Chapter 6

Techniques of approximation

Exercises

6.1 The first-order WKB wavefunction is given in eqn 6.6 in classically allowed regions (note here that $E > V$ since a and x are positive). With $p(x)$ given by eqn 6.1b,

$$p(x) = \{2m[E - V(x)]\}^{1/2} = (2ma)^{1/2}x$$

The first-order WKB wavefunction is

$$\psi(x) = \frac{C}{(2ma)^{\frac{1}{4}}x^{\frac{1}{2}}}\sin\left(\frac{1}{\hbar}\int_0^x (2ma)^{\frac{1}{2}}x\mathrm{d}x + \delta\right) = \frac{C}{(2ma)^{\frac{1}{4}}x^{\frac{1}{2}}}\sin\left(\frac{(2ma)^{\frac{1}{2}}x^2}{2\hbar} + \delta\right)$$
$$= \frac{C}{(2ma)^{\frac{1}{4}}x^{\frac{1}{2}}}\sin\left(\left[\frac{ma}{2\hbar^2}\right]^{1/2}x^2 + \delta\right)$$

6.2 The energies of a two-level system are given by eqn 6.15. Therefore, with all energies in cm^{-1} units,

$$E_{\pm} = \tfrac{1}{2}(5000 + 10000) \pm \tfrac{1}{2}\sqrt{(10000 - 5000)^2 + 4 \times 500^2}$$

yielding $E_+ = 10\,049.51$ cm^{-1} and $E_- = 4950.49$ cm^{-1}.

6.3 The wavefunction for the ground-state harmonic oscillator is given by

$$\psi_0(x) = \left(\frac{\alpha}{\pi^{1/2}}\right)^{1/2} \mathrm{e}^{-\alpha^2x^2/2}$$

The first-order energy correction, eqn 6.24, is

$$E_0^{(1)} = \langle\psi_0|H^{(1)}|\psi_0\rangle = \frac{\alpha}{\pi^{1/2}}\int_0^b ax\mathrm{e}^{-\alpha^2x^2}\mathrm{d}x = \frac{a}{2\alpha\pi^{1/2}}\left(1-\mathrm{e}^{-\alpha^2b^2}\right)$$

6.4 The second-order energy correction is given in eqn 6.30. Here, $H^{(1)} = a$ and $H^{(2)} = 0$. The ground-state wavefunction is given by

$$\psi_0(x) = \left(\frac{\alpha}{\pi^{1/2}}\right)^{1/2}\mathrm{e}^{-\alpha^2x^2/2}$$

and the $v = 1$ wavefunction by

$$\psi_1(x) = \left(\frac{2\alpha^3}{\pi^{1/2}}\right)^{1/2}x\mathrm{e}^{-\alpha^2x^2/2}$$

Since the wavefunctions are real, $H_{01}{}^{(1)} = H_{10}{}^{(1)}$; the denominator of the v =1 contribution to $E^{(2)}$ is $(0 + ½)\,\hbar\omega - (1 + ½)\,\hbar\omega = -\hbar\omega$. The matrix element $H_{01}{}^{(1)}$ is

$$H_{01}^{(1)} = \int_0^\infty a\left(\frac{\alpha}{\pi^{1/2}}\right)^{1/2}\mathrm{e}^{-\alpha^2x^2/2}\left(\frac{2\alpha^3}{\pi^{1/2}}\right)^{1/2}x\mathrm{e}^{-\alpha^2x^2/2}\mathrm{d}x = a\frac{2^{1/2}\alpha^2}{\pi^{1/2}}\left(\frac{1}{2\alpha^2}\right) = \frac{a}{2^{1/2}\pi^{1/2}}$$

Therefore, the contribution to $E^{(2)}$ from v =1 is

$$\frac{H_{01}^{(1)}H_{10}^{(1)}}{E_0^{(0)} - E_1^{(0)}} = \frac{a^2}{2\pi}\times\left(\frac{1}{-\hbar\omega}\right) = -\frac{a^2}{h\omega}$$

6.5 As discussed in Section 6.3, to know the energy correct to order $2n + 1$ in the perturbation, it is sufficient to know the wavefunctions only to nth order in the perturbation. Therefore, if the perturbed wavefunction is known to second order, the energy is accurately known to 5th order.

6.6 Following Example 6.5 in the text, we need to decide which matrix elements $< \mathrm{s}\,|\,y\,|\,n >$ are non-zero. The function for a s-orbital ($l = 0$) is a component of the basis for $\Gamma^{(0)}$ and y is likewise a component of the basis for $\Gamma^{(1)}$. Because $\Gamma^{(0)} \times \Gamma^{(1)} = \Gamma^{(1)}$ by eqn 5.51, we can infer that only p-orbitals can be mixed into the ground state. Furthermore, because the perturbation is in the *y*-direction, only p_y can be mixed.

