Notes for Quantum Mechanics 3 course, CMI Spring 2012
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Contents

• These notes (http://www.cmi.ac.in/ ∼govind/teaching/qm3-e12) are a continuation of the notes from QM1 and QM2, available on this website. They are very sketchy and aren't a substitute for text books or attendance and taking notes at lectures. Some suggested text books have been listed on the course webpage. Please let me know (govind@cmi.ac.in) of any comments or corrections.

1 Time dependent quantum systems (continued)

1.1 Lifetime of an excited state due to spontaneous emission

• Even if an atom isn't exposed to an external electromagnetic wave, it can make a spontaneous transition from a higher to any lower energy level that is allowed by the selection rules. This 'spontaneous' emission is in a sense induced by the electromagnetic radiation that is present even in the vacuum. This is the process by which atoms in excited states decay.

• Suppose an atom is initially in the excited (upper energy) state u and has available to it several lower energy states $l_1, l_2, \ldots l_n$ to which it can spontaneously decay. Each of these is called a decay channel or decay mode. Suppose the spontaneous transition probability from $u \to l_i$ per unit time, i.e., the spontaneous decay rate is $R^{\rm sp}_{u\to l_i}$. This spontaneous decay rate will depend on the electromagnetic radiation present in the vacuum, just as the rate for stimulated emission depends on the electromagnetic radiation incident on the atom. The spontaneous decay rate $R^{\rm sp}_{u\to l_i}$ was called the A-coefficient by Einstein.

• If there are initially N_u atoms in upper state u, then in a time dt the increase in N_u

$$dN_u = -\left(R^{\rm sp}_{u\to l_1} + \cdots + R^{\rm sp}_{u\to l_n}\right) N_u \, dt \tag{1}$$

Thus the expected number of atoms remaining in upper state u at time t is

$$N_u(t) = N_u(t=0) \, \exp\left[-\left(R^{\rm sp}_{u\to l_1} + \cdots + R^{\rm sp}_{u\to l_n}\right) t\right] \tag{2}$$

The time constant for this exponential depletion of population is called the lifetime of the upper state

$$\tau = \frac{1}{R^{\rm sp}_{u\to l_1} + \cdots + R^{\rm sp}_{u\to l_n}} \tag{3}$$

It is the time after which (on average) a fraction $1/e \approx 1/2.718 \approx 0.37$ the population has decayed to *any* of the available lower states, and only about 63% remain in upper state u. If selection rules do not permit any lower state to decay to, then the rates are zero and the lifetime τ infinite.

• Note that spontaneous absorption is almost never seen to occur, an atom in its ground state in vacuum is rarely found to spontaneously get excited. A statistical mechanics argument for this may be offered, using the principle of maximization of entropy. Consider an atom in the presence of electromagnetic radiation present in the vacuum. Suppose the energy difference between the ground and first excited state of the atom is ΔE. There is only one way in which this quantum of energy can be possessed by the atom: by being in the first excited state. On the other hand, this energy can be kept in the radiation field in very many ways, essentially, since the electromagnetic field has very many degrees of freedom, the electric and magnetic fields at each point of space. Since a priori all these possibilities are equally probable, it is entropically favorable for the quantum of energy to be in the vacuum electromagnetic field than in the atom. This explains why atoms are typically found in their ground states and are rarely seen to spontaneously absorb radiation from the vacuum and get excited.

1.2 Relation between spontaneous and stimulated emission (Einstein A & B coefficients)

• To estimate this life time, we need to know the rates for spontaneous emission $R^{\rm sp}_{u\to l}$. To find this rate we could apply first order time-dependent perturbation theory as in the case of stimulated emission/absorption. However, to do so, we will need to know the electromagnetic field in the vacuum, which is not available to us. However, a clever argument of Einstein (1916) relates the spontaneous emission rate to the stimulated emission rate, which we can calculate. See Liboff or Griffiths for more details.

• Suppose we have a box of atoms in thermal equilibrium with EM radiation at temperature T. We already know that EM radiation in equilibrium at temp T has a spectral distribution of energy density given by Planck's black body law. Now suppose the atoms are in one of two states, with N_u in the upper state and N_l in the lower state. In equilibrium these numbers do not change with time. However, this is a dynamic equilibrium where atoms in the upper state decay to l both via spontaneous and stimulated emission (due to the EM waves in the cavity). At the same time, atoms in the lower state get exited to u via stimulated absorption. The rates for these processes are denoted in the obvious way. The rate of change of N_u is (ignoring spontaneous absorption for the above reason)

$$0 = \frac{dN_u}{dt} = -R^{\rm sp}_{u\to l}N_u - R^{\rm st}_{u\to l}N_u + R^{\rm st}_{l\to u}N_l. \tag{4}$$

We have seen that the rates of stimulated emission/absorption are equal $R^{\rm st}_{u\to l} = R^{\rm st}_{l\to u}$. Moreover, as we will shortly see in more detail, they are each proportional to the energy density u in the electromagnetic field at the transition frequency. This is a consequence of Fermi's Golden rule, the transition rate is proportional to the square of the transition matrix element, which is proportional to the square of the electric field for electric dipole transitions. Let us write

$$R^{\rm st}_{u\to l} = R^{\rm st}_{l\to u} = \tilde{R}^{\rm st}_{ul}\; u(\Delta\omega) \tag{5}$$

where we denote the energy difference by $\hbar\Delta\omega = E_u - E_l$. Thus we find a relation between the energy density at the frequency $\Delta\omega$ and transition rates. But this relation must be true no matter what the transition frequency is (since we could consider a different pair of states u and l with a different $\Delta\omega$). For brevity, let us denote $\Delta\omega$ simply by ω:

$$u(\omega)\, d\omega = \frac{R^{\rm sp}_{ul}}{\tilde{R}^{\rm st}_{ul}} \frac{1}{\frac{N_l}{N_u} - 1}\, d\omega. \tag{6}$$

The spontaneous decay rate $R_{ul}^{sp} \equiv A$ is called Einstein's A-coefficient and the stimulated transition rate per energy density $\tilde{R}_{ul}^{\rm st} = B$ is called Einstein's B-coefficient. Now since the atoms are in thermal equilibrium, the populations N_l, N_u are proportional to the Boltzmann factors

$$\frac{N_l}{N_u} = e^{-(E_l - E_u)/kT} = e^{\hbar\Delta\omega/kT} = e^{\hbar\omega/kT}. \tag{7}$$

Thus

$$u(\omega)d\omega = \frac{R_{ul}^{\rm sp}}{\tilde{R}_{ul}^{\rm st}} \frac{1}{e^{\hbar\omega/kT} - 1} d\omega \tag{8}$$

In order to fix $R_{ul}^{\rm sp}/\tilde{R}_{ul}^{\rm st}$ (which is independent of T) we will compare this with the classically known energy density in black-body radiation. At high temperatures or in the semi-classical limit $\hbar\Delta\omega/kT \to 0$, the equilibrium distribution of energy density in cavity radiation is given by the Rayleigh-Jeans law

$$u_{RJ}(\nu)d\nu = \frac{8\pi\nu^2}{c^3} kT\, d\nu \quad \text{or} \quad u_{RJ}(\omega)d\omega = \frac{8\pi\omega^2}{(2\pi)^2 c^3} kT\, d\omega \tag{9}$$

On the other hand, at high temperatures

$$u(\omega)d\omega \overset{\text{high T}}{\longrightarrow} \quad \frac{R_{ul}^{\rm sp}}{\tilde{R}_{ul}^{\rm st}} \frac{kT}{\hbar\omega}\, d\omega. \tag{10}$$

Comparing, we find the ratio of spontaneous and stimulated emission rates

$$\frac{R_{ul}^{\rm sp}}{\tilde{R}_{ul}^{\rm st}} = \frac{8\pi\omega^2\hbar\omega}{c^3(2\pi)^2} \quad \Rightarrow \quad R_{ul}^{\rm sp} = \frac{2}{\pi}\frac{\hbar\omega^3}{c^3}\tilde{R}_{ul}^{\rm st}. \tag{11}$$

Thus we have achieved our objective of expressing the spontaneous emission rate in terms of the stimulated emission rate, which we can calculate using perturbation theory.

• As a byproduct of this argument, we may also obtain the Planck black body spectrum by plugging in this value for $\frac{R_{ul}^{\rm sp}}{\tilde{R}_{ul}^{\rm st}}$ in $u(\omega)$:

$$u(\omega)d\omega = \frac{R_{ul}^{\rm sp}}{\tilde{R}_{ul}^{\rm st}} \frac{d\omega}{e^{\hbar\omega/kT} - 1} = \frac{8\pi\omega^2}{c^3(2\pi)^2} \frac{\hbar\omega\, d\omega}{e^{\hbar\omega/kT} - 1} \quad \Rightarrow \quad u(\nu)d\nu = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1} d\nu \tag{12}$$

which is precisely the Planck distribution ($\omega = 2\pi\nu, h\nu = \hbar\omega$).

