Quantum Mechanics

Homework 9: Time-Independent Perturbation Theory

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017 qfull 00200 3 3 0 tough math: time dependent perturbation, square well

Extra keywords: (MEL-141:5.3), time dependent perturbation, infinite square well

1. At time $t = 0$, an electron of charge $\tilde{e}$ is in the n eigenstate of an infinite square well with potential

$$V(x) = \begin{cases} 0, & x \in [0, a]; \\ \infty & x > a. \end{cases}$$

At that time, a constant electric field $\tilde{E}$ pointed in the positive x direction is suddenly applied. (Note the tildes on charge and electric field are to distinguish these quantities from the natural log base and energy.) **NOTE:** The 1-d infinite square-well eigenfunctions and eigen-energies are, respectively

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \qquad \text{and} \qquad E_n = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 n^2 ,$$

where $n = 1, 2, 3, \ldots$ The sinusoidal eigenfunctions can be expressed as exponentials: let $z = \pi x/a$, and then

$$\sin(nz) = \frac{e^{inz} - e^{-inz}}{2i} .$$

a) Use 1st order time-dependent perturbation theory to calculate the transition probabilities to all **OTHER** states m as a function of time. You should evaluate the matrix elements as explicitly: this is where all the work is naturally.

b) How do the transition probabilities vary with the energy separation between states n and m?

c) Now what is the 1st order probability of staying in the same state n?

SUGGESTED ANSWER:

a) In this case the perturbation potential is given by

$$H^{(1)} = (-\tilde{e})(-\tilde{E})x = \tilde{e}\tilde{E}x . \tag{1}$$

The first order perturbation expression for the coefficent a_m $(m \neq n)$ is then

$$\begin{aligned} a_m &= \frac{1}{i\hbar}\int_0^t e^{i\omega_{mn}t'} H^{(1)}_{mn}(t')\, dt' \\ &= \frac{1}{i\hbar} e^{i\omega_{mn}t/2} \frac{\sin(\omega_{mn}t/2)}{(\omega_{mn}/2)} \tilde{e}\tilde{E}\langle\psi_m|x|\psi_n\rangle , \end{aligned} \tag{2}$$

where

$$\omega_{mn} \equiv \frac{E_m - E_n}{\hbar} . \tag{3}$$

The transition probability is

$$P_{n \text{ to } m}(t) = |a_m|^2 = \frac{1}{\hbar^2} \frac{\sin^2(\omega_{mn}t/2)}{(\omega_{mn}/2)^2} |\tilde{e}\tilde{E}|^2 |\langle\psi_m|x|\psi_n\rangle|^2 . \tag{4}$$

At time zero, the transition probabilities grow everywhere as t^2 as can be seen by a 1st order expansion of the sine function about zero. As time passes, the probabilities begin to oscillate in time. Non-monotonic behavior (which we can call the beginning of oscillation) sets in for state m when

$$\frac{\pi}{2} < \frac{\omega_{mn}t}{2} \tag{5}$$

holds for that state. The probability would continue to grow as t^2 only for states degenerate with state n: i.e., for cases with $\omega_{mn} = 0$. But there are no degenerate states for 1-dimensional infinite square well.

One must recall that 1st order theory can not be valid for long times: i.e., for $P_{n\text{ to }m}(t)$ growing significantly close to 1.

The remaining problem is just to evaluate and simplify the expression for the matrix element:

$$\begin{aligned}
\langle\psi_m|x|\psi_n\rangle &= \frac{2}{a}\int_0^a \sin\left(\frac{m\pi}{a}x\right) x \sin\left(\frac{n\pi}{a}x\right)\,dx \\
&= \frac{2}{a}\frac{1}{(-4)}\left(\frac{a}{\pi}\right)^2\int_0^\pi \left(e^{imz}-e^{-imz}\right) z \left(e^{inz}-e^{-inz}\right)\,dz \\
&= \frac{2a}{\pi^2}\frac{1}{(-4)}\int_0^\pi z\left(e^{i(m+n)z}+e^{-i(m+n)z}-e^{i(m-n)z}-e^{-i(m-n)z}\right)dz\ ,
\end{aligned} \tag{6}$$

where we have used the transformation $z = \pi x/a$. Here we note that

$$\int_0^\pi z e^{i\ell z}\,dz = \frac{\pi}{i\ell}(-1)^\ell + \frac{(-1)^\ell - 1}{\ell^2}\ , \tag{7}$$