6.7 The optimum form of the wavefunction corresponds to a minimum in the Rayleigh ratio. Therefore, we seek the value of *k* such that the derivative of the Rayleigh ratio with respect to *k* vanishes.

$$\frac{\mathrm{d}}{\mathrm{d}k}\left(\frac{\hbar^2 k^2}{2m}-\frac{hcR_\mathrm{H}k}{a_0}\right)=\frac{\hbar^2 k}{m}-\frac{hcR_\mathrm{H}}{a_0}=0$$

and therefore

$$k=\frac{mhcR_\mathrm{H}}{\hbar^2 a_0}=\frac{2\pi mcR_\mathrm{H}}{\hbar a_0}$$

6.8 Use the Hellmann-Feynman theorem, eqn 6.48.

$$\frac{\mathrm{d}E}{\mathrm{d}P}=\langle \partial H/\partial P\rangle=\langle x^2\rangle$$

6.9 The probability of finding the system in state 2 for a degenerate two-level system is given by eqn 6.64. Therefore, we should use this formula to find the time for which a perturbation should be applied to result in $P_2(t)$ = 1/3, and then immediately extinguish the perturbation:

$$\sin^2|V|t=\frac{1}{3}$$

so

$$t=\frac{\arcsin\sqrt{1/3}}{|V|}$$

The perturbation should be applied for this amount of time and then removed.

6.10 The transition rate to a continuum of states is given by Fermi's golden rule, eqn 6.84. The molecular density of states here is

$$\rho_\mathrm{M}=\frac{2.50\times 10^4}{1.50\times 10^{-18}\mathrm{J}}=1.67\ \times 10^{22}\mathrm{J}^{-1}$$

Fermi's golden rule then yields

$$\begin{aligned} W &= 2\pi\hbar|V|^2\rho_M = 2\pi(1.055\times10^{-34}\,\mathrm{Js})(4.50\times10^{12}\,\mathrm{s}^{-1})^2(1.67\times10^{22}\,\mathrm{J}^{-1}) \\ &= 2.24\times10^{14}\,\mathrm{s}^{-1} \end{aligned}$$

6.11 Use the lifetime broadening relation, eqn 6.97.

$$\tau = \frac{\hbar}{\delta E} = \frac{1.055\times10^{-34}\,\mathrm{Js}}{1.92\times10^{-24}\,\mathrm{J}} = 5.49\times10^{-11}\,\mathrm{s}$$

Problems

6.1 First consider $\exp(+\mathrm{i}S_+(x)/\hbar)$. Noting that

$$\frac{\mathrm{d}}{\mathrm{d}x}\exp\left(\frac{\mathrm{i}S}{\hbar}\right) = \frac{\mathrm{i}}{\hbar}\frac{\mathrm{d}S}{\mathrm{d}x}\exp\left(\frac{\mathrm{i}S}{\hbar}\right)$$

we obtain upon substitution of $\exp(+\mathrm{i}S_+(x)/\hbar)$ into eqn 6.1:

$$\hbar^2\left\{\frac{\mathrm{i}}{\hbar}\frac{\mathrm{d}^2S}{\mathrm{d}x^2}\exp\left(\frac{\mathrm{i}S}{\hbar}\right) + \left(\frac{\mathrm{i}}{\hbar}\frac{\mathrm{d}S}{\mathrm{d}x}\right)^2\exp\left(\frac{\mathrm{i}S}{\hbar}\right)\right\} + p^2\exp\left(\frac{\mathrm{i}S}{\hbar}\right) = 0$$

After factoring out the common term of $\exp(+\mathrm{i}S_+(x)/\hbar)$, we obtain

$$\mathrm{i}\hbar\frac{\mathrm{d}^2S}{\mathrm{d}x^2} - \left(\frac{\mathrm{d}S}{\mathrm{d}x}\right)^2 + p^2 = 0$$

which is eqn 6.3 for S_+. Next consider $\exp(-\mathrm{i}S_-(x)/\hbar)$. Noting that

$$\frac{\mathrm{d}}{\mathrm{d}x}\exp\left(\frac{-\mathrm{i}S}{\hbar}\right) = \frac{\text{-i}}{\hbar}\frac{\mathrm{d}S}{\mathrm{d}x}\exp\left(\frac{-\mathrm{i}S}{\hbar}\right)$$

we obtain upon substitution of $\exp(-\mathrm{i}S_-(x)/\hbar)$ into eqn 6.1:

$$\hbar^2\left\{\frac{\text{-i}}{\hbar}\frac{\mathrm{d}^2S}{\mathrm{d}x^2}\exp\left(\frac{-\mathrm{i}S}{\hbar}\right) + \left(\frac{\text{-i}}{\hbar}\frac{\mathrm{d}S}{\mathrm{d}x}\right)^2\exp\left(\frac{-\mathrm{i}S}{\hbar}\right)\right\} + p^2\exp\left(\frac{-\mathrm{i}S}{\hbar}\right) = 0$$

