Ch126
Winter Quarter – 2024
Problem Set 1
Due: 11 January, 2024

1. (10 points) Two operators $\hat{O}$ and $\hat{O}^\dagger$ are defined to be adjoint if their expectation values are complex conjugates of one another. That is:

$$\langle\phi|\hat{O}^\dagger|\phi\rangle = \langle\phi|\hat{O}|\phi\rangle^* \qquad (1)$$

and

$$\left(\hat{O}^\dagger\right)^\dagger = \hat{O}$$

Consider two functions ϕ_1 and ϕ_2 in the domain of adjoint operators $\hat{O}$ and $\hat{O}^\dagger$. Two new functions in this domain, Φ_A and Φ_B, are given by

$$\Phi_A = \phi_1 + \phi_2 \qquad \Phi_B = \phi_1 + i\phi_2$$

where $i = \sqrt{-1}$. Using the foregoing definition of adjoint operators (Eq. 1), with the operators $\hat{O}$ and $\hat{O}^\dagger$ and functions Φ_A and Φ_B to prove the turnover rule:

$$\langle\phi_1|\hat{O}^\dagger|\phi_2\rangle = \langle\hat{O}\phi_1|\phi_2\rangle$$

Some important properties: if z_1 and z_2 are two different complex numbers, then $z_1^* z_2 = (z_2^* z_1)^*$; $z^\dagger = z^*$; $\langle u|^\dagger = |u\rangle$; $\langle u_1|u_2\rangle^\dagger = \langle u_1|u_2\rangle^* = \langle u_2|u_1\rangle$.

2. (10 points) Consider a dynamical quantity F given by the expectation value of the operator $\hat{F}$:

$$\langle F\rangle = \int_{-\infty}^{\infty} \Psi^*(x,y,z,t)\hat{F}\Psi(x,y,z,t)d\tau$$

Use the time-dependent Schrödinger equation and the turnover rule to prove that:

$$\frac{d\langle F\rangle}{dt} = \frac{i}{\hbar}\int_{-\infty}^{\infty} \Psi^*(x,y,z,t)\left[\hat{H}\hat{F} - \hat{F}\hat{H}\right]\Psi(x,y,z,t)d\tau$$

where $\hat{H}$ is the Hamiltonian operator and $\hbar$ is Planck's constant divided by 2π.

3. (10 points) Use the definitions of the orbital angular momentum operators $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ to derive the following commutators:

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z \qquad \left[\hat{L}_y, \hat{L}_z\right] = i\widehat{\hbar L}_x \qquad \left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y$$

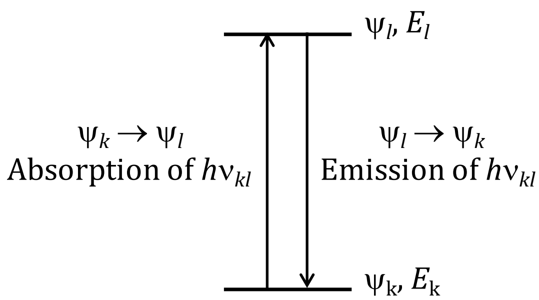
4. (10 points) The linear momentum operator is $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$. Use integration by parts in the following integral to prove that $\hat{p}_x$ is Hermitain (i.e., self-adjoint).

$$\int_{-\infty}^{+\infty}\left(-i\hbar\frac{\partial}{\partial x}\phi_1\right)^{*}\phi_2 dx$$

where the wavefunctions ϕ_1 and ϕ_2 vanish at $\pm\infty$.