1.3 Rate of dipole transitions due to unpolarized polychromatic light incident from all directions in an incoherent superposition

• Our main result from the previous section is an expression for the spontaneous emission rate in terms of the stimulated one

$$R_{u\to l}^{\rm sp} = \frac{2}{\pi} \frac{\hbar(\Delta\omega)^3}{c^3}\, \tilde{R}_{u\to l}^{\rm st} \tag{13}$$

To use this formula, we must calculate the rate of stimulated emission. However, the stimulating EM wave is radiation in a cavity at equilibrium at temperature T. This radiation is not monochromatic (in fact it is an incoherent superposition, a thermal ensemble of electromagnetic

waves following the Planck distribution of energies in the various frequency intervals) and is incident on the atom from all directions and is unpolarized. The fact that it is an incoherent superposition means that we can add the probabilities of transitions for various different incident frequencies, wave vectors and polarizations. If it were a coherent superposition, we would have to add the amplitudes first and then square the total amplitude, leading to interference terms that average to zero in an incoherent superposition. In other words, we need to integrate the rate of electric dipole transitions (found earlier) over all frequencies and average over all polarizations as well as directions of propagation[1].

• Recall that the probability of a transition at first order in time-dependent perturbation theory is

$$P_{i\to f}(t) = \frac{1}{\hbar^2}|\langle f|gH_1|i\rangle|^2 \frac{\sin^2\left(\frac{(\omega\pm\Delta\omega)t}{2}\right)}{(\omega\pm\Delta\omega)^2} \tag{14}$$

Consider electric dipole transitions induced by an $\hat{n}$-polarized monochromatic EM wave propagating along wave vector $\vec{k}$

$$gH_1\cos\omega t = -\vec{d}\cdot\vec{E}_0\cos\omega t, \quad \text{where} \quad \vec{d} = e\vec{r}, \quad \vec{E}_0 = E_0\hat{n} \tag{15}$$

The probability of stimulated emission is (for convenience, we write $\Delta\omega = \omega_u - \omega_l$)

$$P_{u\to d}(t) = \frac{E_0^2}{\hbar^2}\left|\left\langle l|\vec{d}\cdot\hat{n}|u\right\rangle\right|^2 \frac{\sin^2\left(\frac{(\omega-\Delta\omega)t}{2}\right)}{(\omega-\Delta\omega)^2} \tag{16}$$

Now the time-average energy density in the EM wave is

$$u = \left\langle \frac{1}{2}\epsilon_0\vec{E}^2 + \frac{\vec{B}^2}{2\mu_0}\right\rangle_t = \epsilon_0 E_0^2\langle\cos^2(\omega t)\rangle_t = \frac{1}{2}\epsilon_0 E_0^2. \tag{17}$$

Thus for a monochromatic wave of polarization $\hat{n}$ in direction $\vec{k}$, the emission rate is

$$R^{\text{st}}_{u\to l}(t) = \frac{2u}{\epsilon_0\hbar^2}\left|\left\langle l|\vec{d}\cdot\hat{n}|u\right\rangle\right|^2 \frac{\sin^2\left(\frac{(\omega-\Delta\omega)t}{2}\right)}{(\omega-\Delta\omega)^2 t}. \tag{18}$$

For a polychromatic wave, we must integrate over the contributions of all angular frequencies, assuming these probabilities are independent of each other (this is the case for incoherent light)

$$R^{\text{st}}_{u\to l}(t) = \frac{2}{\epsilon_0\hbar^2}\left|\left\langle l|\vec{d}\cdot\hat{n}|u\right\rangle\right|^2 \int_0^\infty \frac{\sin^2\left(\frac{(\omega-\Delta\omega)t}{2}\right)}{(\omega-\Delta\omega)^2 t}\, u(\omega)\,\frac{d\omega}{2\pi}. \tag{19}$$

[1]Incoherent means the initial phases $\sin(\vec{k}\cdot\vec{r}-\omega t+\delta)$ in the electric fields of the various EM waves hitting the atom in the cavity are uncorrelated, i.e. random. To get a sense for what an incoherent superposition means, consider the sum of the wave amplitudes (say electric fields) from the two monochromatic sources $\psi_1 = A\sin(k_1x - \omega_1 t)$ and $\psi_2 = B\sin(k_2x - \omega_2 t + \delta)$. The total amplitude at x, t is $\psi = A\sin(k_1x-\omega_1 t) + B\sin(k_2x-\omega_2 t+\delta)$. The intensity is $|\psi|^2 = |\psi_1|^2 + |\psi_2|^2 + I$ where the interference term is $I = 2AB\sin(k_1x-\omega_1 t)\sin(k_2x-\omega_2 t) = AB\left[\cos((k_1-k_2)x - (\omega_1-\omega_2)t - \delta) - \cos((k_1+k_2)x - (\omega_1+\omega_2)t+\delta)\right]$. Now, for an incoherent superposition we must average over the random phase δ uniformly distributed in $[0, 2\pi]$, we see that $\frac{1}{2\pi}\int_0^{2\pi} I\, d\delta = 0$ since each term in I is sinusoidal in δ with period 2π. Thus, for an incoherent superposition, the total intensity (probability) is given by the sum of the individual probabilities, and we can ignore the interference term.

We have seen that even for moderate times t, $\frac{\sin^2\left(\frac{(\omega-\Delta\omega)t}{2}\right)}{(\omega-\Delta\omega)^2 t}$ is quite sharply peaked at $\omega = \Delta\omega = \omega_u - \omega_l$, so only $u(\Delta\omega)$ contributes, and we may approximate the integral by extending the limits

$$\int_0^\infty \frac{\sin^2\left(\frac{(\omega-\Delta\omega)t}{2}\right)}{(\omega-\Delta\omega)^2 t}\, u(\omega)\frac{d\omega}{2\pi} \approx u(\Delta\omega)\int_{-\infty}^{\infty} \frac{\sin^2\left(\frac{(\omega-\Delta\omega)t}{2}\right)}{(\omega-\Delta\omega)^2 t}\frac{d\omega}{2\pi} = \frac{u(\Delta\omega)}{4\pi}\int_{-\infty}^{\infty}\frac{\sin^2 x}{x^2}\, dx = \frac{\pi\, u(\Delta\omega)}{4\pi} \tag{20}$$

Within these approximations, the emission rate is time-independent and proportional to the square of the dipole matrix element as well as to the energy density of the radiation at the transition frequency

$$R^{\rm st}_{u\to l}(t) = \frac{u(\Delta\omega)}{2\epsilon_0\hbar^2}\ \left|\left\langle l|\vec{d}\cdot\hat{n}|u\right\rangle\right|^2. \tag{21}$$

For brevity, let us denote the matrix element of the dipole momentum vector by $\vec{D} = \left\langle l|\vec{d}\cdot\hat{n}|u\right\rangle$. In general, $\vec{D}$ is a three dimensional vector with complex components so we split it into real and imaginary parts $\vec{D} = \vec{D}_r + i\vec{D}_i$ so that

$$\left|\left\langle l|\vec{d}\cdot\hat{n}|u\right\rangle\right|^2 = |\vec{D}\cdot\hat{n}|^2 = |\vec{D}_r\cdot\hat{n} + i\vec{D}_i\cdot\hat{n}|^2 = |\vec{D}_r\cdot\hat{n}|^2 + |\vec{D}_i\cdot\hat{n}|^2 \tag{22}$$

So far this is for incoherent polychromatic light of a fixed polarization $\hat{n}$ and direction of propagation along the wave vector $\vec{k}$. Now we average over all possible polarizations and directions $\hat{k}$ in which the light is incident on the atom. However, the polarization must always be perpendicular to the direction of propagation of the EM wave. $\vec{D}_r$ and $\vec{D}_i$ are fixed vectors and are not being integrated over, they are given by the matrix elements of the dipole moment between upper and lower state.