After factoring out the common term of $\exp(-\mathrm{i}S_-(x)/\hbar)$, we obtain

$$\text{-i}\hbar\frac{\mathrm{d}^2S}{\mathrm{d}x^2} - \left(\frac{\mathrm{d}S}{\mathrm{d}x}\right)^2 + p^2 = 0$$

which is eqn 6.3 for S_-.

6.4 We begin with eqn 6.13 applied to the wavefunction ψ_- and corresponding energy E_-. Therefore, from eqn 6.17a and eqn 6.15,

$$c_1 = \cos\zeta$$

$$c_2 = \sin\zeta$$

$$E = E_- = \frac{1}{2}\left(E_1^{(0)} + E_2^{(0)}\right) - \frac{1}{2}d$$
$$d = \left\{\left(E_2^{(0)} - E_1^{(0)}\right)^2 + 4|H_{12}^{(1)}|^2\right\}^{1/2}$$

Substitution into eqn 6.13 yields, with $H_{11} = E_1^{(0)}$, $H_{22} = E_2^{(0)}$, and $H_{12} = H_{21} = |\,H_{12}^{(1)}|\,\mathrm{e}^{\mathrm{i}\varphi}$

$$\frac{1}{2}\cos\zeta\left(E_1^{(0)} - E_2^{(0)} + d\right) + \sin\zeta\left|H_{12}^{(1)}\right|\mathrm{e}^{\mathrm{i}\varphi} = 0$$

$$\cos\zeta\left|H_{12}^{(1)}\right|\mathrm{e}^{\mathrm{i}\varphi} + \frac{1}{2}\sin\zeta\left(E_2^{(0)} - E_1^{(0)} + d\right) = 0$$

Multiplication of the first of the equations by $\sin\zeta$ and the second of the equations by $\cos\zeta$ produces

$$\frac{1}{2}\cos\zeta\sin\zeta\left(E_1^{(0)} - E_2^{(0)} + d\right) + \sin^2\zeta\left|H_{12}^{(1)}\right|\mathrm{e}^{\mathrm{i}\varphi} = 0$$

$$\cos^2\zeta\left|H_{12}^{(1)}\right|\mathrm{e}^{\mathrm{i}\varphi} + \frac{1}{2}\sin\zeta\cos\zeta\left(E_2^{(0)} - E_1^{(0)} + d\right) = 0$$

Subtracting the top equation from the bottom equation and using the trigonometric identities

$$\cos 2\zeta = \cos^2\zeta - \sin^2\zeta$$

$$\sin 2\zeta = 2\sin\zeta\cos\zeta$$

yields

$$\cos 2\zeta\left|H_{12}^{(1)}\right|\mathrm{e}^{\mathrm{i}\varphi} + \frac{1}{2}\sin 2\zeta\left(E_2^{(0)} - E_1^{(0)}\right) = 0$$

and therefore, since $\tan 2\zeta = \sin 2\zeta / \cos 2\zeta$,

$$\tan 2\zeta = \frac{-2\left|H_{12}^{(1)}\right|e^{i\varphi}}{E_2^{(0)} - E_1^{(0)}}$$

If we now let $\varphi = \pi$ so that $e^{i\varphi} = -1$, we obtain eqn 6.17b.

6.7 $H = -(\hbar^2/2m)(d^2/dx^2) + mgx$

$H^{(0)} = -(\hbar^2/2m)(d^2/dx^2)$; $H^{(1)} = mgx$

$E^{(1)} = \langle 0|H^{(1)}|0\rangle = mg\,\langle x\rangle = \underline{\tfrac{1}{2}mgL}$

The first-order correction disregards the adjustment of the location of the particle in the gravitational field, so $E^{(1)}$ is the potential energy of a particle at its average height ($\tfrac{1}{2}L$).