where ℓ is an integer. The first terms from right-hand side of equation (7) that appear in integral of equation (6) all cancel out in fact. The second terms from right-hand side of equation (7) that appear in integral of equation (6) yield the factor

$$2\frac{[(-1)^{m-n}-1]}{(m+n)^2} + 2\frac{[(-1)^{m-n}-1]}{(m-n)^2} = \frac{-8mn}{(m^2-n^2)^2}[(-1)^{m-n}-1]\ , \tag{8}$$

where we have use the fact that if $m+n$ is even then $m-n$ is even too, and so $(-1)^{m+n} = (-1)^{m-n}$. The final results are

$$\langle\psi_m|x|\psi_n\rangle = \frac{8a}{\pi^2}\frac{mn}{(m^2-n^2)^2}\left\{\frac{[(-1)^{m-n}-1]}{2}\right\} \tag{9}$$

and

$$|\langle\psi_m|x|\psi_n\rangle|^2 = \frac{64a^2}{\pi^4}\frac{m^2n^2}{(m^2-n^2)^4}\left\{\frac{[(-1)^{m-n}-1]}{2}\right\}^2\ . \tag{10}$$

We can see from the matrix element that all even transitions (i.e., those with $m-n$ even) vanish in 1st order theory.

b) How does energy separation of states m and n affect the matrix elements? Recall from equation E_n is proportional n^2 and is always greater than zero. Consider the function

$$f(r) = \frac{rb}{(r-b)^4}\ . \tag{11}$$

The derivative is

$$\frac{df(r)}{dr} = -\frac{b(b+3r)}{(r-b)^5}\ . \tag{12}$$

Evidently, the function $f(r)$ for $r > 0$ and $b > 0$ decreases with r for $r > b$ and increases with r for $r < b$. Thus $f(r)$ decreases always as $|r-b$ increases. In our case $r = m^2$ and $b = n^2$. We can see that the squared modulus of the odd matrix element decreases with increasing energy separation. Thus the transition probabilities decrease with increasing energy separation between states n and m.

c) The first order amplitude for staying in the same state is

$$\begin{aligned}
a_m &= \frac{1}{i\hbar}\int_0^t H^{(1)}_{nn}(t')\,dt' \\
&= \frac{1}{i\hbar}t\tilde{e}\tilde{E}\langle\psi_n|x|\psi_n\rangle\ .
\end{aligned} \tag{13}$$

Now

$$\begin{aligned}
\langle\psi_n|x|\psi_n\rangle &= \frac{2}{a}\int_0^a x\sin^2\left(\frac{n\pi}{a}x\right)\,dx = \frac{2}{a}\left(\frac{a}{n\pi}\right)^2\int_0^{n\pi} z\sin^2(z)\,dz \\
&= \frac{2}{a}\left(\frac{a}{n\pi}\right)^2\left\{\frac{z}{2}\left[z-\frac{\sin(2z)}{2}\right]\Bigg|_0^{n\pi} - \int_0^{n\pi}\frac{1}{2}\left[z-\frac{\sin(2z)}{2}\right]\,dz\right\} \\
&= \frac{2}{a}\left(\frac{a}{n\pi}\right)^2\left\{\frac{(n\pi)^2}{2}-\frac{1}{2}\left[\frac{z^2}{2}+\frac{\cos(2z)}{4}\right]\Bigg|_0^{n\pi}\right\} \\
&= \frac{2}{a}\left(\frac{a}{n\pi}\right)^2\frac{(n\pi)^2}{4} \\
&= \frac{a}{2}
\end{aligned} \tag{14}$$

Then we find

$$P(t) = \frac{t^2}{\hbar^2}|\tilde{e}\tilde{E}|^2\frac{a^2}{4}\ . \tag{15}$$

The 1st order probability of no transition increases quadratically with time. Note a 1st order calculation for no transition is probably not that great. One should probably do a 2nd order calculation.

Redaction: Jeffery, 2001jan01

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024 qmult 01600 1 4 4 easy deducto-memory: Einstein stimulated em.

2. "Let's play *Jeopardy*! For \$100, the answer is: An effect discovered by Einstein by means of a thermodynamic equilibrium detailed balance argument."

What is ____________, Alex?

a) spontaneous emission b) special relativity c) the photoelectric effect
d) stimulated emission e) spontaneous omission

SUGGESTED ANSWER: (d)

Wrong answers:

e) I'm subject to this effect myself.