• Let us consider first the term involving $\vec{D}_r$. $\vec{D}_i$ can be treated in the same way. Now $\vec{D}_r$ and the direction of propagation $\hat{k}$ are a pair of vectors. Let us define the plane they span to be the $y-z$ plane and moreover, choose the z-axis to point along $\hat{k}$. We label the angle made by $\vec{D}_r$ with the z-axis $0 \le \theta < \pi$. The polarization vector $\hat{n}$ must lie in the $x-y$ plane as it must be perpendicular to $\vec{k}$. Suppose $\hat{n}$ makes an angle $0 \le \phi < 2\pi$ with the $\hat{x}$ axis. Then the projection of $\vec{D}_r$ on the $x-y$ plane is the vector $|\vec{D}_r|\sin\theta\,\hat{y}$. Thus

$$\vec{D}_r\cdot\hat{n} = |\vec{D}_r|\sin\theta\cos(\pi/2-\phi) = |\vec{D}_r|\sin\theta\sin\phi \quad\Rightarrow\quad |\vec{D}_r\cdot\hat{n}|^2 = |\vec{D}_r|^2\sin^2\theta\ \sin^2\phi \tag{23}$$

Averaging over direction of polarization and direction of incidence while holding $\vec{D}_r$ fixed is merely an average over all possible angles $d\Omega = \sin\theta\, d\theta\, d\phi$:

$$\left\langle|\vec{D}\cdot\hat{n}|^2\right\rangle_\Omega = \frac{1}{4\pi}\int\left(|\vec{D}_r|^2 + |\vec{D}_i|^2\right)\sin^2\theta\ \sin^2\phi\ \sin\theta d\theta d\phi \tag{24}$$

Let us denote $|\vec{D}|^2 = |\vec{D}_r|^2 + |\vec{D}_i|^2$. Then

$$\left\langle\left|\left\langle l|\vec{d}\cdot\hat{n}|u\right\rangle\right|^2\right\rangle_{\theta,\phi} = \frac{1}{4\pi}|\vec{D}|^2\iint\sin^2\theta\sin^2\phi\ \sin\theta\, d\theta\, d\phi = \frac{1}{4\pi}\frac{4}{3}\frac{2\pi}{2}|\vec{D}|^2 = \frac{|\vec{D}|^2}{3} = \frac{1}{3}\left|\left\langle l|\vec{d}|u\right\rangle\right|^2 \tag{25}$$

Thus the rate of stimulated emission by unpolarized incoherent light incident from all directions is proportional to the absolute square of the dipole matrix element and the electromagnetic energy density

$$R^{\rm st}_{u\to l} \approx \frac{u(\Delta\omega)}{6\epsilon_0\hbar^2}\ \left|\left\langle l|\vec{d}|u\right\rangle\right|^2. \tag{26}$$

Recall that $\vec{d} = e\vec{r}$, and assume that $|u\rangle$ and $|l\rangle$ are *normalized* states, then

$$|\vec{D}|^2 = \left|\left\langle l|\vec{d}|u\right\rangle\right|^2 = e^2\left[|\langle l|x|u\rangle|^2 + |\langle l|y|u\rangle|^2 + |\langle l|z|u\rangle|^2\right] \tag{27}$$

Combining with Einstein's relation, the rate of spontaneous emission is

$$A \equiv R^{\rm sp}_{u\to l} = \frac{2}{\pi}\frac{\hbar(\Delta\omega)^3}{c^3}\,\tilde{R}^{\rm st}_{u\to l} = \frac{1}{3\pi\epsilon_0\hbar}\frac{(\Delta\omega)^3}{c^3}\left|\left\langle l|\vec{d}|u\right\rangle\right|^2. \tag{28}$$

The lifetime τ of the excited state u due to spontaneous decay to state l is the reciprocal of $R^{\rm sp}_{u\to l}$. To find it we need to know the matrix elements of the components of $\vec{r}$ between the upper and lower states.

1.4 Frequency-time relation for harmonic perturbations

We briefly discuss a relation between the frequency of a harmonic perturbation (e.g. EM waves) and the time for which it has acted to cause a transition between states of a system (e.g. an atom). This relation is often written in a form similar to the uncertainty principle, though it differs from the energy-time uncertainty inequality in many crucial ways.

• Recall that the probability of transitions from state i to state f due a harmonic perturbation $gH_1\cos\omega t$ acting for a time t on a system with hamiltonian H_0 and energy levels $E_i = \hbar\omega_i$ is given to first order by

$$P_{i\to f}(t) \approx \frac{1}{\hbar^2}\,|\langle f|gH_1|i\rangle|^2\,\frac{\sin^2\left(\frac{(\omega\pm\omega_{fi})t}{2}\right)}{(\omega\pm\omega_{fi})^2}. \tag{29}$$

where $\omega_{fi} = \omega_f - \omega_i$ is the Bohr frequency associated with the transition between i and f. Let us consider the case of absorption (excitation) $\omega_{fi} > 0$, though a similar argument applies to emission (decay). We consider the transition probability (or the rate P/t) as a function of incident frequency ω. $P_{i\to f}(t)$ is quite sharply peaked around $\omega = \omega_{fi}$, but has a finite spread. In other words, it is not only the resonant frequency that is effective in inducing a transition, but a narrow range around it. Roughly, this band of frequencies lies somewhere in the interval between the two nearest zeros of $P_{i\to f}(t)$ around the central maximum at $\omega = \omega_{fi}$.

$$\text{These zeros occur at}\quad (\omega-\omega_{fi})\frac{t}{2} = \pm\pi. \tag{30}$$

So the probability of excitation after a time t is most significant for a range of frequencies lying within

$$\omega_{fi} - \frac{2\pi}{t} \lesssim \omega \lesssim \omega_{fi} + \frac{2\pi}{t}. \tag{31}$$

Note that these are not inviolable inequalities, frequencies which are outside this interval can also induce transitions from i to f, though with a much lower probability. Moreover, frequencies at the edges of this band cannot induce transitions since the probability goes to zero.

• Within these approximations, the frequencies lying in the central region of the band

$$|\omega - \omega_{fi}| \lesssim \frac{2\pi}{t} \tag{32}$$

are particularly effective in inducing a transition from i to f after a time t. Let us denote the central half the above range of frequencies by $\Delta\omega$[2]. Then after a time t, frequencies lying in a band of width $\Delta\omega \approx 2\pi/t$ about ω_{fi} are effective in causing transitions from i to f:

$$\Delta\omega\, t \approx 2\pi \tag{33}$$

Sometimes, we multiply through by $\hbar$ and express the frequency band as a range of energies $\Delta E \equiv \hbar\Delta\omega$

$$\Delta E\, t \approx h. \tag{34}$$

Sometimes, this is loosely called an uncertainty relation. But t here is not the uncertainty in a measurement of time. Moreover, this relation between the band of effective frequencies and the time the perturbation acted is not an inequality but just an estimate relevant to harmonic perturbations.

• The definitions of ΔE and t here are different from what they meant in the Mandelstam-Tamm version of the energy-time uncertainty *inequality* $\Delta E\Delta t \geq \frac{\hbar}{2}$. In this inequality, ΔE is the standard deviation in possible measurements of energy of a system in a given state ψ. And Δt is the time it takes for the expectation value (in state ψ) of a chosen observable A to change by an amount equal to one standard deviation in the distribution of possible measured values of A: $\Delta t|\partial_t\langle A\rangle_\psi| = \Delta A$.

• Our new relation simply says that if the perturbation acts only for a short time, then a wide band of frequencies can cause transitions. Indeed, as is easily seen by taking $t \to 0$, for short times, $P_{i\to f}$ is independent of ω, all frequencies are equally effective in inducing transitions if they act for a very short time. But after the perturbation has acted for a long time, the band of effective frequencies is much narrower, tending eventually to the resonant frequency *alone*, as $t \to \infty$.

• In this discussion, the EM wave is treated classically. The photon concept does not play a role. This works in the high intensity regime where a large number of photons are present, and the energy in a monochromatic EM wave is supplied in a nearly continuous manner. Within this framework, energy is conserved. Irrespective of what the frequency of the EM wave is, an energy of $\hbar\omega_{fi}$ is absorbed by the atom in going from $i \to f$.

• One way to interpret this relation is to imagine an ensemble of atoms all in state i. A monochromatic harmonic perturbation is applied to each atom for a time t. However, we scan uniformly through a whole range of frequencies ω. So a bunch of atoms receive frequency ω_1, another bunch of atoms receive a slightly higher frequency and so on. So each bunch of atoms experiences a slightly different frequency of light. After a common time t some atoms would have been excited to a given final state f with energy E_f. The above argument says that the incident frequencies most effective in inducing a transition from $i \to f$ are clustered around $\omega = \omega_{fi}$ with an approximate spread given by $\Delta\omega \approx 2\pi/t$.

• Another way to interpret this formula: suppose all the atoms in state i receive light of the same frequency ω. But suppose there are several closely-spaced possible final states with energies E_f (to which transitions are not forbidden!). Let the harmonic perturbation act for a time t. Then we tabulate the energies E_f of the atoms that have made transitions to various possible excited states. Then we will find that among the atoms that have been excited, a vast majority would

[2] $\Delta\omega$ isn't the standard deviation of the distribution $P(\omega)$.

have been excited to states f with energies E_f satisfying

$$|E_f - (E_i + \hbar\omega)| \lesssim \frac{h}{t}. \tag{35}$$

In other words, the absorbed energies are centered around $\hbar\omega$ but with a spread of roughly h/t.

