Chapter 6

Techniques of approximation

All the following material © P.W. Atkins and R.S. Friedman.

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

$$\psi(x) = \frac{C}{(2ma)^{1/2}} \sin \left( \frac{1}{\hbar} \int_0^x (2ma)^{1/2} dx + \delta \right) = \frac{C}{(2ma)^{1/2}} \sin \left( \frac{(2ma)^{1/2} x^2}{2\hbar} + \delta \right)$$

$$= \frac{C}{(2ma)^{1/2}} \sin \left( \frac{ma}{2\hbar^2} \frac{1}{2} x^2 + \delta \right)$$

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

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

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

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

The first-order energy correction, eqn 6.24, is
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

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

and the $\nu = 1$ wavefunction by

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

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

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

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

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

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 $n$th order in the perturbation. Therefore, if the perturbed wavefunction is known to second order, the energy is accurately known to $5^{th}$ order.

6.6 Following Example 6.5 in the text, we need to decide which matrix elements $<s | y | n>$ 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.

\[
\frac{d}{dk} \left( \frac{\hbar^2 k^2}{2m} \frac{h c R_H(k)}{a_0} \right) = 0
\]

and therefore

\[
k = \frac{m h c R_H}{\hbar^2 a_0} = \frac{2 \pi m c R_H}{\hbar a_0}
\]

6.8 Use the Hellmann-Feynman theorem, eqn 6.48.

\[
\frac{dE}{dP} = \langle \frac{\partial H}{\partial P} \rangle = \langle x^2 \rangle
\]

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

\[
\rho_M = \frac{2.50 \times 10^4}{1.50 \times 10^{-18}} = 1.67 \times 10^{22} \text{J}^{-1}
\]
Fermi’s golden rule then yields

\[ W = 2\pi\hbar|V|^2\rho_M = 2\pi(1.055 \times 10^{-34} J s)(4.50 \times 10^{12} s^{-1})^2(1.67 \times 10^{22} J^{-1}) = 2.24 \times 10^{14} s^{-1} \]

**6.11** Use the lifetime broadening relation, eqn 6.97.

\[ \tau = \frac{\hbar}{\delta E} = \frac{1.055 \times 10^{-34} J s}{1.92 \times 10^{-24} J} = 5.49 \times 10^{-11} s \]

**Problems**

**6.1** First consider \( \exp(+iS_+\chi/\hbar) \). Noting that

\[ \frac{d}{dx}\exp(\frac{iS}{\hbar}) = \frac{i}{\hbar} \frac{dS}{dx}\exp(\frac{iS}{\hbar}) \]

we obtain upon substitution of \( \exp(+iS_+\chi/\hbar) \) into eqn 6.1:

\[ \hbar^2 \left( \frac{i}{\hbar} \frac{d^2S}{dx^2}\exp(\frac{iS}{\hbar}) + \left( \frac{i}{\hbar} \frac{dS}{dx} \right)^2 \exp(\frac{iS}{\hbar}) + p^2 \exp(\frac{iS}{\hbar}) \right) = 0 \]

After factoring out the common term of \( \exp(+iS_+\chi/\hbar) \), we obtain

\[ i\hbar \frac{d^2S}{dx^2} - \left( \frac{dS}{dx} \right)^2 + p^2 = 0 \]

which is eqn 6.3 for \( S_+ \). Next consider \( \exp(-iS_-\chi/\hbar) \). Noting that

\[ \frac{d}{dx}\exp(\frac{-iS}{\hbar}) = -\frac{i}{\hbar} \frac{dS}{dx}\exp(\frac{-iS}{\hbar}) \]

we obtain upon substitution of \( \exp(-iS_-\chi/\hbar) \) into eqn 6.1:

\[ \hbar^2 \left( -\frac{i}{\hbar} \frac{d^2S}{dx^2}\exp(\frac{-iS}{\hbar}) + \left( \frac{i}{\hbar} \frac{dS}{dx} \right)^2 \exp(\frac{-iS}{\hbar}) \right) + p^2 \exp(\frac{-iS}{\hbar}) = 0 \]

After factoring out the common term of \( \exp(-iS_-\chi/\hbar) \), we obtain

\[ -i\hbar \frac{d^2S}{dx^2} - \left( \frac{dS}{dx} \right)^2 + p^2 = 0 \]

which is eqn 6.3 for \( S_- \).
6.4 We begin with eqn 6.13 applied to the wavefunction $\psi$ and corresponding energy $E$.