Redaction: Jeffery, 2001jan01

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024 qmult 01900 1 1 2 easy memory: electric dipole transitions

3. Typically, strong atomic and molecular transitions are ____________ transitions.

a) electric quadrupole b) electric dipole c) magnetic dipole d) electric monopole
e) magnetic metropole

SUGGESTED ANSWER: (b)

Wrong Answers:

e) Metropole is not in my dictionary, but I think it is a word meaning metropolis. If I recall correctly, Wallace Stevens uses metropole in cute poem.

Redaction: Jeffery, 2001jan01

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024 qfull 00300 2 5 0 moderate thinking: classical EM scattering

Extra keywords: reference Mi-83

4. Say we had a classical simple harmonic oscillator (SHO) consisting of a particle with mass m and charge e and a restoring force $m\omega_0^2$ where ω_0 is the simple harmonic oscillator frequency. This SHO is subject to driving force caused by traveling electromagnetic field (i.e., light):

$$\vec{F}_{\rm drive} = e\vec{E}_0 e^{i\omega t}\ ,$$

where $\vec{E}_0$ is the amplitude, ω is the driving frequency, and we have used the complex exponential form for mathematical convenience: the real part of this force is the real force. The magnetic force can be neglected for non-relativistic velocities. The Lorentz force is

$$\vec{F} = e\left(\vec{E}+\frac{\vec{v}}{c}\times\vec{B}\right)$$

(Ja-238) and $\vec{E}$ and $\vec{B}$ are comparable in size for electromagnetic radiation, and so the magnetic force is of order v/c smaller than the electric force. (See also MEL-130.) An oscillating charge is an accelerating charge and will radiate electromagnetic radiation. The power radiated classically is

$$P = \frac{2e^2a^2}{3c^3} ,$$

where $\vec{a}$ is the charge acceleration. This radiation causes an effective damping force given approximately by

$$\vec{F}_{\rm damp} = -m\gamma\vec{v} ,$$

where

$$\gamma = \frac{2e^2\omega_0^2}{3mc^3} .$$

The full classical equation of motion of the particle is

$$m\vec{a} = -m\omega_0^2\vec{r} + e\vec{E}_0 e^{i\omega t} - m\gamma\vec{v} .$$

a) Solve the equation of motion for $\vec{r}$ and $\vec{a}$. **HINTS:** The old trial solution approach works. Don't forget to take the real parts although no need to work out the real part explicitly: i.e., Re[solution] is good enough for the moment.

b) Now solve for the time average of the power radiated by the particle. **HINT:** You will need the explicit real acceleration now.

c) The average power radiated must equal the average power absorbed. Let's say that the particle is in radiation flux from a single direction with specific intensity

$$I_0 = \frac{cE_0^2}{8\pi}$$

(Mi-9), where time averaging is assumed *como usual*. The power absorbed from this flux is $\sigma(\omega)I_0$, where $\sigma(\omega)$ is the cross section for energy removed. Solve for $\sigma(\omega)$ and then find show that it can be approximated by a Lorentzian function of ω with a coefficient $\pi e^2/(mc)$. **HINT:** It is convenient to absorb some of the annoying constants into another factor of γ.

d) Now rewrite the cross section as a function of $\nu = \omega/(2\pi)$ (i.e., the ordinary frequency) and then integrate over ν to get the frequency integrated cross section $\sigma_{\nu\ \rm int}$ of the system. What is the remarkable thing about $\sigma_{\nu\ \rm int}$? Think about how it relates to the system from which we derived it. Evaluate this frequency integrated cross section for an electron. **HINT:** The following constants might be useful

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137.036} , \qquad \hbar = 1.05457 \times 10^{-27}\,{\rm erg\,s} , \qquad \text{and} \qquad m_e = 9.10939 \times 10^{-28}\,{\rm g} .$$

SUGGESTED ANSWER:

a) Let $\vec{r} = \vec{r}_0 e^{i\omega t}$ and substitute this into the equation of motion and cancel out the exponential factor:

$$-\omega^2 m\vec{r}_0 = -m\omega_0^2\vec{r}_0 + e\vec{E}_0 - i\omega m\gamma\vec{r}_0 .$$