• Yet another way to look at it is to consider an ensemble of atoms or other particles in an unstable state i. However, suppose we do not know the energy E_i (or the mass of the unstable particle). We wait a time t (e.g. the life time) after which a fraction of the atoms have decayed, say via a specific channel to a particular (say stable) final state f, whose energy is known. In the process, radiation of some sort is also emitted and we measure how much energy is carried away by radiation in each decay. However, according to the above argument, in different members of the ensemble, we will find that a slightly different amount of energy has been carried away by radiation leading to a distribution of radiated energies that are clustered around a central value E_0 (determined experimentally), with a spread in energies given by $\Delta E \approx 2h/t$. In this manner, we can reconstruct a distribution of possible energies of the initial state E_i or a distribution of possible masses of the unstable particle i. We would predict that E_i would lie approximately in the interval

$$E_0 + E_f - \frac{h}{t} \lesssim E_i \lesssim E_0 + E_f + \frac{h}{t}. \tag{36}$$

1.5 Adiabatic or quasi-static time dependence & perturbations

• An adiabatic change is a slow change, slow compared to the natural time-scales of the system.

• The slow precession of the Earth's rotation axis (mainly due to the gravitational force between the earth and sun, which are not perfect spheres) takes 26k years. This is an adiabatic (slow or quasi-static) change superimposed on the Earth's (fast i.e., daily) rotation about its axis.

• The slow stretching of the string supporting an oscillating stone is a slow adiabatic change compared to the fast oscillations of the stone. The effect of this adiabatic perturbation is to lengthen the time period of the pendulum. It is handled by finding the time period $T = 2\pi\sqrt{L/g}$ assuming the string is of fixed length and then letting $L \to L(t)$.

• An adiabatic change is to be contrasted with a sudden perturbation. An adiabatic change is at the other extreme. Suppose we place a pen on a paper which is on a table. If the paper is suddenly pulled from under the pen, this is a sudden change/perturbation. The pen remains in its original state (location with respect to the table and at rest). Under a sudden perturbation, the state of the system is unchanged. An example of an adiabatic change is when we slowly move the paper around the table, carrying the pen with it. The state of the pen (location on the table) is altered. But the pen remains in the corresponding state of the new system (location w.r.to the moving paper is unaltered.). This is typical of adiabatic changes. Adiabatic changes to a system take the particle to the *corresponding* state of the new system.

• A swinging pendulum whose support is adiabatically transported continues to oscillate in the same plane. Here adiabatic means the time scale over which the support is moved is much longer than the time period of the pendulum. If the change is performed much faster, the plane of oscillation will not be maintained, indeed the bob may oscillate wildly (and not in a single plane) if the support is shaken at a rate comparable to the period of the undisturbed pendulum.

• In general, suppose l is some (external, 'environmental') parameter involved in the specification of a system. A slow and continuous change of l is an adiabatic change. For example, it could be the length of a pendulum string, the spring constant of an SHO, the width of an infinite square-well or the external magnetic field applied to an atomic electron. As the external parameter is changed, some classical and quantum properties of the system may remain unchanged. These are called adiabatic invariants.

• For e.g. if a particle is in the g.s. of an infinite square well of length L and if L is slowly increased, the particle will remain in the g.s. of the new square well as L grows. In this case, the property of being in the g.s. is an adiabatic invariant, as we will show. However, the state itself is changed, since the g.s. wave function depends on L, also the energy is not an adiabatic invariant, it decreases $E_{gs} \propto \frac{1}{L^2}$ as the particle loses energy to the walls as they yield to the force it imparts to them in collisions.

• Moreover, the number of nodes of the wave function is an adiabatic invariant. It is an integer and an integer cannot change under continuous deformation of the system parameters.

• In general, for a process to be adiabatic, the rate at which external parameters are varied must be much slower than the rate of the internal dynamics. Suppose a quantum system is in an initial energy eigenstate E_i (e.g. its ground state ψ_i) and is subjected to a time-dependent perturbation which varies over a time-scale of τ. For simplicity, the perturbation may even be introduced and then withdrawn. We ask whether the system makes a transition to a different eigenstate E_f. We expect this will not happen (and this is a consequence of the adiabatic theorem) as long as the change is adiabatic, i.e. as long as $\tau \gg \frac{\hbar}{|E_i - E_f|}$. The longest of the internal time-scales $\max_f \frac{\hbar}{|E_i - E_f|}$ is determined by the level which is closest in energy to E_i. If there is another state ψ_f with the *same* energy $E_i = E_f$, then we can no longer guarantee that the state will not change upon an adiabatic perturbation.

• For an electron in a molecule, the electronic motion within the individual atoms is fast while the relative motion of atoms is slow and may be treated in an adiabatic approximation. For example, consider a collision between two polyatomic molecules. Initially, each molecule is in a particular state of vibrational excitation and the electrons in the atoms are in particular electronic states. In a collision between molecules, it is found that the electronic state is unaltered. But the vibrational state of the molecule as a whole is altered after the collision. The time-scale of the molecular collision is much longer than electronic time scales but is comparable to those of vibrational modes. This is because the energy gaps between electronic energy levels is quite large, while the vibrational modes are spaced quite close together. In fact, the adiabatic approximation allows us to ignore any change in atomic/nuclear/subnuclear state in a molecular process.

• A model for an adiabatic perturbation is $H(t) = H_0 + gH_1(t)$ where the time scale over which $H_1(t)$ changes is much longer than an appropriate time scale associated to H_0, e.g. maximal value of $\frac{\hbar}{|E_f^0 - E_i^0|}$.

• In some perturbative treatments, one asks that the fractional change in H_1 over the characteristic time-scale of the unperturbed system be small in the following sense. Suppose ω is a characteristic frequency of the unperturbed system, i.e., $\omega = |E_i - E_f|/\hbar$, which corresponds to a time period $2\pi/\omega$. For the perturbation to be adiabatic (with regard to the possibility of a

transition between i and f) one requires

$$\left| \frac{\langle f| \frac{\partial H_1}{\partial t} \frac{2\pi}{\omega} |i\rangle}{\langle f|H_1|i\rangle} \right| \ll 1. \tag{37}$$

We have seen that a given perturbation may be perceived to be adiabatic (slow) by certain degrees of freedom and non-adiabatic (fast) by other degrees of freedom.

• Suppose we start in an eigenstate $|n(0)\rangle$ of H_0 at $t = 0$ and let the system evolve under $H(t) = H_0 + gH_1(t)$ where $H_1(t)$ changes very slowly. Suppose $|n(t)\rangle$ is the corresponding eigenstate of $H(t)$

$$H(t)|n(t)\rangle = E_n(t)|n(t)\rangle \tag{38}$$

Then the adiabatic theorem (originally due to Born and Fock) says that the system will be in the eigenstate $|n(t)\rangle$. E.g. If the system started in the g.s. of H_0, it will evolve into the g.s. of $H(t)$ at time t. We will sketch why this is the case in the next section.

• As an example (see Shankar) of an adiabatic perturbation consider a 1d SHO that is initially in its g.s. It is perturbed by a linear potential which is slowly turned on at $t = -\infty$ and then turned off as $t \to \infty$

$$H = H_0 + gH_1, \quad H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2, \quad gH_1 = gx\, e^{-t^2/\tau^2}. \tag{39}$$

Adiabatic means τ is very large. Roughly, we expect it must be much larger than the characteristic time scale of oscillations of the SHO, $\frac{1}{\omega}$ which is also the maximal value of $\hbar/|E_i - E_f|$. The transition probability to state $n \neq 0$ at time $t = \infty$ is given by the absolute square of

$$d_n(\infty) = -\frac{ig}{\hbar}\int_{-\infty}^{\infty} \langle n|x|0\rangle e^{-t^2/\tau^2} e^{-i(E_0 - E_n)t/\hbar} = -\frac{ig}{\hbar}\langle n|x|0\rangle \int_{-\infty}^{\infty} e^{-t^2/\tau^2} e^{in\omega t}\, dt \tag{40}$$

Recall that $a + a^\dagger = \sqrt{2}\beta x$ where $\beta = \sqrt{m\omega/\hbar}$ and $a^\dagger|0\rangle = |1\rangle$. Only d_1, d_0 are non-vanishing. Completing the square $t^2 - at = (t - \frac{a}{2})^2 - a^2/4$ where $a = i\omega\tau^2$

$$\int e^{-t^2/\tau^2} e^{i\omega t} dt = \int e^{-\frac{1}{\tau^2}(t^2 - i\omega\tau^2 t)} = e^{a^2/4\tau^2}\tau \int e^{-x^2} dx = \tau\sqrt{\pi} e^{-\omega^2\tau^2/4} \quad \text{where} \quad \tau x = t - a/2. \tag{41}$$

we get

$$d_1(\infty) = -\frac{ig}{\hbar}\frac{1}{\sqrt{2}\beta}\int_{-\infty}^{\infty} e^{-t^2/\tau^2} e^{i\omega t}\, dt = -\frac{ig\tau\sqrt{\pi}}{\sqrt{2m\omega\hbar}} e^{-\omega^2\tau^2/4}. \tag{42}$$

The probability of a transition $0 \to 1$ due to this perturbation that is turned on and then removed is

$$P(0 \to 1) = |d_1|^2 = \frac{\pi g^2 \tau^2}{2m\omega\hbar} e^{-\omega^2\tau^2/2}. \tag{43}$$

Now, if the perturbation is adiabatic, then the time-scale τ over which H_1 varies, must be much larger than $\frac{\hbar}{E_1 - E_0} = \frac{1}{\omega}$, i.e., $\omega\tau \gg 1$. In the adiabatic limit we find that the probability of excitation is exponentially suppressed in this example. The system remains in the corresponding state if the perturbation is sufficiently slowly varying (adiabatic). A similar argument works for other perturbing potentials gH_1, which are not necessarily linear in x.

