# EXAMPLES CLASS IN MATHEMATICAL PHYSICS

## IX. Quantum Theory (5.5.99)

In this final sheet we apply a number of important mathematical principles and techniques to problems in quantum physics. It is quite long, but this is mainly because we have included revision material, some of it from earlier sheets, at the start of each section. You need not work through these recap sections if you have already mastered the material (and remember it).

[We have also included an optional section on Green functions, which are useful for both classical and quantum problems.]

### A. Eigenfunction expansions in quantum mechanics

**A1. Recap on eigenfunctions.** Consider a quantum mechanical system governed by a Hamiltonian $H$. Subject to given boundary conditions (which *must* be specified), $H$ is self-adjoint (hermitian). In this case it has a *complete* set of *orthogonal* eigenfunctions $\phi_n(x)$:

$$H\phi_n(x) = E_n\phi_n(x) \ .$$

Assuming the $\phi_n(x)$ to be normalized, the orthogonality condition is

$$\int \phi_m^*(x)\phi_n(x)\,dx = \delta_{mn} \ . \tag{1}$$

Any function $f(x)$ can then be expanded in terms of the complete set of eigenfunctions:

$$f(x) = \sum_n c_n\phi_n(x) \tag{2}$$

where

$$c_m = \int \phi_m^*(x)\, f(x)\, dx \ . \tag{3}$$

[If you are unsure of this equation, prove it by substitution of (2) in (3) and using (1).]

**A2. Particle in a box.** Consider now the "particle in a box" problem with wave functions defined on the interval $0 \le x \le L$; the Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \ . \tag{4}$$

Since $\hbar^2/2m$ is a constant, the eigenfunctions of $H$ are those of the operator $\partial^2/\partial x^2$. *These depend on the boundary conditions.* Finding the boundary conditions appropriate to a given physical situation is an important part of setting up the problem in mathematical terms.

(i) What are the boundary conditions for a quantum particle trapped in a box?

(ii) Confirm that the normalized eigenfunctions in this case are

$$\phi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad , \quad n = 1, 2, 3... \tag{5}$$

and sketch the first three.

(iii) Use the results of Q. A1 to show that any real function $f(x)$, defined on the interval $0 \le x \le L$, can be expanded as follows:

$$f(x) = \sum_{n=1}^{\infty} a_n \ \sin\left(\frac{n\pi x}{L}\right) \tag{6}$$

$$a_n = \frac{2}{L}\int_0^L f(x)\ \sin\left(\frac{n\pi x}{L}\right) dx \tag{7}$$

These equations resemble ones you will have seen in the theory of Fourier analysis.

**A3. The time evolution problem.** The importance of eigenfunctions in the study of differential equations in physics stems from the fact that their time dependence is simple. A specified initial condition can be decomposed into eigenfunctions, these evolved according to simple rules, and the behaviour at a later time synthesized by superposing the time-evolved functions. The method is most familiar in quantum mechanics (this question) but applies equally to many other problems such as heat conduction, diffusion, and wave motion.

Consider the following problem:

"A particle of mass $m$ is in the groundstate of a 1-D box, $0 < x < L/2$. At time $t = 0$, the wall at $x = L/2$ is suddenly displaced to $x = L$. What is the wavefunction $\psi(x, t)$ at a subsequent time $t$?"

To solve this:

(i) Sketch the initial wavefunction, and write down its normalized form.

[Ans: $\psi(x, 0) = \sqrt{\frac{4}{L}} \sin\left(\frac{2\pi x}{L}\right), \quad 0 < x < L/2$; $\psi(x, 0) = 0 \quad , L/2 < x < L$.]

(ii) Use (6) to write $\psi(x, 0)$ as a sum over the eigenfunctions $\phi_n(x)$ of the new (larger) box, and find the coefficients $a_n$. To simplify this procedure, first show that $a_n = 0$ for all even $n$ except $n = 2$; then calculate $a_2$. Also, you may use without proof the following formula which applies for $n$ odd:

$$\int_0^{L/2} \sin\left(\frac{2\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) dx = \frac{L}{\pi}(-1)^{(n+1)/2} \frac{2}{n^2 - 4} \quad . \tag{8}$$

(iii) Use the time dependent Schrödinger equation,

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \tag{9}$$

to show that the eigenfunctions evolve according to

$$\phi_n(t) = \phi_n(0) e^{-iE_n t/\hbar}$$

and give an expression for the $E_n$.