Therefore, from eqn 6.17a and eqn 6.15,

$$c_1 = \cos \zeta$$

$$c_2 = \sin \zeta$$

$$E = E_\pm = \frac{1}{2} \left( E_1^{(0)} + E_2^{(0)} \right) - \frac{1}{2} d$$

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

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

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

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

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

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

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

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

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

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

C06  p. 5
\[
\tan 2\zeta = \frac{-2|H^{(1)}_{12}|e^{i\varphi}}{E^{(0)}_2 - E^{(0)}_1}
\]

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

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

\[H^{(0)} = -(\hbar^2/2m)(d^2/dx^2); \quad H^{(1)} = mxg\]

\[E^{(1)} = \langle 0|H^{(1)}|0 \rangle = mg \langle x \rangle = \frac{1}{2} mgL\]

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 \((\frac{1}{2}L)\).

For \(m = m_e\),

\[E^{(1)}/L = \frac{1}{2}mg = 4.47 \times 10^{-30} \text{ J m}^{-1}\]

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

\[E^{(1)}_0 = \langle 0|H^{(1)}|0 \rangle\]

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

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

and the perturbation hamiltonian is

\[H^{(1)} = ax^3 + bx^4\]
The following standard integrals will be useful:

\[
\int_0^\infty x^3 e^{-cx^2} \, dx = \frac{1}{2c^2}
\]

\[
\int_0^\infty x^4 e^{-cx^2} \, dx = \frac{3}{8c^2} \left( \frac{\pi}{c} \right)^{1/2}
\]

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

\[
\int_{-\infty}^{0} f(x) \, dx = \int_{0}^{\infty} f(x) \, dx
\]

and if the function is odd, then

\[
\int_{-\infty}^{0} f(x) \, dx = -\int_{0}^{\infty} f(x) \, dx
\]

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

\[
E_0^{(1)} = \left( \frac{\alpha}{\pi^{1/2}} \right) \int_{-\infty}^{\infty} e^{-\alpha^2 x^2} (ax^3 + bx^4) \, dx
\]

\[
= \left( \frac{\alpha}{\pi^{1/2}} \right) \left[ 0 + \frac{3b \pi^{1/2}}{4\alpha^5} \right]
\]

\[
= \frac{3b}{4\alpha^4}
\]

(b) The anharmonic perturbation is only present during bond expansion so \( H_0^{(1)} \) vanishes for \( x < 0 \).
\[
E_0^{(1)} = \left( \frac{\alpha}{\pi^{1/2}} \right) \int_0^\infty e^{-x^2} (ax^3 + bx^4) dx
\]

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

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

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

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

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

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

**Exercise:** Repeat the problem for the \(v = 1\) harmonic oscillator wavefunction.

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

(b) \(l, \psi_0\) 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 \(\text{ClO}_2\) is \(\underline{2B_1}\). What symmetry species of excited states are admixed?

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

Form the secular determinant by using
\[ H_{m_l}^{(1)} = (\varepsilon/2\pi) \int_0^{2\pi} e^{-i(m_l' - m_l)\phi} (e^{2i\phi} + e^{-2i\phi} - 2) d\phi/(-4) \]

\[ = -3(\varepsilon/8\pi) \int_0^{2\pi} \{ e^{i(2-m_l+m_l')\phi} + e^{i(-2-m_l+m_l')\phi} - 2e^{-i(m_l'-m_l)\phi} \} d\phi \]

\[ = -3(\varepsilon/4) \{ \delta_{m_l',m_l+2} + \delta_{m_l',m_l-2} - 2\delta_{m_l',m_l} \} \]