1.5.1 Adiabatic 'theorem'

• If the hamiltonian is time independent, then a system that begins in the n^{th} eigenstate remains in the same state. We can write the stationary state wave function in terms of the energy eigenvalue

$$\psi_n(t) = \psi_n(0)e^{-iE_nt/\hbar} = \psi_n(0)e^{-\frac{i}{\hbar}\int_0^t E_n\, dt'} \tag{44}$$

More generally, if the system started in the superposition of energy eigenstates $\Psi(0) = \sum_n c_n\psi_n$ then

$$\Psi(t) = \sum_n c_n\psi_n e^{-\frac{i}{\hbar}\int_0^t E_n\, dt'} \quad \text{for} \quad H \ \text{ time-independent.} \tag{45}$$

Now suppose some 'environmental' parameters appearing in the hamiltonian are slowly changed, so that the hamiltonian $H(t)$ becomes time-dependent. If the time-dependence is adiabatic, i.e. $\dot{H}(t)$ is small in an appropriate sense, how do these formulae change? Note that the dependence of H on time is in many interesting cases, not explicit but via its dependence on certain parameters which we may denote $l_1, \cdots, l_p$. For example these may be lengths of the sides of an expanding box containing the system or components of an external magnetic field that is being slowly turned off etc. So

$$\dot{H} = \frac{\partial H}{\partial t} + \sum_{i=1}^{p} \frac{\partial H}{\partial l_i}\frac{\partial l_i}{\partial t} = \frac{\partial H}{\partial t} + \vec{\nabla}H \cdot \frac{\partial \vec{l}}{\partial t} \tag{46}$$

• The adiabatic 'theorem' asserts that if the system started in the n^{th} eigenstate of $H(0)$, the system will be in the n^{th} eigenstate of $H(t)$ after a time t. However, the state-vector picks up a phase generalizing $e^{-iE_nt/\hbar}$. The adiabatic approximation was developed by Born and Fock and one can read more about it in Bransden and Joachain or Griffiths. Assuming $H(t)$ is hermitian at all t, it has a complete set of orthonormal eigenstates $\psi_n(t)$ and energy eigenvalues (assumed non-degenerate) $E_n(t)$ for each t

$$H(t)\psi_n(t) = E_n(t)\psi_n(t). \tag{47}$$

Note that $\psi_n(t)$ are merely instantaneous eigenstates. They do not know yet, anything about Schrödinger time evolution. In particular, if the initial state was $\psi_n(0)$, there is no reason to believe a priori that the state at time t is $\psi_n(t)$. However, in the adiabatic approximation, this is indeed nearly true (i.e. up to a phase), as we will see.

• We seek solutions of the SE

$$i\hbar\frac{\partial\Psi(t)}{\partial t} = H(t)\Psi(t) \tag{48}$$

in the form of linear combinations of the complete sets of instantaneous eigenstates.

$$\Psi(t) = \sum_n d_n(t)\psi_n(t) \tag{49}$$

Without loss of generality we are free to write the coefficients $d_n(t)$ in a notation that mimics the case of a time-independent hamiltonian

$$\Psi(t) = \sum_n c_n(t)e^{i\theta_n(t)}\psi_n(t) \quad \text{where} \quad \theta_n(t) = -\frac{1}{\hbar}\int_0^t E_n(t')\, dt'. \tag{50}$$

We have merely separated out a factor from $d_n(t)$ which would be present even for a time-independent hamiltonian. Now $c_n(t)$ are to be determined by solving the time-dependent SE.

• Aim: find $c_n(t)$ in the adiabatic approximation, i.e., when $\dot{H}(t)$ is appropriately small. Note that by the fundamental theorem of calculus

$$\dot{\theta}_n(t) = -\frac{E_n(t)}{\hbar}. \tag{51}$$

So the requirement that $\Psi(t)$ solve the SE implies

$$i\hbar \sum_n \left(\dot{c}_n \psi_n + c_n \dot{\psi}_n + i c_n \psi_n \dot{\theta}_n \right) e^{i\theta_n} = \sum_n c_n E_n \psi_n e^{i\theta_n} \quad \text{or} \quad \sum_n \dot{c}_n \psi_n e^{i\theta_n} = -\sum_n c_n \dot{\psi}_n e^{i\theta_n}. \tag{52}$$

Taking the inner product with $\psi_m(t)$, we separate the $n = m$ 'diagonal' term in the sum

$$\dot{c}_m = -\sum_n c_n \langle \psi_m | \dot{\psi}_n \rangle e^{i(\theta_n - \theta_m)} = -c_m \langle \psi_m | \dot{\psi}_m \rangle - \sum_{n \neq m} c_n \langle \psi_m | \dot{\psi}_n \rangle e^{i(\theta_n - \theta_m)}. \tag{53}$$

Soon we'll argue that the sum on the rhs is small for adiabatic $H(t)$ with non-degenerate levels. Assuming this is so, we find that the coefficients $c_m(t)$ are proportional to their initial values

$$\dot{c}_m = -c_m \langle \psi_m | \dot{\psi}_m \rangle \quad \Rightarrow \quad c_m(t) = c_m(0) e^{i \int_0^t \langle \psi_m(t') | i \dot{\psi}_m(t') \rangle \, dt'}. \tag{54}$$

If a particular eigenstate was absent in the initial linear combination, then under adiabatic time dependence, the corresponding eigenstate cannot sneak in. In the adiabatic approximation, if the system begins in the n^{th} state, with $\Psi(0) = \psi_n(0)$ ($c_m(0) = \delta_{mn}$), then it remains in the corresponding state. The state-vector just picks up a phase

$$\Psi(t) = \psi_n(t) e^{-\frac{i}{\hbar} \int_0^t E_n(t') \, dt'} e^{i \int_0^t \langle \psi_n(t') | i \dot{\psi}_n(t') \rangle \, dt'} \tag{55}$$

The first phase angle is called a dynamical phase since it depends on the energy and time elapsed

$$\theta_n^D = -\frac{1}{\hbar} \int_0^t E_n(t') \, dt'. \tag{56}$$

The second phase angle is called a geometric phase in anticipation of its significance in a cyclic adiabatic process. We denote it

$$\theta_n^G = \gamma_n = \int_0^t \langle \psi_n(t') | i \dot{\psi}_n(t') \rangle \, dt'. \tag{57}$$

Show that θ_n^G is real, so that we are justified in calling it a phase angle. For a time-independent hamiltonian, $\theta_n^G = 0$, as the eigenstates are time independent.

• It remains to show that $\sum_{n \neq m} c_n \langle \psi_m | \dot{\psi}_n \rangle e^{i(\theta_n - \theta_m)}$ is small. We'll argue that each of the terms is ignorable if $\dot{H}$ is very small and the spectrum non-degenerate. Differentiating the instantaneous energy eigenvalue equation in time we have

$$\dot{H}\psi_n + H\dot{\psi}_n = \dot{E}_n \psi_n + E_n \dot{\psi}_n. \tag{58}$$

Taking an inner product with ψ_m for $m \neq n$ we have

$$\langle \psi_m | \dot{H} | \psi_n \rangle + \langle \psi_m | H | \dot{\psi}_n \rangle = E_n \langle \psi_m | \dot{\psi}_n \rangle \quad \Rightarrow \quad \langle \psi_m | \dot{\psi}_n \rangle = \frac{\langle \psi_m | \dot{H} | \psi_n \rangle}{E_n - E_m} \quad \text{for } m \neq n \tag{59}$$

Assuming the energy levels are non-degenerate at all times and that H is slowly varying so that $\dot{H}$ is small, we drop these terms. The only term that cannot be ignored is the diagonal one $m = n$, which we already accounted for. Thus we have the adiabatic 'theorem'.

1.5.2 Criterion for validity of adiabatic approximation

• We take a 2^{nd} look at the above argument for the adiabatic 'theorem'. We argued that eigenstates absent in the initial state remain absent subsequently, in the adiabatic approximation. We wish to estimate the growth of these initially absent amplitudes and determine under what conditions they are small.