(iv) Hence obtain a general expression for $\psi(x, t)$ at times $t > 0$.

[Ans: $\frac{1}{\sqrt{L}} \sin\left(\frac{2\pi x}{L}\right) e^{-\frac{i\hbar}{2m}\left(\frac{2\pi}{L}\right)^2 t} + \frac{8}{\pi\sqrt{L}} \sum_{n \text{ odd}} \frac{(-1)^{(n+1)/2}}{n^2 - 4} \sin\left(\frac{n\pi x}{L}\right) e^{-\frac{i\hbar}{2m}\left(\frac{n\pi}{L}\right)^2 t}$.]

(v) The quantum whispering gallery (Schrödinger's gallery). At what later time(s) is the particle definately in the interval $(0, L/2)$? All the initial information about the system is preserved as time evolves. The phases of the normal modes conspire to reconstitute, for an instant, the initial particle distribution.

## B. Wave packets in quantum mechanics

**B1. Recap on wave packets.** Recall the treatment of the propagation of a wave packet in the earlier sheet on waves. We defined a general one-dimensional problem in which we set up a wave packet at time $t = 0$, which we will assume to be symmetrical about the origin. This defines the initial condition of the problem: we must evolve forwards in time to find the disturbance $\psi(x,t)$. The evolution is governed by an arbitrary dispersion relation $\omega(k)$. The "carrier" wave, that is the basic wave underlying the initial pulse, has wavenumber $q$ and it is assumed that the envelope function of the pulse $A(x)$ is much broader than one wavelength. The initial profile is thus

$$\psi(x,0) = A(x)e^{iqx} \,.$$

(i) Show that the total disturbance can be written initially as

$$\psi(x,0) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk \, e^{i(k+q)x} B(k)$$

where

$$B(k) = \int_{-\infty}^{\infty} dx \, e^{-ikx} A(x) \,.$$

This corresponds to a distribution of Fourier components $B(k)e^{i(k+q)x}$ centred (in wavenumber space) around the carrier wave $e^{iqx}$.

(ii) Assume that each Fourier component evolves in time according to some arbitrary dispersion relation $\omega(q)$. Show that the disturbance at time $t$ can be written as:

$$\psi(x,t) = e^{i(qx-\omega(q)t)} \times \frac{1}{2\pi}\int_{-\infty}^{\infty} B(k)\, e^{ik(x-\omega'(q)t)} \times e^{-i\frac{1}{2}\omega''(q)k^2 t + \dots} \, dk \qquad (10)$$

where $\omega'(q) \equiv \frac{d\omega}{dq}$ and $\omega''(q) \equiv \frac{d^2\omega}{dq^2}$. By considering separately each of the three exponential factors, interpret this formula physically and derive expressions for (a) the *phase velocity* of a particular crest; (b) the *group velocity* of the wave train; and (c) the time it takes for the train to spread or alter its shape appreciably. [Note that for times much longer than this, the neglected terms (+...) in the third exponential may become important and the treatment starts to break down.]

**B2. Quantum wave packet.** The wave function $\psi(x,t)$ of a free particle obeys Schrödinger's equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = i\hbar\frac{\partial\psi}{\partial t}$$

(i) What is the dispersion relation for particle waves?

(ii) Consider a gaussian wavepacket with carrier wave $q$ and amplitude function $A(x) = A_o e^{-x^2/4\lambda^2}$, where $A_o$ is a suitable normalization constant. Show that at time zero this describes a particle localised at the origin with mean-square deviation $\langle\Delta x^2\rangle^{1/2} = \lambda$. What is its mean velocity? [Answer: $\hbar q/m$].

(iii) Show that, for particle waves, Eq. (10) is exact even for arbitrarily long times. [Hint: consider the neglected terms (+...) in the third exponential factor.]

(iv) Use Eq. (10) above to show that $\langle\Delta x(t)^2\rangle = (\lambda^4 + (\hbar t/2m)^2)/\lambda^2$. Why does the wavepacket spread with time? Interpret your result physically in terms of Heisenberg's uncertainty principle for $\Delta p\Delta x$. [You may assume without proof the formula for "completing the square":

$$\int dy\, e^{-y^2/2\kappa+\mu y} = \sqrt{2\pi\kappa}\, e^{\mu^2\kappa/2}$$

which applies for arbitrary complex $\kappa$ and $\mu$.]