For $m = m_e$,

$$E^{(1)}/L = \tfrac{1}{2}mg = \underline{4.47 \times 10^{-30}\ \mathrm{J\ m^{-1}}}$$

6.10 The first-order correction to the energy is given by eqn 6.24:

$$E_0^{(1)} = \langle 0|H^{(1)}|0\rangle$$

where the state $|0\rangle$ is the ground-state harmonic oscillator wavefunction of Section 2.14:

$$\psi_0(x) = \left(\frac{\alpha}{\pi^{1/2}}\right)^{1/2} e^{-\alpha^2x^2/2} \qquad \alpha = \left(\frac{mk}{\hbar^2}\right)^{1/4}$$

and the perturbation hamiltonian is

$$H^{(1)} = ax^3 + bx^4$$

The following standard integrals will be useful:

$$\int_0^\infty x^3 \mathrm{e}^{-cx^2}\mathrm{d}x = \frac{1}{2c^2}$$

$$\int_0^\infty x^4 \mathrm{e}^{-cx^2}\mathrm{d}x = \frac{3}{8c^2}\left(\frac{\pi}{c}\right)^{1/2}$$

We also use the result that if the function $f(x)$ in the integrand is an even function of x, then

$$\int_{-\infty}^0 f(x)\mathrm{d}x = \int_0^\infty f(x)\mathrm{d}x$$

and if the function is odd, then

$$\int_{-\infty}^0 f(x)\mathrm{d}x = -\int_0^\infty f(x)\mathrm{d}x$$

(a) The anharmonic perturbation is present for all values of x.

$$\begin{aligned} E_0^{(1)} &= \left(\frac{\alpha}{\pi^{1/2}}\right)\int_{-\infty}^{\infty} \mathrm{e}^{-\alpha^2x^2}(ax^3+bx^4)\mathrm{d}x \\ &= \left(\frac{\alpha}{\pi^{1/2}}\right)\left[0+\frac{3b\pi^{1/2}}{4\alpha^5}\right] \\ &= \frac{3b}{4\alpha^4} \end{aligned}$$

(b) The anharmonic perturbation is only present during bond expansion so $H^{(1)}$ vanishes for $x < 0$.

$$E_0^{(1)} = \left(\frac{\alpha}{\pi^{1/2}}\right)\int_0^{\infty} \mathrm{e}^{-\alpha^2x^2}(ax^3 + bx^4)\mathrm{d}x$$

$$= \left(\frac{\alpha}{\pi^{1/2}}\right)\left[\frac{a}{2\alpha^4} + \frac{3b\pi^{1/2}}{8\alpha^5}\right]$$

$$= \frac{a}{2\alpha^3\pi^{1/2}} + \frac{3b}{8\alpha^4}$$

(c) The anharmonic perturbation is only present during bond compression so $H^{(1)}$ vanishes for $x > 0$.

$$E_0^{(1)} = \left(\frac{\alpha}{\pi^{1/2}}\right)\int_{-\infty}^{0} \mathrm{e}^{-\alpha^2x^2}(ax^3 + bx^4)\mathrm{d}x$$

$$= \left(\frac{\alpha}{\pi^{1/2}}\right)\left[-\frac{a}{2\alpha^4} + \frac{3b\pi^{1/2}}{8\alpha^5}\right]$$

$$= -\frac{a}{2\alpha^3\pi^{1/2}} + \frac{3b}{8\alpha^4}$$

Exercise: Repeat the problem for the $v = 1$ harmonic oscillator wavefunction.

6.13 **(a)** $x\psi_0$ spans $B_1 \times A_1 = B_1$ in C_{2v}; hence $\underline{B_1}$ states are admixed.

(b) $l_x\psi_0$ spans $B_2 \times A_1 = B_2$ in C_{2v}; hence $\underline{B_2}$ states are admixed.

Exercise: : The symmetry of the ground state of ClO_2 is $^2B_1$. What symmetry species of excited states are admixed?

6.16 $H^{(1)} = \varepsilon \sin^2\phi$

Form the secular determinant by using

$$H^{(1)}_{m_l'm_l} = (\varepsilon/2\pi)\int_0^{2\pi} \mathrm{e}^{-\mathrm{i}(m_l'-m_l)\phi}(\mathrm{e}^{2\mathrm{i}\phi}+\mathrm{e}^{-2\mathrm{i}\phi}-2)\mathrm{d}\phi/(-4)$$

$$= -(\varepsilon/8\pi)\int_0^{2\pi}\{\mathrm{e}^{\mathrm{i}(2-m_l'+m_l)\phi}+\mathrm{e}^{\mathrm{i}(-2-m_l'+m_l)\phi}-2\mathrm{e}^{-\mathrm{i}(m_l'-m_l)\phi}\}\mathrm{d}\phi$$

$$= -(\varepsilon/4)\{\delta_{m_l',m_l+2}+\delta_{m_l',m_l-2}-2\delta_{m_l',m_l}\}$$