5. (10 points) Consider the two-state system shown in the figure below.

$$h\nu_{kl} = E_l - E_k$$



The rate of spontaneous emission from state ψ_l is $A \times N_l$, the rate of stimulated emission from state ψ_l is $B \times N_l \times \rho(\nu_{kl})$, and rate of light absorption from state ψ_k is $B \times N_k \times \rho(\nu_{kl})$, where: N_k and N_l are the populations of states ψ_k and ψ_l, respectively; A is the Einstein coefficient for spontaneous emission; B is the Einstein coefficient for stimulated absorption and stimulated emission; and $\rho(\nu_{kl})$ is the radiation density of frequency ν_{kl}. The total population of the two states is N_{total}. Suppose that $N_k = N_{total}$ before light of constant intensity is switched on at time $t = 0$.

a. Write down the differential equations describing the rate of change in N_k and N_l with time.

b. Solve the differential equations from part (a) to obtain N_k and N_l as functions of time.

c. What are the limiting populations of states ψ_k and ψ_l, as $t \rightarrow \infty$?

d. Is it possible to create a population inversion (*i.e.*, $N_l > N_k$) by increasing the light intensity (*i.e.*, increasing $\rho(\nu_{kl})$)?

6. (10 points) An Excel file containing a spreadsheet of the solar spectrum above the Earth's atmosphere (zero air mass) and at its surface is posted on the Canvas website. The spectrum reports intensity in units of watts per square meter per nanometer ($W \cdot m^{-2} \cdot nm^{-1}$) as a function of the wavelength of light in units of nanometers (nm).

a. Make an overlay plot of intensity vs. wavelength of the two spectra using the units provided in the file.

b. What fraction of the light power at the Earth's surface is in the visible spectral region (400-700 nm)?

c. Use Planck's equation for the energy of a photon ($E = h\nu$) to make a new overlay plot of photon flux vs. wavelength of the two spectra using flux units of Einsteins per second per square meter per nanometer ($Einstein \cdot s^{-1} \cdot m^{-2} \cdot nm^{-1}$). The Einstein unit is defined to be 1 mole of photons.

d. What fraction of the photons reaching the Earth's surface is in the visible spectral region (400-700 nm)?

e. The light absorbance of a sample is defined by the equation: $Abs = -log_{10}\left(\frac{I_t}{I_0}\right)$, where I_0 is the intensity of light incident on the sample and I_t is the intensity of light transmitted through the sample. Use the data in the Excel file to plot the absorbance of the atmosphere as a function of wavelength in nanometers.

1. $\langle \Phi_A | \hat{O}^\dagger | \Phi_A \rangle = \langle \Phi_A | \hat{O} | \Phi_A \rangle^*$ $\quad \langle \Phi_B | \hat{O}^\dagger | \Phi_B \rangle = \langle \Phi_B | \hat{O} | \Phi_B \rangle^*$

$\Phi_A = \phi_1 + \phi_2 \qquad \Phi_B = \phi_1 + i\phi_2$

$$\langle \phi_1 + \phi_2 | \hat{O}^\dagger | \phi_1 + \phi_2 \rangle = \langle \phi_1 + \phi_2 | \hat{O} | \phi_1 + \phi_2 \rangle^*$$
$$+ \ \langle \phi_1 + i\phi_2 | \hat{O}^\dagger | \phi_1 + i\phi_2 \rangle = \langle \phi_1 + i\phi_2 | \hat{O} | \phi_1 + i\phi_2 \rangle^*$$

complex conj.

$$\langle 2\phi_1 + (1+i)\phi_2 | \hat{O}^\dagger | 2\phi_1 + (1+i)\phi_2 \rangle = \langle 2\phi_1 + (1+i)\phi_2 | \hat{O} | 2\phi_1 + (1+i)\phi_2 \rangle^*$$

$$\langle 2\phi_1 + (1+i)\phi_2 | \hat{O}^\dagger | 2\phi_1 + (1+i)\phi_2 \rangle = \langle 2\phi_1 + (1+i)^*\phi_2 | \hat{O}^* | 2\phi_1 + (1+i)^*\phi_2 \rangle$$

$$\langle 2\phi_1 + (1-i)\phi_2 | \hat{O}^\dagger | 2\phi_1 + (1-i)\phi_2 \rangle^* = \langle 2\phi_1 + (1+i)^*\phi_2 | \hat{O}^* | 2\phi_1 + (1+i)^*\phi_2 \rangle$$

$$\langle 2\phi_1 + (1-i)\phi_2 | \hat{O}^\dagger | 2\phi_1 + (1-i)\phi_2 \rangle = \langle 2\phi_1 + (1+i)^*\phi_2 | \hat{O}^* | 2\phi_1 + (1+i)^*\phi_2 \rangle^*$$

because if $A^* = B$ then $A = B^*$

$$\langle 2\phi_1 + (1-i)\phi_2 | \hat{O}^\dagger | 2\phi_1 + (1-i)\phi_2 \rangle = \langle 2\phi_1 + (1+i)\phi_2 | \hat{O} | 2\phi_1 + (1+i)\phi_2 \rangle$$