Well we find

$$\vec{r}_0 = \frac{(e/m)\vec{E}_0}{\omega_0^2 - \omega^2 + i\gamma\omega} ,$$

and so

$$\vec{r} = {\rm Re}\left[\frac{(e/m)\vec{E}_0 e^{i\omega t}}{\omega_0^2 - \omega^2 + i\gamma\omega}\right]$$

and

$$\vec{a} = \mathrm{Re}\left[\frac{-\omega^2(e/m)\vec{E}_0 e^{i\omega t}}{\omega_0^2-\omega^2+i\gamma\omega}\right] .$$

b) Behold:

$$\vec{a} = -\omega^2(e/m)\vec{E}_0\frac{(\omega_0^2-\omega^2)\cos(\omega t)+\gamma\omega\sin(\omega t)}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2} .$$

The time average of the square of the magnitude of $\vec{a}$ is

$$\langle a^2\rangle = \left[\omega^2(e/m)\vec{E}_0\right]^2\frac{1}{2}\frac{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2}{[(\omega_0^2-\omega^2)^2+\gamma^2\omega^2]^2} = \left[\omega^2(e/m)\vec{E}_0\right]^2\frac{1}{2}\frac{1}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2} ,$$

where we have used the facts that

$$\frac{1}{2\pi}\int_0^{2\pi}\sin^2(x)\,dx = \frac{1}{2\pi}\int_0^{2\pi}\cos^2(x)\,dx = \frac{1}{2} \qquad \text{and} \qquad \frac{1}{2\pi}\int_0^{2\pi}\sin(x)\cos(x)\,dx = 0 .$$

The time-averaged power is then

$$\langle P\rangle = \frac{e^4\omega^2E_0^2}{3m^2c^3}\frac{1}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2} ,$$

c) Behold:

$$\sigma(\omega) = \frac{\langle P\rangle}{I_0} = \frac{8\pi e^4\omega^4}{3m^2c^4}\frac{1}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2} .$$

Given the denominator, $\sigma(\omega)$ may well be sharply peaked about the SHO frequency ω_0. Thus only the strongest variation on ω needs to be retained. One can approximate ω elsewhere by ω_0. Well the big trick, and I admit to never having thought of it myself, is to make the following approximation

$$\omega_0^2-\omega^2 = (\omega_0+\omega)(\omega_0-\omega) \approx 2\omega_0(\omega_0-\omega) .$$

One then approximates the ω^4 by ω_0^4, divides numerator and denomitor by $4\omega_0^2$, and absorbs some constants into another γ factor to get

$$\sigma(\omega) = \frac{\pi e^2}{mc}\frac{\gamma}{(\omega_0-\omega)^2+(\gamma/2)^2} .$$

d) Well

$$\sigma(\nu) = \frac{\pi e^2}{mc}\frac{1}{\pi}\frac{\gamma/(4\pi)}{(\nu_0-\nu)^2+(\gamma/4\pi)^2} .$$

The normalized Lorentzian is

$$L(x) = \frac{1}{\pi}\frac{\Gamma/2}{(x-\bar{x})^2+(\Gamma/2)^2} ,$$

where Γ is the FWHM (i.e., full-width at half maximum) and $\bar{x}$ is the mean value of the distribution. It follows that

$$\sigma_{\nu\ \mathrm{int}} = \frac{\pi e^2}{mc} .$$

The remarkable thing about this frequency integrated cross section is that it is independent of the restoring force of the simple harmonic oscillator. It is sort of a universal result. Now microscopic systems are not classical nor often exactly simple harmonic oscillators, and thus one does not expect $\sigma_{\nu\ \mathrm{int}}$ to apply. However, $\sigma_{\nu\ \mathrm{int}}$ evaluated for an electron is frequently used as a unit of frequency integrated cross sections. Atomic frequency integrated cross sections can be written out

$$\sigma_{\nu\ \mathrm{int\ atomic}} = \frac{\pi e^2}{mc}f_{ij} ,$$

where f_{ij} is a dimensionaless quantity called the oscillator strength of the transition from lower level i to upper level j. Only for the strongest atomic transitions does $_{ij}$ approach unity (Mi-84).

For an electron, we find

$$\sigma_{\nu\ \mathrm{int}} = \frac{\pi e^2}{mc} = \frac{\pi\hbar\alpha}{m} = 0.02654\,\mathrm{cm}^2/\mathrm{s}\ .$$

We note that the units are area per time. The per time is there because we integrated over frequency.

Fortran Code

```
print*
pi=acos(-1.)
finestr=1./137.036
hbar=1.05457e-27
emass=9.10939e-28
oscon=(pi*hbar*finestr/emass)
print*,'The classical frequency integrated cross section is'
print*,'oscon=',oscon   !  0.0265400279
```

Redaction: Jeffery, 2001jan01