Consequently,

$$H^{(1)}_{1,1} = \tfrac{1}{2}\varepsilon, \quad H^{(1)}_{-1,-1} = \tfrac{1}{2}\varepsilon, \quad H^{(1)}_{1,-1} = -\tfrac{1}{4}\varepsilon, \quad H^{(1)}_{-1,1} = -\tfrac{1}{4}\varepsilon$$

$$S_{1,1} = S_{-1,-1} = 1; \quad S_{1,-1} = S_{-1,1} = 0$$

$$\det|H^{(1)} - SE| = \begin{vmatrix} \tfrac{1}{2}\varepsilon - E & -\tfrac{1}{4}\varepsilon \\ -\tfrac{1}{4}\varepsilon & \tfrac{1}{2}\varepsilon - E \end{vmatrix} = (\tfrac{1}{2}\varepsilon - E)^2 - (-\tfrac{1}{4}\varepsilon)^2 = 0$$

Consequently, $E = \tfrac{1}{2}\varepsilon \pm \tfrac{1}{4}\varepsilon = \tfrac{3}{4}\varepsilon$ and $\tfrac{1}{4}\varepsilon$. Find the coefficients from the secular equations and $|c_1|^2 + |c_2|^2 = 1$ (or by intuition):

$$\left.\begin{aligned}(\tfrac{1}{2}\varepsilon - E)c_1 - \tfrac{1}{4}\varepsilon c_2 &= 0\\ -\tfrac{1}{4}\varepsilon c_1 + (\tfrac{1}{2}\varepsilon - E)c_2 &= 0\end{aligned}\right\}\left\{\begin{aligned}\phi_{\frac{3}{4}} &= (\psi_1 - \psi_{-1})/\sqrt{2}\\ \phi_{\frac{1}{4}} &= (\psi_1 + \psi_{-1})/\sqrt{2}\end{aligned}\right.$$

For the first-order energies we have $E = \tfrac{3}{4}\varepsilon$ and $\tfrac{1}{4}\varepsilon$. If desired, check this as follows:

$$H^{(1)}_{3/4,3/4} = \tfrac{1}{2}(H^{(1)}_{1,1} + H^{(1)}_{-1,-1} - H^{(1)}_{1,-1} - H^{(1)}_{-1,1}) = \tfrac{1}{2}(\varepsilon + \tfrac{1}{2}\varepsilon) = \tfrac{3}{4}\varepsilon$$

$$H^{(1)}_{1/4,1/4} = \tfrac{1}{2}(H^{(1)}_{1,1} + H^{(1)}_{-1,-1} + H^{(1)}_{1,-1} + H^{(1)}_{-1,1}) = \tfrac{1}{2}(\varepsilon - \tfrac{1}{2}\varepsilon) = \tfrac{1}{4}\varepsilon$$

$$H^{(1)}_{3/4,1/4} = \tfrac{1}{2}(H^{(1)}_{1,1} - H^{(1)}_{-1,-1} + H^{(1)}_{1,-1} - H^{(1)}_{-1,1}) = 0$$

This calculation confirms that $H^{(1)}$ is diagonal in the $\phi_{\frac{3}{4}}, \phi_{\frac{1}{4}}$ basis, and that its eigenvalues are $\frac{3}{4}\varepsilon$ and $\frac{1}{4}\varepsilon$.

For the second-order energies we require the following matrix elements:

$$H^{(1)}_{m_l,\frac{3}{4}} = (1/\sqrt{2})\{H^{(1)}_{m_l,1} - H^{(1)}_{m_l,-1}\}$$

$$= \begin{cases} (1/\sqrt{2})H^{(1)}_{3,1} & = -(\varepsilon/4\sqrt{2}) \quad \text{for } m_l = 3 \\ -(1/\sqrt{2})H^{(1)}_{-3,-1} & = +(\varepsilon/4\sqrt{2}) \quad \text{for } m_l = -3, \text{ all others zero} \end{cases}$$

$$H^{(1)}_{m_l,\frac{1}{4}} = (1/\sqrt{2})\{H^{(1)}_{m_l,1} + H^{(1)}_{m_l,-1}\}$$

$$= \begin{cases} (1/\sqrt{2})H^{(1)}_{3,1} & = -(\varepsilon/4\sqrt{2}) \quad \text{for } m_l = 3 \\ (1/\sqrt{2})H^{(1)}_{-3,-1} & = -(\varepsilon/4\sqrt{2}) \quad \text{for } m_l = -3, \text{ all others zero} \end{cases}$$

$$E^{(0)}_{m_l} = m_l^2\hbar^2/2mr^2 = m_l^2 A, \text{ with } A = \hbar^2/2mr^2$$