$-(1-i)\phi_2 \quad -2\phi_1 \qquad -(1-i)\phi_2 \quad -2\phi_1$

$$\langle 2\phi_1 | \hat{O}^\dagger | (1-i)\phi_2 \rangle = \langle 2\phi_1 - \phi_2 | \hat{O} | (1+i)\phi_2 \rangle$$

2. $\langle F \rangle = \int_{-\infty}^{\infty} \Psi^*(x,y,z,t)\, \hat{F}\, \Psi(x,y,z,t)\, d\tau$

Prove that

$$\frac{d\langle F \rangle}{dt} = \frac{i}{\hbar} \int_{-\infty}^{\infty} \Psi^*(x,y,z,t) [\hat{H}\hat{F} - \hat{F}\hat{H}] \Psi(x,y,z,t)\, d\tau$$

$$\frac{\partial}{\partial t}\langle \hat{F} \rangle = \int \left[\frac{\partial \psi}{\partial t}^* \hat{F} \psi + \psi^* \cancel{\frac{\partial \hat{F}}{\partial t}}^{\,0} \psi + \psi^* \hat{F} \frac{\partial \psi}{\partial t} \right)\Big] d\tau$$

$\hat{F}$ is time-independent

time dependent Schrodinger: $i\hbar \dfrac{\partial \psi}{\partial t} = \hat{H}\psi$

$\rightarrow$ complex. conj. $-i\hbar \dfrac{\partial \psi^*}{\partial t} = \psi^* \hat{H}$

$$\frac{\partial}{\partial t}\langle \hat{F} \rangle = \int_{-\infty}^{\infty} \frac{1}{i\hbar} \left[-\psi^* \hat{H}\hat{F}\psi + \psi^* \hat{F}\hat{H}\psi \right] d\tau$$
$$= \int_{-\infty}^{\infty} \left(\frac{i}{i}\right) \frac{1}{i\hbar} \left[\psi^* \hat{F}\hat{H}\psi - \psi^* \hat{H}\hat{F}\psi \right] d\tau$$

$$= \int_{-\infty}^{\infty} \frac{i}{\hbar} \left[\psi^* \hat{H} \hat{F} \psi - \psi^* \hat{F} \hat{H} \psi \right] d\tau$$

$$\boxed{\frac{\partial}{\partial t} \langle \hat{F} \rangle = \frac{i}{\hbar} \int_{-\infty}^{\infty} \psi^*(x,y,z,t) \left(\hat{H}\hat{F} - \hat{F}\hat{H} \right) \psi(x,y,z,t)\, d\tau}$$

3. Derive :

$$[\hat{L}_x , \hat{L}_y] = i\hbar \hat{L}_z \qquad \hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$$
$$[\hat{L}_y , \hat{L}_z] = i\hbar \hat{L}_x \qquad \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z$$
$$[\hat{L}_z , \hat{L}_x] = i\hbar \hat{L}_y \qquad \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$

$$[\hat{L}_x , \hat{L}_y] = [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y , \hat{z}\hat{p}_x - \hat{x}\hat{p}_z]$$
$$[\hat{L}_x , \hat{L}_y] = [\hat{y}\hat{p}_z , \hat{z}\hat{p}_y] - [\hat{y}\hat{p}_z , \hat{x}\hat{p}_z] - [\hat{z}\hat{p}_y , \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y , \hat{x}\hat{p}_z]$$

x & p_x, y & p_y, z & p_z don't commute

$$[\hat{L}_x , \hat{L}_y] = [\hat{y}\hat{p}_z , \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y , \hat{x}\hat{p}_z]$$
$$[\hat{L}_x , \hat{L}_y] = \hat{y}\hat{p}_x [\hat{p}_z , \hat{z}] + \hat{x}\hat{p}_y [\hat{z} , \hat{p}_z]$$