Consequently,

\[ H_{1,1}^{(1)} = \frac{1}{2} \varepsilon, \quad H_{-1,-1}^{(1)} = \frac{1}{2} \varepsilon, \quad H_{1,-1}^{(1)} = -\frac{1}{4} \varepsilon, \quad H_{-1,1}^{(1)} = -\frac{1}{4} \varepsilon \]

\[ S_{1,1} = S_{-1,-1} = 1; \quad S_{1,-1} = S_{-1,1} = 0 \]

\[ \det [H^{(1)} - SE] = \begin{vmatrix} \frac{1}{2} \varepsilon - E & -\frac{1}{4} \varepsilon \\ -\frac{1}{4} \varepsilon & \frac{1}{2} \varepsilon - E \end{vmatrix} = (\frac{1}{2} \varepsilon - E)^2 - (-\frac{1}{4} \varepsilon)^2 = 0 \]

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

\[ \begin{align*}
(\frac{1}{2} \varepsilon - E)c_1 - \frac{1}{4} \varepsilon c_2 &= 0 \\
-\frac{1}{4} \varepsilon c_1 + (\frac{1}{2} \varepsilon - E)c_2 &= 0
\end{align*} \]

\[ \begin{cases} 
\phi_1 = (\psi_1 - \psi_{-1})/\sqrt{2} \\
\phi_2 = (\psi_1 + \psi_{-1})/\sqrt{2}
\end{cases} \]

For the first-order energies we have \( E = \frac{1}{2} \varepsilon \) and \( \frac{1}{4} \varepsilon \). If desired, check this as follows:

\[ H_{3/4,3/4}^{(1)} = \frac{1}{2} (H_{1,1}^{(1)} + H_{-1,-1}^{(1)} - H_{1,-1}^{(1)} - H_{-1,1}^{(1)}) = \frac{1}{2} (\varepsilon + \frac{1}{4} \varepsilon) = \frac{3}{4} \varepsilon \]

\[ H_{1/4,1/4}^{(1)} = \frac{1}{2} (H_{1,1}^{(1)} + H_{1,-1}^{(1)} + H_{-1,1}^{(1)} + H_{-1,-1}^{(1)}) = \frac{1}{2} (\varepsilon - \frac{1}{4} \varepsilon) = \frac{1}{4} \varepsilon \]

\[ H_{3/4,1/4}^{(1)} = \frac{1}{2} (H_{1,1}^{(1)} - H_{-1,-1}^{(1)} + H_{1,-1}^{(1)} - H_{-1,1}^{(1)}) = 0 \]
This calculation confirms that $H^{(1)}$ is diagonal in the $\phi_{1/4}$ basis, and that its eigenvalues are $\frac{1}{4}\varepsilon$ and $\frac{1}{4}\varepsilon$.

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

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

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

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

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

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

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

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

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

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

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

$$= |H^{(1)}_{1/4, 3}|^2 / (-8A) + |H^{(1)}_{1/4, -3}|^2 / (-8A) = -\varepsilon^2 / 128A$$
[The \( m_l = 0 \) does not in fact make a contribution to the sum.] The energies to second order are therefore

\[
E_{3/4} = A + \frac{3}{4} \varepsilon - \frac{\varepsilon^2}{128A}, \quad E_{1/4} = A + \frac{1}{4} \varepsilon - \frac{\varepsilon^2}{128A}
\]

**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:

\[
\int (a_2')^2 d\tau = \frac{1}{2} \int (s_A + s_C)^2 d\tau = \frac{1}{2} \int (s_A^2 + s_C^2 + 2s_As_C) d\tau = 1 + S_{AC}
\]

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

Therefore,

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

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

Now construct the matrix elements of \( H \):

\[
\int a'_1Ha'_1d\tau = \alpha
\]

\[
\int a'_2Ha'_2d\tau = \int (s_A + s_C)H(s_A + s_C)d\tau / 2(1 + S_{AC}) = (\alpha + \gamma)/(1 + S_{AC})
\]

\[
\int a''Ha''d\tau = (\alpha - \gamma)/(1 - S_{AC})
\]
\[
\int a'_1 H a'_2 d\tau = \int s_b H(s_A + s_C) d\tau / \{2(1 + S_{AC})\}^{1/2} = \{2/(1 + S_{AC})\}^{1/2} \beta
\]
\[
\int a'_1 a'_2 d\tau = \{2/(1 + S_{AC})\}^{1/2} S_{AB} \quad [S_{AB} = S_{BC}]
\]