## C. Variational method in quantum mechanics

**C1. Recap on method of undetermined multipliers.** Recall from the examples sheet on variational calculus the method for finding the function $y(x)$ that makes a functional

$$I[y(x)] = \int_a^b F(y, y', x)\, dx$$

stationary subject to a constraint, for instance that a second functional,

$$J[y(x)] = \int_a^b G(y, y', x)\, dx$$

is held constant. The constraint restricts the allowed types of variation $\eta(x)$ and hence the criterion for stationarity of $I$ is modified. A restricted set of variations $\bar{\eta}(x)$ about a given function $y(x)$ may be defined as those that obey

$$\delta J[y(x), \bar{\eta}(x)] = 0\ .$$

These variations are those that satisfy the constraint; hence the condition on $y(x)$ that $I$ is stationary, subject to the constraint of constant $J$, may be written

$$\delta I[y(x), \bar{\eta}(x)] = 0 \qquad \forall\ \bar{\eta}(x) \tag{11}$$

Show that the following condition on $y(x)$ is sufficient to ensure (11) holds:

$$\delta I[y(x), \eta(x)] + \lambda\, \delta J[y(x), \eta(x)] = 0 \qquad \forall\ \eta(x) \tag{12}$$

where $\eta(x)$ is now an *unconstrained* variation and $\lambda$ is an arbitrary constant.

Clearly, Eq. (12) is equivalent to seeking stationary values of a modified functional $K = I + \lambda J$, where the problem is to be solved now with *no* constraint on the type of variation allowed. The undetermined multiplier $\lambda$ is treated as a parameter, which can later be fixed from considering boundary conditions, etc.

**C2. Variational approach to the Schrödinger equation.** Consider variations in the Lagrangian $L$,

$$L = \text{K.E.} - \text{P.E.} = \int \left[ \frac{1}{2m} \left( \frac{\hbar}{i} \frac{\partial \psi^*}{\partial x} \right) \left( \frac{\hbar}{i} \frac{\partial \psi}{\partial x} \right) - V(x) \psi^* \psi \right] dx\ , \tag{13}$$

constrained by the normalization condition

$$J = \int \psi^* \psi \, dx \ \ (= 1) \, . \tag{14}$$

(i) Defining $K = L + \lambda J$, show that $K$ is stationary if $\psi$ satisfies

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V(x)\psi = \lambda\psi. \tag{15}$$

[Hint: to deal with the fact that $\psi$ is complex, write it as $\psi = \chi + i\phi$ with $\chi$ and $\phi$ two real functions, and make $F$ stationary w.r.t. variations in both $\chi$ and $\phi$. Alternatively, think of the two independent quantities as $\psi$ and $\psi^*$. Take variations with respect to $\psi^*$.]

We may identify (15) as the time-independent Schrödinger equation, $H\psi = \lambda\psi$, where $H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$. This equation is therefore equivalent to the "variational principle" $\delta K = 0$. In this formalism, the energy eigenvalue $\lambda$ plays the role of an undetermined multiplier, which ensures that the only variations permitted for $\psi$ are those that preserve the normalization of the wavefunction.

(ii) Show that $L = -\int dx \psi^* H \psi$. (Assume appropriate boundary conditions on $\psi$ at infinity.)

Thus we may identify $-L$ with $\langle H \rangle$. Hence **the solutions to Schrödinger's equation are those functions that make the expectation value of the Hamiltonian stationary**. This forms the basis of the Rayleigh-Ritz method for estimating the lowest eigenvalue of Schrödinger's equation.

**C3. The Rayleigh-Ritz method.** Consider the following functional:

$$\bar{E}[\psi(x)] = \frac{\int \psi^* H \psi \, dx}{\int \psi^* \psi \, dx}. \tag{16}$$

This is another way of writing the expectation value of $H$, now without any explicit normalisation constraint. (The normalisation chosen obviously cancels top and bottom since both terms are quadratic in $\psi$.) We have seen that this expectation value is stationary whenever $\psi$ is an eigenfunction of the Schrödinger equation.