while $[\hat{z} , \hat{p}_z] = i\hbar$

$$[\hat{L}_x , \hat{L}_y] = \hat{y}\hat{p}_x (-i\hbar) + \hat{x}\hat{p}_y (i\hbar)$$
$$[\hat{L}_x , \hat{L}_y] = i\hbar (\hat{x}\hat{p}_y - \hat{y}\hat{p}_x)$$
$$[\hat{L}_x , \hat{L}_y] = i\hbar \hat{L}_z$$

repeat same approach for $[\hat{L}_y , \hat{L}_z]$ and $[\hat{L}_z , \hat{L}_x]$

4. $\hat{p}$ is self-adjoint by showing $\langle \hat{p}\phi_1 | \phi_2 \rangle = \langle \phi_1 | \hat{p}\phi_2 \rangle$

$$\langle \hat{p}\phi_1 | \phi_2 \rangle = \int_{-\infty}^{\infty} \left(-i\hbar \frac{\partial}{\partial x} \phi_1 \right)^* \phi_2 \, dx$$

$$= i\hbar \int_{-\infty}^{\infty} \frac{\partial}{\partial x} \phi_1^* \phi_2 \, dx$$

$u = \phi_2 \qquad dv = \frac{\partial}{\partial x} \phi_1^*$

$du = \frac{\partial}{\partial x} \phi_2 \qquad v = \phi_1^*$

$$= i\hbar \left[[\phi_2 \phi_1^*]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \phi_1^* \frac{\partial}{\partial x} \phi_2 \, dx \right]$$
$$= 0 + \int_{-\infty}^{\infty} \phi_1^* \left(-i\hbar \frac{\partial}{\partial x} \phi_2 \right) dx$$

$$\langle \hat{p}\phi_1 | \phi_2 \rangle = \langle \phi_1 | \hat{p}\phi_2 \rangle$$

5. a) $R_{SE} = N_\ell A$

$R_{STE} = -BN_\ell \rho(\nu_{k\ell})$

$\frac{dN_{tot}}{dt} = \phi = \frac{dN_k}{dt} + \frac{dN_\ell}{dt}$

$R_A = -BN_k \rho(\nu_{k\ell})$

$\frac{dN_k}{dt} = -\frac{dN_\ell}{dt}$

$$\frac{dN_k}{dt} = N_\ell A - N_k B\rho(\nu_{k\ell}) + N_\ell B\rho(\nu_{k\ell})$$

$$\frac{dN_\ell}{dt} = -N_\ell A + N_k B\rho(\nu_{k\ell}) - N_\ell B\rho(\nu_{k\ell})$$

b) $\frac{dN_k}{dt} = N_\ell A - N_k B\rho(\nu_{k\ell}) + N_\ell B\rho(\nu_{k\ell})$

$\frac{dN_k}{dt} = N_\ell(A + B\rho(\nu_{k\ell})) - N_k B\rho(\nu_{k\ell})$

$\mu = e^{\int B\rho(\nu_{k\ell})\,dt} = e^{B\rho(\nu_{k\ell})t}$

$\frac{dN_k}{dt} + N_k B\rho(\nu_{k\ell}) = N_\ell(A + B\rho(\nu_{k\ell}))$

$e^{B\rho(\nu_{k\ell})t}\left(\frac{dN_k}{dt} + N_k B\rho(\nu_{k\ell})\right) = e^{B\rho(\nu_{k\ell})t} N_\ell(A + B\rho(\nu_{k\ell}))$

$e^{B\rho(\nu_{k\ell})t}\frac{dN_k}{dt} + e^{B\rho(\nu_{k\ell})t} N_k B\rho(\nu_{k\ell}) = e^{B\rho(\nu_{k\ell})t} N_\ell(A + B\rho(\nu_{k\ell}))$

$\frac{(e^{B\rho(\nu_{k\ell})t} N_k)}{dt} = e^{B\rho(\nu_{k\ell})t} N_\ell(A + B\rho(\nu_{k\ell}))$