Hence, the $2 \times 2$ secular determinant is

\[
\det |H - ES| = \left| \begin{array}{cc}
\alpha - E & \frac{(\beta - ES_{AB})\sqrt{5}}{\sqrt{1 + S_{AC}}} \\
\frac{(\beta - ES_{AB})\sqrt{5}}{\sqrt{1 + S_{AC}}} & \left(\frac{\alpha + \gamma}{1 + S_{AC}}\right) - E
\end{array} \right|
\]

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

\[
\det |H - ES| = \left| \begin{array}{cc}
\alpha - E & 1.219(\beta - 0.723E) \\
1.219(\beta - 0.723E) & (\alpha + 0.477\beta)/1.345 - E
\end{array} \right|
\]

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

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

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 $\lambda$, 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

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

\[ c_{2p}(t) = \frac{1}{\hbar} (2p_z | e_z | 1s) \int_0^t \mathcal{E}(\tau)e^{i\omega_{2p,1s}\tau} d\tau \quad [H_{2p,1s}^{(1)}(t) = -\mu e\mathcal{E}(t) = e\varepsilon E(t)] \]
Set \( E(t) = \gamma t \); note that \( \omega_{2p,1s} = \frac{3}{4} \hbar c R_H / \hbar = (3\pi/2)c R_H \). For simplicity of notation, write \( \omega = \omega_{2p,1s} \)

\[
c_{2p}(t) = \gamma (e^{i\frac{\hbar}{\omega}})(2p_z | 1s) \int_0^t e^{i\omega t} dt
= (e^{i\frac{\hbar}{\omega}})(2p_z | 1s) \{ t/(i\omega) e^{i\omega t} + (1/i\omega^2)(e^{i\omega t} - 1) \}
\]

\[
|c_{2p}(t)|^2 = (e^{i\frac{\hbar}{\omega}})^2(2p_z | 1s)^2(2/\omega^2) \{ 1 - \cos \omega t - \omega t \sin \omega t + \frac{1}{2} \omega^2 t^2 \}
\]

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

**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 \( R_{n\ell}Y_{\ell m} \), where the radial functions are listed in Table 3.4 and the spherical harmonics in Table 3.2; the transition frequency \( \nu \) 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 \( \mu_z \) for the \( 3p_z \rightarrow 2s \) transition.

\[
\mu_z = -e \int \psi_{3p_z}^* \psi_{2s}^* \, d\tau = -\frac{3^3 \times 2^{10}}{5^6} e a_0
= -1.769 e a_0 = -1.500 \times 10^{-29} \text{ C m}
\]

Since the lower (2s) state of the atom is spherically symmetrical, the contributions for \( 3p_x, 3p_y \) and \( 3p_z \) are identical. Therefore

\[
|\mu|^2 = |\mu_z|^2 + |\mu_x|^2 + |\mu_y|^2 = 3 \times 3.131 e^2 a_0^2 = 6.752 \times 10^{-58} \text{ C}^2 \text{ m}^2
\]
The Einstein coefficient of stimulated emission is

\[ B = \frac{|\mu|^2}{6\epsilon_0\hbar^2} = 1.143 \times 10^{21} \text{ J}^{-1} \text{ m}^3 \text{ s}^{-2} \]

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

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

and so it follows that

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

At 1000 K and for the transition frequency,

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

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

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

**6.28** We use eqn 6.97 to estimate the lifetime \( \tau \) from the full width at half maximum, which we denote \( \Delta \). The latter is converted from a wavenumber to an energy in joules by multiplication by \( \hbar c \); the full width as an energy in joules is then identified with \( \delta E \).

\[ \tau = \frac{h}{(\delta E)} = \frac{1}{2\pi c \Delta} \]
(a) \( \tau = (2\pi \times 2.9979 \times 10^{10} \text{ cm s}^{-1} \times 0.010 \text{ cm}^{-1})^{-1} = 5.3 \times 10^{-10} \text{ s} = 530 \text{ ps} \)

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

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

**Exercise:** What is the full width of the spectral peak if the lifetime of the upper state is 1.0 \( \mu \text{s} \)?