Both ϕ linear combinations correspond to $|m_l| = 1$, and so for them $E^{(0)} = A$. For the $\phi_{\frac{3}{4}}$ combination:

$$E^{(2)} = \sum_{m_l \neq 0} \left\{ H^{(1)}_{3/4,m_l} H^{(1)}_{m_l,3/4} / (1-m_l^2)A \right\}$$

$$= |H^{(1)}_{3/4,3}|^2/(-8A) + |H^{(1)}_{3/4,-3}|^2/(-8A) = -\varepsilon^2/128A$$

For the $\phi_{1/4}$ combination:

$$E^{(2)} = \sum_{m_l \neq 0} \left\{ H^{(1)}_{1/4,m_l} H^{(1)}_{m_l,1/4} / (1-m_l^2)A \right\}$$

$$= |H^{(1)}_{1/4,3}|^2/(-8A) + |H^{(1)}_{1/4,-3}|^2/(-8A) = -\varepsilon^2/128A$$

[The $m_l = 0$ does not in fact make a contribution to the sum.] The energies to second order are therefore

$$\underline{E_{3/4} = A + \tfrac{3}{4}\varepsilon - \varepsilon^2/128A}, \underline{E_{1/4} = A + \tfrac{1}{4}\varepsilon - \varepsilon^2/128A}$$

Exercise: Find the first- and second-order energy corrections for a particle subject to $H^{(1)} = \varepsilon \sin^4\phi$.

6.19 First, normalize the linear combinations to 1:

$$\int (a_2')^2 \mathrm{d}\tau = \tfrac{1}{2}\int (\mathrm{s_A} + \mathrm{s_C})^2 \mathrm{d}\tau = \tfrac{1}{2}\int (\mathrm{s_A^2} + \mathrm{s_C^2} + 2\mathrm{s_A s_C})\mathrm{d}\tau$$

$$= 1 + S_{\mathrm{AC}}$$

$$\int (a'')^2 \mathrm{d}\tau = 1 - S_{\mathrm{AC}}$$

Therefore,

$$a_2' = (\mathrm{s_A} + \mathrm{s_C})/\{2(1 + S_{\mathrm{AC}})\}^{1/2}$$

$$a'' = (\mathrm{s_A} - \mathrm{s_C})/\{2(1 - S_{\mathrm{AC}})\}^{1/2}$$

Now construct the matrix elements of H:

$$\int a_1' H a_1' \mathrm{d}\tau = \alpha$$

$$\int a_2' H a_2' \mathrm{d}\tau = \int (\mathrm{s_A} + \mathrm{s_C}) H (\mathrm{s_A} + \mathrm{s_C}) \mathrm{d}\tau / 2(1 + S_{\mathrm{AC}})$$

$$= (\alpha + \gamma)/(1 + S_{\mathrm{AC}})$$

$$\int a'' H a'' \mathrm{d}\tau = (\alpha - \gamma)/(1 - S_{\mathrm{AC}})$$

$$\int a_1' H a_2' \mathrm{d}\tau = \int s_B H(s_A + s_C)\mathrm{d}\tau/\{2(1+S_{AC})\}^{1/2} = \{2/(1+S_{AC})\}^{1/2}\beta$$

$$\int a_1' a_2' \mathrm{d}\tau = \{2/(1+S_{AC})\}^{1/2} S_{AB} \quad [S_{AB} = S_{BC}]$$

Hence, the 2 × 2 secular determinant is

$$\det|H - ES| = \begin{vmatrix} \alpha - E & \frac{(\beta - ES_{AB})\sqrt{2}}{\sqrt{(1+S_{AC})}} \\ \frac{(\beta - ES_{AB})\sqrt{2}}{\sqrt{(1+S_{AC})}} & \left(\frac{\alpha+\gamma}{1+S_{AC}}\right) - E \end{vmatrix}$$

Set $\gamma = (S_{AC}/S_{AB})\beta$; then with $S_{AB} = 0.723$ and $S_{AC} = 0.345$,

$$\det|H - ES| = \begin{vmatrix} \alpha - E & 1.219(\beta - 0.723E) \\ 1.219(\beta - 0.723E) & (\alpha + 0.477\beta)/1.345 - E \end{vmatrix}$$

$$= 0.223E^2 + (1.794\beta - 1.744\alpha)E$$

$$+ (0.355\alpha\beta + 0.744\alpha^2 - 1.486\beta^2)$$

Therefore, we must solve

$$E^2 + (8.045\beta - 7.821\alpha)E + (1.592\alpha\beta + 3.336\alpha^2 - 6.664\beta^2) = 0$$