$\int \frac{(e^{B\rho(\nu_{k\ell})t} N_k)}{dt}\,dt = \int e^{B\rho(\nu_{k\ell})t} N_\ell(A + B\rho(\nu_{k\ell}))\,dt$

let $u = B\rho(\nu_{k\ell})t$

$du = B\rho(\nu_{k\ell})\,dt$

$e^{B\rho(\nu_{k\ell})t} N_k = \int e^u \frac{N_\ell(A + B\rho(\nu_{k\ell}))}{B\rho(\nu_{k\ell})}\,du$

$e^{B\rho(\nu_{k\ell})t} N_k = \frac{N_\ell(A + B\rho(\nu_{k\ell}))}{B\rho(\nu_{k\ell})} e^{B\rho(\nu_{k\ell})t} + C$

$N_k = \left(\frac{N_\ell A}{B\rho(\nu_{k\ell})} + 1\right) + Ce^{-B\rho(\nu_{k\ell})t}$ when $N_k(0) = N_{tot}$

$N_{tot} = \left(\frac{N_\ell A}{B\rho(\nu_{k\ell})} + 1\right) + Ce^{-B\rho(\nu_{k\ell})0}$

$N_{tot} = \frac{N_\ell A}{B\rho(\nu_{k\ell})} + 1 + C(1)$

$C = \frac{N_\ell A}{B\rho(\nu_{k\ell})} + 1 - N_{tot}$

$$\boxed{N_k = \frac{N_\ell A}{B\rho(\nu_{k\ell})} + \left(\frac{N_\ell A}{B\rho(\nu_{k\ell})} + 1 - N_{tot}\right)e^{-B\rho(\nu_{k\ell})t} + 1}$$

$$\frac{dN_\ell}{dt} = -N_\ell A + N_k B\rho(\nu_{k\ell}) - N_\ell B\rho(\nu_{k\ell})$$

$$\frac{dN_\ell}{dt} - N_\ell(A + B\rho(\nu_{k\ell})) = N_k B\rho(\nu_{k\ell}) \qquad \mu = e^{\int -(A+B\rho(\nu_{k\ell}))dt} = e^{(A+B\rho(\nu_{k\ell}))t}$$

$$e^{-(A+B\rho(\nu_{k\ell}))t}\left[\frac{dN_\ell}{dt} - N_\ell(A + B\rho(\nu_{k\ell}))\right] = e^{-(A+B\rho(\nu_{k\ell}))t} N_k B\rho(\nu_{k\ell})$$

$$\frac{[e^{-(A+B\rho(\nu_{k\ell}))t} N_\ell]}{dt} = e^{-(A+B\rho(\nu_{k\ell}))t} N_k B\rho(\nu_{k\ell})$$

$$\int \frac{[e^{-(A+B\rho(\nu_{k\ell}))t} N_\ell]}{dt} dt = \int e^{-(A+B\rho(\nu_{k\ell}))t} N_k B\rho(\nu_{k\ell})\, dt$$

let $u = -(A+B\rho(\nu_{k\ell}))t$

$du = -(A+B\rho(\nu_{k\ell}))dt$

$$e^{-(A+B\rho(\nu_{k\ell}))} N_\ell = \frac{-1}{(A+B\rho(\nu_{k\ell}))} \int e^u N_k B\rho(\nu_{k\ell})\, du$$

$$e^{-(A+B\rho(\nu_{k\ell}))} N_\ell = \frac{-1}{(A+B\rho(\nu_{k\ell}))} e^{-(A+B\rho(\nu_{k\ell}))t} N_k B\rho(\nu_{k\ell}) + C$$

$$N_\ell = \frac{-N_k B\rho(\nu_{k\ell})}{(A+B\rho(\nu_{k\ell}))} + Ce^{(A+B\rho(\nu_{k\ell}))t} \qquad \text{when } N_\ell(0) = 0$$

$$0 = \frac{-N_k B\rho(\nu_{k\ell})}{(A+B\rho(\nu_{k\ell}))} + Ce^{(A+B\rho(\nu_{k\ell}))0}$$

