suppose a magnetic field is present. How does $\mathcal{P}(T)$ depend on it?

11.13 $H\Psi = \mathcal{E}\Psi$, $\Psi = a\psi + \sum_n b_n\phi_n$; $\quad H^{(\text{bath})}\phi_n = E_n\phi_n$.

ψ should be interpreted as $\psi_{\text{system}} f_{\text{bath}}$ and ϕ as $\phi_{\text{bath}}\, g_{\text{system}}$, with $H^{(\text{bath})} f_{\text{bath}} = 0$ and $H^{(\text{sys})} g_{\text{system}} = 0$ (so that in each case no energy resides in the relevant component).

Then

$$H\Psi = aE\psi + \sum_n b_n E_n\phi_n + H'a\psi + \sum_n b_n H'\phi_n$$

$$= \mathcal{E}a\psi + \sum_n b_n\mathcal{E}\phi_n$$

Multiply by (a) ψ* and integrate, (b) ϕ_n^* and integrate (follow that by setting $n' \to n$):

$$(E - \mathcal{E})a + V\sum_n b_n = 0 \qquad [\langle \psi|\phi_n\rangle = 0, \langle \psi|H'|\psi\rangle = 0]$$

$$V_a + (E_n - \mathcal{E})b_n = 0 \qquad [\langle \phi_n|\psi\rangle = 0, \langle \phi_n|H'|\phi_{n'}\rangle = 0]$$

Then, $b_n = \{V/(\mathcal{E} - E_n)\}a$.

Substitute this expression for b_n back into the first equation of the pair:

$$(E - \mathcal{E}) + V^2\sum_n \{1/\{\mathcal{E} - E_n)\} = 0$$

Then, with $\mathcal{E} - E_n = \gamma\varepsilon - n\varepsilon$ and $\rho = 1/\varepsilon$,

$$E - \mathcal{E} = -(V^2/\varepsilon)\sum_n \{1/\{\gamma - n)\}$$

$$= \underline{(V^2\rho)\pi \cot(\pi\gamma)}$$

As Ψ is normalized to unity, $a^2 + \sum_n b_n^2 = 1$; consequently [from above]

$$a^2 + a^2V^2\sum_n \{1/(E_n - \mathcal{E})^2\} = 1$$

Since

$$\sum_{n=-\infty}^{\infty}(\gamma - n)^{-2} = \pi^2\text{cosec}^2\pi\gamma$$

[*Handbook of mathematical functions*]

$$a^2 = \{1 + \pi^2\rho^2V^2\text{cosec}^2(\pi\gamma)\}^{-1}$$

$$= \{1 + \pi^2\rho^2V^2 + \pi^2\rho^2V^2 \cot^2(\pi\gamma)\}^{-1}$$

$$= \{1 + \pi^2\rho^2V^2 + \pi^2\rho^2V^2[(E - \mathcal{E})/\pi\rho V^2]^2\}^{-1}$$

$$= \underline{\frac{V^2}{(E - \mathcal{E})^2 + V^2 + (\pi V^2\rho)^2}}$$

Exercise: Find an expression for $\sum_n b_n^4$.