Write $E/\alpha = \varepsilon$ and $\beta/\alpha = \lambda$; then

$$\varepsilon^2 + (8.045\lambda - 7.821)\varepsilon + (1.592\lambda + 3.336 - 6.664\lambda^2) = 0$$

$$\varepsilon = 3.911 - 4.023\lambda \pm \sqrt{\{22.845\lambda^2 - 33.052\lambda + 11.956\}}$$

which can be plotted as a function of λ, Fig. 6.2. (The result from Problem 6.18, $\varepsilon = 1 \pm \lambda\sqrt{2}$, is also shown.)

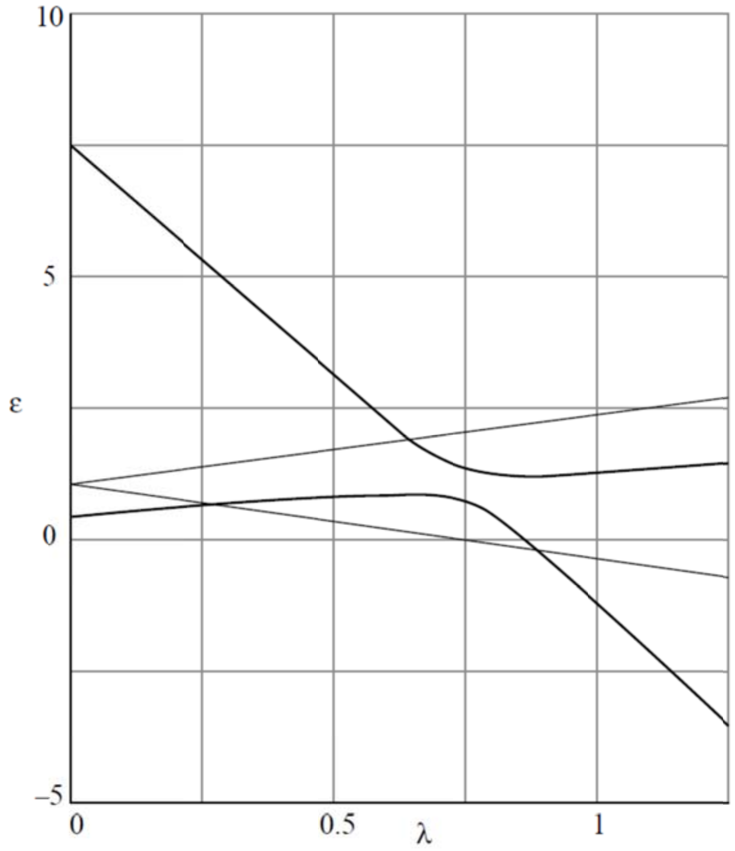

Figure 6.2: The energies calculated in Problem 6.19. The straight lines are the energies calculated in Problem 6.18.

Exercise: Include overlap in the *Exercise* attached to Problem 6.18.

6.22

$$c_f(t) = (1/\mathrm{i}\hbar)\int_0^t H_{\mathrm{fi}}^{(1)}(t)\mathrm{e}^{\mathrm{i}\omega_{\mathrm{fi}}t}\mathrm{d}t \quad \text{[eqn 6.71]}$$

$$c_{2\mathrm{p}}(t) = (1/\mathrm{i}\hbar)\langle 2\mathrm{p}_z|ez|1\mathrm{s}\rangle \int_0^t \mathcal{E}(t)\mathrm{e}^{i\omega_{2\mathrm{p},1s}t}\mathrm{d}t \qquad [H^{(1)}(t) = -\mu_z\mathcal{E}(t) = ez\mathcal{E}(t)]$$

Set $\mathcal{E}(t) = \gamma t$; note that $\omega_{2\mathrm{p},1\mathrm{s}} = \frac{3}{4}hc\mathrm{R}_\mathrm{H}/\hbar = (3\pi/2)c\mathrm{R}_\mathrm{H}$. For simplicity of notation, write $\omega = \omega_{2p,1\mathrm{s}}$

$$c_{2\mathrm{p}}(t) = \gamma(e/\mathrm{i}\hbar)\langle 2\mathrm{p}_z|z|1\mathrm{s}\rangle\int_0^t t\mathrm{e}^{\mathrm{i}\omega t}\mathrm{d}t$$

$$= (e\gamma/\mathrm{i}\hbar)\langle 2\mathrm{p}_z|z|1\mathrm{s}\rangle\{(t/\mathrm{i}\omega)\mathrm{e}^{\mathrm{i}\omega t} + (1/\omega^2)(\mathrm{e}^{\mathrm{i}\omega t} - 1)\}$$

$$|c_{2\mathrm{p}}(t)|^2 = (e\gamma/\hbar)^2\langle 2\mathrm{p}_z|z|1\mathrm{s}\rangle^2(2/\omega^4)\{1 - \cos\omega t - \omega t\sin\omega t + \tfrac{1}{2}\omega^2 t^2\}$$

Exercise: Find $|c_{2\mathrm{p}}(t)|^2$ in the case where the perturbation is turned on quadratically ($\mathcal{E} \propto t^2$).