(i) Prove directly from (15) that the stationary value of $\bar{E}$ is equal to the energy eigenvalue $\lambda$. This means that if we can find a stationary value of $\bar{E}$, we have found an eigenvalue of the Schrödinger equation. The case of the *lowest* eigenvalue must therefore correspond to the lowest stationary value or *global minimum* of $\bar{E}$.

Even if we can't solve the Schrödinger equation, we can still estimate the lowest eigenvalue, $\lambda_o$, in the following way. Since $\lambda_o$ is a global minimum, we have the inequality

$$\lambda_o \leq \bar{E}[\psi(x)] \, .$$

Hence any guess for $\psi$ can be used in (16) to provide an upper bound for $\lambda_o$. Of course, the estimate will be closest to the real answer when $\psi$ is similar to the true eigenfunction.

(ii) Estimate the ground state energy of a particle confined to an infinite square well ($\psi$ finite for $0 < x < 1$, zero for $x \geq 1$, $x \leq 0$). Take as a guess $\psi = x(1-x)$ since it has roughly the right sort of shape, and obeys the boundary conditions. Find the exact solution and compare it to your estimate. Why is the method so good here? [Answer: $m\lambda_o/\hbar^2 \leq 5$; exact value $\pi^2/2 = 4.935$.]

## D. Green functions

**D1. Green function for the diffusion equation.** Green functions arise often in mathematical physics; for example in *boundary value* or *initial value* problems. Consider first the diffusion equation (in one dimension for simplicity)

$$\frac{\partial \rho(x,t)}{\partial t} - D\frac{\partial^2 \rho(x,t)}{\partial x^2} = 0 \tag{17}$$

as seen on earlier sheets. Here $D$ is the diffusivity; $\rho(x,t)$ is the concentration of diffusing particles. The diffusion process leads to a smearing of inhomogeneities in concentration, and we saw earlier that an initially localised distribution (such as a square pulse) broadens into a gaussian whose width increases as $\sqrt{2Dt}$. In the limit that all the particles start off from time zero at a point $x_0$, we can represent the initial concentration by a $\delta$-function, $\rho(x,0) = \delta(x - x_0)$. Show that for later times the normalized gaussian

$$\rho(x,t) = \sqrt{\frac{1}{4\pi Dt}} \exp\left[-(x - x_0)^2/4Dt\right] \tag{18}$$

is a solution of the diffusion equation satisfying the required initial condition.

In dealing with Eq. (17) it is often the case that we know $\rho(x,t_0)$ at some time $t_0$ and need to calculate it for a later time $t$ (an initial value problem). We now define a Green function $G(x_0,x,t_0,t)$ by

$$\left[\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2}\right] G(x_0,x,t_0,t) = 0 \qquad \text{for } t > t_0 \tag{19}$$

$$G(x_0,x,t_0,t) = \delta(x - x_0) \qquad \text{for } t = t_0 \,. \tag{20}$$

Show that a formal solution of the initial value problem is then

$$\rho(x,t) = \int_{-\infty}^{\infty} G(x_0,x,t_0,t)\rho(x_0,t_0)\, dx_0 \tag{21}$$

where $x_0$ is a dummy variable, and

$$G(x_0,x,t_0,t_0+\tau) \equiv G(x_0,x,\tau) = \sqrt{\frac{1}{4\pi D\tau}} \exp\left[-(x - x_0)^2/4D\tau\right] \,. \tag{22}$$

In (21), $\rho(x_0,t_0)$ specifies the initial condition in terms of dummy variable $x_0$.

[**Aside remark**: Green functions can also be used to solve *inhomogeneous problems*, such as $\frac{\partial\rho(x,t)}{\partial t} - D\frac{\partial^2\rho(x,t)}{\partial x^2} = f(x,t)$, with $f(x,t)$ a specified function. The definition of $G(x_0,x,t_0,t)$ is then $\left[\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2}\right] G(x_0,x,t_0,t) = \delta(x - x_0)\,\delta(t - t_0)$, and the solution is $\rho(x,t) = \int_{-\infty}^{\infty} dx_0 \int_{-\infty}^{t} dt_0 G(x_0,x,t_0,t) f(x_0,t_0)$. It turns out that this definition of the Green function is mathematically equivalent to Eqs.(19) and(20).]