• To simplify the calculation, it is convenient to use the freedom to pick the phase of instantaneous eigenfunctions $\psi_n(t)$ of $H(t)$. Let us define new orthonormal instantaneous eigenstates of $H(t)$ by absorbing the phases $\theta_n^G = \gamma_n$

$$\phi_n(t) = e^{i\gamma_n(t)}\psi_n(t) \quad \text{with} \quad H(t)\phi_n(t) = E_n(t)\phi_n(t). \tag{60}$$

Note that this choice of phases *may not* always be possible. In particular, if we consider an adiabatic process where the environmental parameters $l_i(0) = l_i(T)$ return to their initial values after a time T, then $H(T) = H(0)$ but $\gamma_n(T)$ may not equal $\gamma_n(0) = 0$ even modulo 2π. In such a situation, we would *not* be free to consistently absorb the geometric phase into the instantaneous wave functions: we would have two *different* sets of wave functions $\phi_n(0) = \psi_n(0)$ and $\phi_n(T)$ for the *same* hamiltonian $H(0) = H(T)$. Indeed, for cyclic adiabatic processes, the geometric phase cannot simply be absorbed into the instantaneous wave functions. It has observable physical consequences. We will address cyclic adiabatic processes later on. For now we assume that the set of environmental parameters do not ever return to the values they held before, so that we may consistently absorb the phases γ_n into the instantaneous wave functions.

• Then $\dot{\phi}_n = e^{i\gamma_n}\dot{\psi}_n + i\dot{\gamma}_n\phi_n$ and

$$\langle\phi_n|\dot{\phi}_n\rangle = \langle\psi_n e^{i\gamma_n}|e^{i\gamma_n}\dot{\psi}_n\rangle + \langle\psi_n e^{i\gamma_n}|i\dot{\gamma}_n\phi_n\rangle = \langle\psi_n|\dot{\psi}_n\rangle + i\dot{\gamma}_n\langle\phi_n|\phi_n\rangle = -i\dot{\gamma}_n + i\dot{\gamma}_n = 0. \tag{61}$$

So by a choice of phase, we ensured that the instantaneous eigenfunctions are orthogonal to their own time derivatives. Hereon, we assume the phases of ψ_n are chosen so that $\langle\psi_n|\dot{\psi}_n\rangle = 0$.

• Now recall that the Schrödinger equation for time evolution of $\Psi(t) = \sum_n c_n e^{i\theta_n}\psi_n$ implies

$$\dot{c}_m = -c_m\langle\psi_m|\dot{\psi}_m\rangle - \sum_{n\neq m} c_n\langle\psi_m|\dot{\psi}_n\rangle e^{i(\theta_n-\theta_m)}. \tag{62}$$

Since this is true for any choice of instantaneous eigenfunctions, we suppose that the phases are chosen such that $\langle\psi_n|\dot{\psi}_n\rangle = 0$ which implies

$$\dot{c}_m = -\sum_{n\neq m} c_n\langle\psi_m|\dot{\psi}_n\rangle e^{i(\theta_n-\theta_m)}. \tag{63}$$

Now we insert our formula for $\langle\psi_m|\dot{\psi}_n\rangle$ and get the system of 1st order ODEs for the coefficients

$$\dot{c}_m = -\sum_{n\neq m} c_n\frac{\langle\psi_m|\dot{H}|\psi_n\rangle}{E_n - E_m}e^{i(\theta_n-\theta_m)}. \tag{64}$$

Introduce the 'Bohr frequencies' by analogy with the frequencies of light emitted in atomic transitions

$$\omega_{mn}(t) = \hbar^{-1}\left(E_m - E_n\right) \tag{65}$$

Then we may write

$$\dot{c}_m(t) = \sum_{n \neq m} c_n(t) \frac{\langle \psi_m | \dot{H} | \psi_n \rangle}{\hbar \omega_{mn}(t)} e^{i \int_0^t \omega_{mn}(t')\, dt'} \tag{66}$$

So far, no approximation has been made. We merely wrote the time-dependent SE in this basis of instantaneous eigenstates. In general, it is difficult to solve this coupled system of ODEs. Let us suppose that initially we are in the eigenstate $\psi_i(0)$, i.e., $c_n(0) = \delta_{ni}$.

• In the adiabatic limit, we argued that $c_m(t) = 0$ for $m \neq i$, so that the above equation reads $\dot{c}_i = 0$ and the coefficient $c_i = 1$ of this initially present state is unchanged. We would like to improve on this 'zeroth order' approximation just as we do in perturbation theory.

• We are particularly interested in the probability of a transition to a final state ψ_f different from the initial one ψ_i. So let us consider c_f for $f \neq i$ and see what the above equation implies for their growth. For an adiabatic process, H is slowly varying with time, so that $\dot{H}$ is appropriately small. This suggests we treat $\dot{H}$ as a constant on the rhs of (66). Similarly, the c_n on the rhs of (66) are also slowly varying in time and we assign to them their values from the above zero-order approximation $c_n = \delta_{ni}$. Thus only the $n = i$ term survives on the rhs and we get

$$\dot{c}_f(t) \approx \frac{\langle \psi_f | \dot{H} | \psi_i \rangle}{\hbar \omega_{fi}(t)} e^{i \int_0^t \omega_{fi}(t')\, dt'} \quad \text{for} \quad f \neq i. \tag{67}$$

This may be integrated to give

$$c_f(t) \approx \int_0^t \frac{\langle \psi_f | \dot{H} | \psi_i \rangle}{\hbar \omega_{fi}(t')} e^{i \int_0^{t'} \omega_{fi}(t'')\, dt''}\, dt' \quad \text{for} \quad f \neq i. \tag{68}$$

While a reasonable approximation, this formula is not very revealing, as the integrations are yet to be done. A quick and dirty estimate for c_f may be obtained by assuming that since H is slowly varying in time, $\dot{H}$ on the rhs may be taken to be approximately time-independent, in so far as its contribution to the growth of c_f is concerned. In a similar spirit, the Bohr frequencies ω_{fi} and instantaneous eigenstates are also slowly varying and we approximate them by constants on the rhs to get a crude estimate for c_f

$$c_f \approx \frac{\langle \psi_f | \dot{H} | \psi_i \rangle}{\hbar \omega_{fi}} \frac{e^{i\omega_{fi} t} - 1}{i \omega_{fi}} \quad \text{for} \quad f \neq i. \tag{69}$$

Thus the probability of a transition to a state distinct from the initial one is

$$P_{i \to f}(t) = |c_{f \neq i}|^2 \approx \frac{|\langle \psi_f | \dot{H} | \psi_i \rangle|^2}{\hbar^2 \omega_{fi}^4} \times 4 \sin^2 \left(\frac{\omega_{fi} t}{2} \right) \quad \text{for} \quad f \neq i. \tag{70}$$

Within these approximations, the probability for a transition out of the initial state is oscillatory in time, and remains bounded by

$$P_{i \to f}(t) \leq 4 \frac{|\langle \psi_f | \dot{H} | \psi_i \rangle|^2}{\hbar^2 \omega_{fi}^4} \tag{71}$$

This probability is small $P_{i \to f}(t) \ll 1$ if

$$\frac{|\langle \psi_f | \dot{H} | \psi_i \rangle|}{|\omega_{fi}|} \ll \frac{1}{2} \hbar |\omega_{fi}| \tag{72}$$

Let us define the 'Bohr' time period $T_{fi} = 2\pi/|\omega_{fi}|$, which sets the scale of the 'internal' dynamics associated to the transition from $i \to f$. Then a criterion for the probability of a transition to be small is

$$T_{fi} \left| \left(\dot{H}\right)_{fi} \right| \ll \frac{\pi}{2} \left| E_f - E_i \right| . \tag{73}$$

Thus our condition for the validity of the adiabatic approximation applied to a system in the initial state ψ_i is this: the matrix element of the change in the hamiltonian over the largest internal 'Bohr' time period must be small compared to energy gap to the closest energy level ψ_f.

1.5.3 Example: Spin in a slowly varying magnetic field

• Let us illustrate the adiabatic theorem by the commonly studied example of a spin magnetic moment subjected to a time-dependent magnetic field.

• Earlier, we saw that a spin half magnetic moment $\vec{\mu} = \frac{-ge}{2m}\vec{S}$ at rest (say at the origin) subject to a constant magnetic field $\vec{B}$ executes Larmor precession. Here the magnetic moment may arise due to the spin of an electron of mass m and charge $-e$, say in an atom. The expectation value of the spin vector operator $\langle\psi(t)|\vec{S}|\psi(t)\rangle$ precesses about the direction of the magnetic field at a fixed angular frequency, the Larmor frequency $\omega_l = \frac{|e|B}{m}$. The angle between $\langle\vec{S}\rangle$ and $\vec{B}$ remains constant and is determined by the initial conditions. In particular, if the spin $\langle\vec{S}\rangle$ is initially along the direction of the magnetic field, then it remains that way and there is no precession. Now suppose $\langle\vec{S}\rangle$ was initially along the direction of $\vec{B}$. In fact, suppose the initial state is an up spin in the direction of $\vec{B}$. Now the magnetic field $\vec{B}(t)$ is slowly changed in direction, while its magnitude is held fixed. Then we expect from the adiabatic theorem that the spin will be carried along by the magnetic field. The electron should remain in a spin up state *with respect to the instantaneous direction of the magnetic field.* Let us see in what sense this is true.