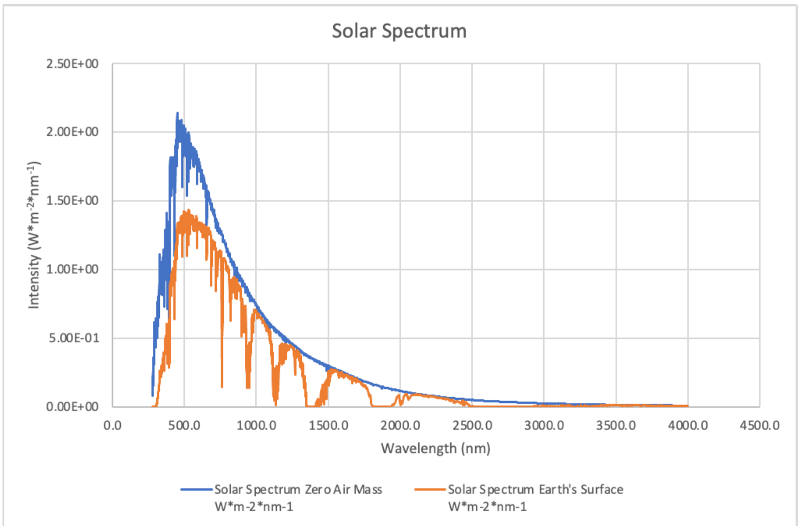
$$0 = \frac{-N_k B\rho(\nu_{k\ell})}{(A+B\rho(\nu_{k\ell}))} + C(1)$$

$$C = \frac{N_k B\rho(\nu_{k\ell})}{(A+B\rho(\nu_{k\ell}))} \qquad \boxed{N_\ell = \frac{N_k B\rho(\nu_{k\ell})}{(A+B\rho(\nu_{k\ell}))}\left(e^{(A+B\rho(\nu_{k\ell}))t} - 1\right)}$$

c) As $t \to \infty$ the population tends toward populating ψ_ℓ and depopulating ψ_k exponentially.

d) It is impossible to create a population inversion, not in a two energy levels system as there the population will continue this trend unless there is a 3rd energy level to populate/depopulate.

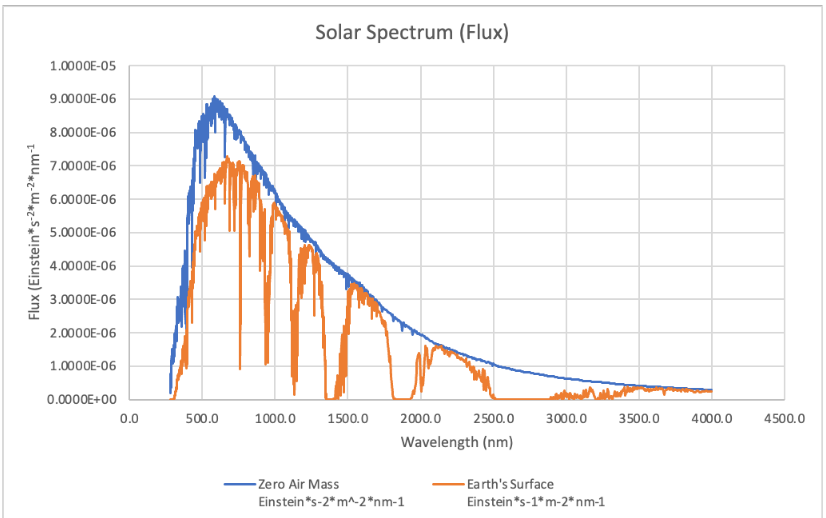
6. a)



b) 42%

c) $J s^{-1} m^{-2} nm^{-1} \times \frac{1\ mol}{6.02\times10^{23}\ phot} = \frac{I}{(hc/\lambda)N_A}$

$I \times \left(\frac{\lambda \times 10^{-9}\ m}{6.626\times10^{-34}\ J\cdot s \times 3.0\times10^{8}\ m/s \times 6.02\times10^{23}} \right)$



d) 29%

e)