The Green function (22) can be interpreted as the *conditional probability* that a diffusing particle is at $x$ at time $t_1 = t_0 + \tau$, given that it was at $x_0$ at time $t_0$. [The second notation for $G$ emphasizes that only the time *difference* is involved.] What, in these terms, is the interpretation of Eq. (21)?

Now suppose we know an initial state $\rho(x_0, t_0)$ and want to find the state at a later time $t_2 = t_0 + 2\tau$. There are two ways to do this: (i) by using the Green function for a time interval $2\tau$ directly on $\rho(x_0, t_0)$; or (ii) by "propagating" the system forward by a time $\tau$ to a state $\rho(x_1, t_1)$ (where $t_1 = t_0 + \tau$), and then repeating this procedure to get from $\rho(x_1, t_1)$ to $\rho(x_2, t_2)$. Show generally that the equivalence of these two methods implies

$$G(x_0, x_2, 2\tau) = \int G(x_0, x_1, \tau)\, G(x_1, x_2, \tau) dx_1 \ . \tag{23}$$

**D2. Green function for the Schrödinger equation.** In terms of physical mechanism, quantum mechanics and diffusion have nothing whatever in common: the latter is a completely classical (though random) process. However, there is a deep *mathematical* analogy. To see the correspondence, show that Schrödinger's equation for a free particle can be written in the form of Eq. (17)

$$\frac{\partial \psi(x,t)}{\partial t} - D\frac{\partial^2 \psi(x,t)}{\partial x^2} = 0 \tag{24}$$

so long as we choose $D = i\hbar/2m$. You may assume without proof that all the formulae of the previous section remain valid for imaginary $D$. [This *can* be proved, but takes time!]

Hence (without repeating the details of previous derivations) find a formal solution to Schrödinger's equation, for a specified initial state $\psi(x_0, 0)$, in the form

$$\psi(x, \tau) = \int_{-\infty}^{\infty} G(x_0, x, \tau)\psi(x_0, 0)\, dx_0 \tag{25}$$

where the Green function for Schrödinger's equation may be written

$$G(x_0, x, \tau) = \sqrt{\frac{-im}{2\pi\hbar\tau}}\ \exp\left[i\frac{m(x-x_0)^2}{2\hbar\tau}\right] \ . \tag{26}$$

**D3. Green functions and eigenfunction expansion.** Suppose we have a Schrödinger equation

$$i\hbar\frac{\partial \psi}{\partial t} = H\psi \tag{27}$$

where $H$ is a hermitian operator. This has a complete set of normalized eigenfunctions $\phi_n(x)$ obeying

$$H\phi_n(x) = E_n\phi_n(x) \ . \tag{28}$$

(i) Using the fact that the eigenfunctions are orthogonal and complete, show that

$$G(x_0, x, t) = \sum_n \phi_n^*(x_0)\phi_n(x)e^{-iE_nt/\hbar} \tag{29}$$

is a suitable Green function for this equation. [Hint: it is easiest to prove this directly from the defining equation Eq. (25) for the Green function.]

(ii) Consider solutions to Schrödinger's equation for a free particle on an interval $x = [0, L]$ with *periodic* boundary conditions. What are the eigenfunctions, and the corresponding energy levels?

(iii) Express the Green function as an eigenfunction expansion, and show that as $L \to \infty$, the result may be written

$$G(x_0, x, t) = (2\pi)^{-1} \int_{-\infty}^{\infty} e^{ik(x-x_0)}\, e^{-i\hbar k^2 t/2m}\, dk \ . \tag{30}$$

Confirm that this is equivalent to Eq. (26). [Use the integral given in Q. B2.]

**D4. Particle in a box again.** Consider a particle trapped in a one-dimensional box $0 < x < L$. Derive (as an eigenfunction expansion) a Green function that describes the evolution of the wave function. Suppose that at time $t = 0$ the particle is equally likely to be anywhere in the box: $\psi(x, 0) = 1/\sqrt{L}$. Find the wave function after a time $t$ has elapsed.

[Ans: $\frac{4}{\pi\sqrt{L}} \sum_{n \text{ odd}} \frac{1}{n} \sin\left(\frac{n\pi x}{L}\right) e^{-\frac{i\hbar}{2m}\left(\frac{n\pi}{L}\right)^2 t}$.]