• The magnetic moment is fixed at the origin and is subjected to a magnetic field of constant magnitude B whose direction (for simplicity) sweeps out a cone of opening angle θ at a constant angular speed ω

$$\vec{B}(t) = B\left[\hat{z}\cos\theta + \hat{x}\sin\theta\cos\omega t + \hat{y}\sin\theta\sin\omega t\right] = B\hat{n}(t) \tag{74}$$

where $\hat{n}(t)$ is the unit vector with polar coordinates $\theta, \phi = \theta, \omega t$. The hamiltonian

$$\begin{aligned} H(t) &= -\vec{\mu}\cdot\vec{B} = -\frac{g(-e)}{2m}\vec{S}\cdot\vec{B} = \frac{e}{m}\vec{B}\cdot\vec{S} = \frac{\hbar eB}{2m}\left[\sigma_z\cos\theta + \sigma_x\sin\theta\cos\omega t + \sigma_y\sin\theta\sin\omega t\right] \\ &= \frac{\hbar\omega_l}{2}\begin{pmatrix}\cos\theta & e^{-i\omega t}\sin\theta \\ e^{i\omega t}\sin\theta & -\cos\theta\end{pmatrix} = \omega_l\,\vec{S}\cdot\hat{n} \quad \text{is hermitian and traceless always.} \end{aligned} \tag{75}$$

$\omega_l = eB/m$ is the Larmor frequency which sets the scale for the fast 'internal' dynamics. The direction of the magnetic field is the environmental parameter that is varied in this example. The speed at which the magnetic field is rotated, ω, would be much slower than ω_l in the adiabatic approximation $\omega \ll \omega_l$.

• $H(t)$ is simply (up to a constant ω_l) the component of the spin operator in the direction of the instantaneous magnetic field. Since the component of the spin operator in any direction $\vec{S}\cdot\hat{n}$

has eigenvalues $\pm\hbar/2$, the eigenvalues of $H(t)$ are *independent of time* (primarily because the magnitude of $\vec{B}$ was held fixed for calculational simplicity) and equal to $E_\pm = \pm\hbar\omega_l/2$. Thus the Larmor frequency sets the scale for the energy difference between instantaneous eigenstates of $H(t)$. The corresponding instantaneous normalized eigenstates $\psi_\pm(t)$ are time dependent and are the spin up and spin down states with respect to the instantaneous direction of magnetic field. As shown in the homework, we can take them to be

$$\psi_+(t) = \begin{pmatrix} \cos(\theta/2) \\ e^{i\omega t}\sin(\theta/2) \end{pmatrix} \quad \text{and} \quad \psi_-(t) = \begin{pmatrix} e^{-i\omega t}\sin(\theta/2) \\ -\cos(\theta/2) \end{pmatrix}. \tag{76}$$

As before we write the solution of the SE as the linear combination

$$\psi(t) = c_+(t)\psi_+(t)e^{i\theta_+^D(t)} + c_-(t)\chi_-(t)e^{i\theta_-^D(t)}. \tag{77}$$

In this case the dynamical phases $\theta_\pm^D$ are linear in time as the energy levels $E_\pm = \pm\hbar\omega_l/2$ are constant

$$\theta_\pm^D = -\frac{1}{\hbar}\int_0^t E_\pm\, dt' = \mp\frac{\omega_l}{2}t \quad \text{and} \quad \theta_-^D - \theta_+^D = \omega_l t. \tag{78}$$

The SE implies the following coupled equations for $c_\pm(t)$

$$\begin{aligned} \dot{c}_+ &= -c_+\langle\psi_+|\dot{\psi}_+\rangle - c_-\langle\psi_+|\dot{\psi}_-\rangle e^{i(\theta_- - \theta_+)} \\ \dot{c}_- &= -c_-\langle\psi_-|\dot{\psi}_-\rangle - c_+\langle\psi_-|\dot{\psi}_+\rangle e^{i(\theta_+ - \theta_-)}. \end{aligned} \tag{79}$$

The inner products evaluate to

$$\langle\psi_+|\dot{\psi}_+\rangle = -\langle\psi_-|\dot{\psi}_-\rangle = i\omega\sin^2(\theta/2), \quad \langle\psi_+|\dot{\psi}_-\rangle = -\frac{i\omega}{2}e^{-i\omega t}\sin\theta, \quad \langle\psi_-|\dot{\psi}_+\rangle = -\frac{i\omega}{2}e^{i\omega t}\sin\theta.$$

So the SE in the basis of instantaneous eigenstates $\chi_\pm$ becomes the coupled pair of ODEs for $c_\pm$

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix} c_+ \\ c_- \end{pmatrix} = -\frac{\hbar\omega}{2}\begin{pmatrix} -2\sin^2(\theta/2) & e^{i(\omega_l-\omega)t}\sin\theta \\ e^{-i(\omega_l-\omega)t}\sin\theta & 2\sin^2(\theta/2) \end{pmatrix}\begin{pmatrix} c_+ \\ c_- \end{pmatrix}. \tag{80}$$

The fact that the matrix on the rhs is hermitian ensures the evolution preserves the norm of the state $||\psi||^2 = |c_+(t)|^2 + |c_-(t)|^2 = 1$ (we will show this later). The trace of the matrix on the rhs is zero mirroring $\text{tr } H = 0$. The difficulty in solving this system lies in the time-dependence of the coefficients (the off-diagonal matrix entries). If we could somehow make the matrix entries time-independent, then we could decouple the system by diagonalizing the matrix (passage to normal modes). We will pursue this in the problem set. Here we recall that in the adiabatic limit, we can ignore the off-diagonal entries. A heuristic reason for this is that in the adiabatic limit the internal (Larmor) frequency is much larger than the frequency with which the magnetic field rotates $\omega_l - \omega \approx \omega_l$. So on time steps t large compared to the internal time scale $t \gg 2\pi/\omega_l$, the phase $e^{\pm i(\omega_l-\omega)t}$ is rapidly oscillating and on average, does not contribute. In this approximation, we get

$$\dot{c}_+ = -i\omega\sin^2(\theta/2)\, c_+ \quad \text{and} \quad \dot{c}_- = i\omega\sin^2(\theta/2)\, c_- \quad \Rightarrow \quad c_\pm(t) = c_\pm(0)e^{i\gamma_\pm(t)} \tag{81}$$

with the (geometric) phases (whose significance will be discussed soon)

$$\theta_\pm^G = \gamma_\pm(t) = \mp\omega\sin^2(\theta/2)t = \pm\frac{\omega t}{2}(\cos\theta - 1) \tag{82}$$

In particular, if the electron started out in a spin-up state $\psi(0) = \psi_+(0)$, then at time t it is approximately still in an up spin state with respect to the instantaneous direction of the magnetic field:

$$\psi(t) = e^{-\frac{i}{\hbar}E_+ t} e^{\frac{i\omega t}{2}(\cos\theta - 1)} \psi_+(t) \tag{83}$$

In the homework, we will justify (83) by solving the SE exactly and taking the adiabatic limit $\omega/\omega_l \to 0$.

1.5.4 Dynamical and geometric phases for cyclic adiabatic processes

• We showed that for a hamiltonian $H(t)$ with adiabatic time-dependence and instantaneous eigenfunctions $\psi_n(t)$, the wave function evolves from

$$\Psi(0) = \sum_n c_n(0)\psi_n(0) \qquad \text{approximately to} \qquad \Psi(t) = \sum_n c_n(0)\psi_n(t) e^{i\theta_n^D} e^{i\theta_n^G} \tag{84}$$

where the dynamical and geometric phases are

$$\theta_n^D = -\frac{1}{\hbar}\int_0^t E(t')dt', \quad \text{and} \quad \theta_n^G = \int_0^t \langle \psi_n(t')|\, i\,\dot{\psi}_n(t')\rangle. \tag{85}$$

It is particularly interesting to consider a cyclic adiabatic process, where the environmental parameters are varied adiabatically from their initial values $l_i(0)$ and returned to their initial values after a time T, $l_i(T) = l_i(0)$; so that $H(0) = H(T)$. The adiabatic theorem says that if the initial state was an eigenstate of $H(0)$, then the final state will be along the same eigenstate, though the state vector could pick up a phase given by the sum of the dynamical and geometric phases. This total phase may be called the Pancharatnam phase. The remarkable thing is that the Pancharatnam and geometric phases can be non-trivial for a closed loop and can have observable consequences. This is despite the fact that two state vectors that differ by a phase describe the same physical state.

• This phenomenon was discovered in optics by Pancharatnam (1956) while studying the change in phase of a beam of light whose polarization is varied in a cyclic manner. The adiabatic approximation is not necessary for this phenomenon. The geometric phase for quantum systems subject to cyclic adiabatic changes was discovered by Berry (1984). So the geometric phase is also called Berry's phase.