6.25 We use eqn 6.87 for the rate of stimulated emission, taking the value of B from eqn 6.88 and the density of states of the radiation field from eqn 6.92b. The transition dipole moment is calculated by using the hydrogen orbitals $R_{nl}Y_{lm_l}$ where the radial functions are listed in Table 3.4 and the spherical harmonics in Table 3.2; the transition frequency ν is obtained from the energies in eqn 3.66. For the rate of spontaneous emission, use the relation between A and B in eqn 6.93.

First consider the transition dipole moment μ_z for the $3\mathrm{p}_z \rightarrow 2\mathrm{s}$ transition.

$$\mu_z = -e\int\psi^*_{3\mathrm{p}_z} z\psi_{2\mathrm{s}}\mathrm{d}\tau = -\frac{3^3\times 2^{10}}{5^6}ea_0$$

$$= -1.769ea_0 = -1.500 \times 10^{-29}\ \mathrm{C\ m}$$

Since the lower (2s) state of the atom is spherically symmetrical, the contributions for $3\mathrm{p}_x$, $3\mathrm{p}_y$ and $3\mathrm{p}_z$ are identical. Therefore

$$|\mu|^2 = |\mu_x|^2 + |\mu_y|^2 + |\mu_z|^2 = 3 \times 3.131e^2a_0^2 = 6.752 \times 10^{-58}\ \mathrm{C^2\ m^2}$$

The Einstein coefficient of stimulated emission is

$$B = \frac{|\mu|^2}{6\varepsilon_0 \hbar^2} = 1.143 \times 10^{21}\ \mathrm{J^{-1}\ m^3\ s^{-2}}$$

The frequency of the transition (with R the Rydberg constant) is

$$\nu = \left(\frac{1}{2^2} - \frac{1}{3^2}\right) cR = 4.567 \times 10^{14}\ \mathrm{Hz}$$

and so it follows that

$$A = \frac{8\pi h\nu^3}{c^3} B = 6.728 \times 10^7\ \mathrm{s^{-1}}$$

At 1000 K and for the transition frequency,

$$\rho_{\mathrm{rad}} = \frac{8\pi h\nu^3/c^3}{\mathrm{e}^{h\nu/kT} - 1} = 1.782 \times 10^{-23}\ \mathrm{J\ Hz^{-1}\ m^{-3}}$$

It then follows that the rate of stimulated emission is $B\rho_{\mathrm{rad}} = 2.036 \times 10^{-2}\ \mathrm{s^{-1}}$ whereas that of spontaneous emission is $A = 6.728 \times 10^7\ \mathrm{s^{-1}}$.

Exercise: Find the dependence on atomic number of the rates of stimulated and spontaneous emission for the 3p → 2s transition in hydrogenic atoms at 1000 K.

6.28 We use eqn 6.97 to estimate the lifetime τ from the full width at half maximum, which we denote Δ. The latter is converted from a wavenumber to an energy in joules by multiplication by hc; the full width as an energy in joules is then identified with δE.

$$\tau = \frac{\hbar}{(\delta E)} = \frac{1}{2\pi c\Delta}$$

(a) $\tau = (2\pi \times 2.9979 \times 10^{10}\ \text{cm s}^{-1} \times 0.010\ \text{cm}^{-1})^{-1} = 5.3 \times 10^{-10}\ \text{s} = \underline{530\ \text{ps}}$

(b) $\tau = (2\pi \times 2.9979 \times 10^{10}\ \text{cm s}^{-1} \times 1.5\ \text{cm}^{-1})^{-1} = 3.5 \times 10^{-12}\ \text{s} = \underline{3.5\ \text{ps}}$

(c) $\tau = (2\pi \times 2.9979 \times 10^{10}\ \text{cm s}^{-1} \times 40\ \text{cm}^{-1})^{-1} = 13 \times 10^{-14}\ \text{s} = \underline{130\ \text{fs}}$

Exercise: What is the full width of the spectral peak if the lifetime of the upper state is 1.0 μs?