• Let us see why Berry's phase is called a geometric phase. Suppose the time dependence of the hamiltonian is entirely due to the time-dependence of the p parameters $l_i(t)$ as we go round a closed curve C in parameter space. Then[3]

$$\dot{\psi}_n(t) = \sum_{i=1}^{p} \frac{\partial\psi}{\partial l_i}\frac{dl_i}{dt} = \vec{\nabla}\psi_n \cdot \frac{d\vec{l}}{dt} \tag{86}$$

So we may write Berry's phase as

$$\theta_n^G = \int_0^T \langle\psi_n(t')|i\dot{\psi}_n(t')\, dt' = i\oint_C \langle\psi_n|\vec{\nabla}\psi_n\rangle \cdot d\vec{l} \tag{87}$$

[3]The gradient is with respect to the parameters l_i, not with respect to $\vec{x}$.

Using Stokes theorem, this line integral may also be expressed as a surface integral. If the space of environmental parameters is three dimensional, we get the flux of the vector field $\nabla\times\langle\psi_n|\vec{\nabla}\psi_n\rangle$ through any surface whose boundary is the closed loop C:

$$\theta_n^G = i\int_S \vec{\nabla}\times\langle\psi_n|\vec{\nabla}\psi_n\rangle\cdot d\vec{S} \quad \text{if} \quad p=3 \quad \text{and} \quad \partial S = C. \tag{88}$$

Berry's phase is independent of the time T, it only depends on closed curve C (and the energy eigenstate ψ_n at each point along C). Thus it is called a geometric phase. On the other hand, the dynamical phase $\theta_n^D = -\frac{1}{\hbar}\int_0^T E(t)dt$ depends on the time taken to complete the cyclic process.

1.5.5 Example of Berry's geometric phase: spin in an adiabatically rotated magnetic field

• Let us return to the electron spin subject to a magnetic field of constant magnitude B but slowly varying direction which traces out a cone of opening angle θ at angular speed ω with apex at the electron location. If the state is initially spin-up with respect to the direction of $\vec{B}(0)$, we found that in the adiabatic approximation, the state at time t is still up-spin with respect to the instantaneous direction of $\vec{B}(t)$

$$\psi(t) = e^{-\frac{i}{\hbar}E_+ t}e^{\frac{i\omega t}{2}(\cos\theta-1)}\psi_+(t) \tag{89}$$

We identified the dynamical and geometric phase angles

$$\theta_+^D = -\frac{1}{\hbar}E_+ t = -\frac{\omega_l t}{2} \quad \text{and} \quad \theta_+^G = \frac{\omega t}{2}(\cos\theta-1). \tag{90}$$

appearing in the statement of the adiabatic theorem

$$\Psi_n(t) = \psi_n(t)e^{i\theta_n^D}e^{i\theta_n^G} \quad \text{where} \quad \theta_n^D = -\frac{1}{\hbar}\int_0^t E_n(t')\,dt', \quad \theta_n^G = \int_0^t \langle\psi_n(t')|i\dot{\psi}_n(t')\rangle\,dt'. \tag{91}$$

For a cyclic adiabatic process, we wait till a time $t = T = 2\pi/\omega$ when the magnetic field has returned to its initial direction. Then the dynamical phase angle is $\theta_+^D = -\pi\frac{\omega_l}{\omega}$ proportional to the total time and to the angular speed of the fast process (Larmor frequency). On the other hand, Berry's phase

$$\theta_+^G = \pi(\cos\theta-1) = -\frac{1}{2}\Omega \quad \text{where} \quad \Omega = 2\pi(1-\cos\theta). \tag{92}$$

is a purely geometric quantity proportional to the solid angle Ω swept out by the cone. The solid angle subtended at the apex of a cone is defined as the surface area (lying within the cone) of a concentric unit sphere. For a cone of opening angle θ, this area/solid angle is

$$\Omega = \int_0^\theta \sin\theta'\,d\theta'\int_0^{2\pi} d\phi = 2\pi(1-\cos\theta). \tag{93}$$

This relation between Berry's phase and the solid angle is valid in greater generality. Suppose the magnetic field is constant in magnitude but its direction traces out a cone (not necessarily right circular) defined by the curve C which is the locus of the tip of $\vec{B}$ on a sphere of radius

B. The instantaneous direction of $\vec{B}$ is defined by the spherical polar angles $\theta(t), \phi(t)$, whose dependence on time could be quite complicated:

$$\vec{B} = B[\hat{z}\cos\theta + \hat{x}\sin\theta\cos\phi + \hat{y}\sin\theta\sin\phi]. \tag{94}$$

And the instantaneous up-spin state is

$$\psi_+(t) = \begin{pmatrix} \cos\frac{1}{2}\theta(t) \\ e^{i\phi(t)}\sin\frac{1}{2}\theta(t) \end{pmatrix} \tag{95}$$

Then Berry's phase is

$$\theta_+^G = \int_0^T \langle\psi_+(t)|i\dot{\psi}_+(t')\rangle\, dt' = i\oint_C \langle\psi_+(t)|\nabla\psi_+(t)\rangle\cdot d\vec{l} \tag{96}$$

Let us denote the magnitude of $\vec{B}$ by $r = B$. The gradient $\nabla = \hat{r}\frac{\partial}{\partial r} + \frac{\hat{\theta}}{r}\frac{\partial}{\partial\theta} + \frac{\hat{\phi}}{r\sin\theta}\frac{\partial}{\partial\phi}$ of ψ_+,

$$\nabla\psi_+ = \frac{\hat{\theta}}{2r}\begin{pmatrix} -\sin\frac{1}{2}\theta \\ e^{i\phi}\cos\frac{1}{2}\theta \end{pmatrix} + \frac{\hat{\phi}}{r\sin\theta}\begin{pmatrix} 0 \\ ie^{i\phi}\sin\frac{1}{2}\theta \end{pmatrix}. \tag{97}$$

is a two-component spinor in spin space as well as a vector in the three dimensional space of magnetic fields at the location of the spin. The inner product of ψ_+ with its gradient points in the $\hat{\phi}$ direction

$$\vec{A} \equiv \langle\psi_+|\nabla\psi_+\rangle = i\frac{\sin^2(\theta/2)}{r\sin\theta}\hat{\phi} = \frac{i\hat{\phi}}{2r}\tan\frac{1}{2}\theta, \quad \text{where} \quad r = B. \tag{98}$$

However, evaluating the line integral of this vector field along the curve C on the sphere of radius B cannot be performed directly. We have not specified C explicitly by giving $\theta(t), \phi(t)$. Nevertheless, by Stokes' theorem we may express Berry's phase as a surface integral

$$\theta_+^G = i\int_S \vec{\nabla}\times\langle\psi_+|\vec{\nabla}\psi_+\rangle\cdot d\vec{S} \tag{99}$$

In our case the curl $\nabla\times A_\phi(r,\theta)\,\hat{\phi} = \frac{\hat{r}}{r\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\, A_\phi(\theta))$ points radially

$$\nabla\times\langle\psi_+|\nabla\psi_+\rangle = \frac{i\hat{r}}{r^2\sin\theta}\partial_\theta\left(\sin^2\frac{1}{2}\theta\right) = \frac{i}{2r^2}\hat{r} \tag{100}$$

while the area element on the sphere also points radially $d\vec{S} = r^2 d\Omega\hat{r}$. Thus Berry's phase

$$\theta_+^G = -\frac{1}{2}\int_S \frac{\hat{r}}{r^2}\cdot d\vec{S} = -\frac{1}{2}\int_S d\Omega = -\frac{1}{2}\Omega. \tag{101}$$

is minus half the solid angle swept by the magnetic field vector, as found in the special case of the right-circular cone.

1.5.6 Some remarks on the geometric phase and adiabatic approximation

• The geometric phase is defined modulo 2π since only $e^{i\gamma_n(t)}$ appears in the wave function in the adiabatic approximation.

• The geometric phase vanishes if the instantaneous eigenstates of $H(t)$ can be chosen real. For, in this case both $\psi_n(t)$ and $\dot{\psi}_n(t)$ are real, so that

$$\gamma_n(t) = i\int_0^t \langle\psi_n(t')|\dot{\psi}_n(t')\rangle dt' \tag{102}$$

is purely imaginary. But we know that the geometric phase is real. So in this case it must be zero. E.g. the geometric phase vanishes for a 2d square-well whose walls are slowly moved out, since the instantaneous eigenfunctions $(2/L(t))\sin(n\pi x/L(t))\sin(m\pi y/L(t))$ may be taken real. However, in the case of a spin magnetic moment in a time-dependent magnetic field, the instantaneous energy eigenstates cannot be chosen real, they are essentially complex. E.g. $\psi_+(t) = \big(\cos\theta(t)/2,\ e^{i\phi(t)}\sin\theta(t)/2\big)$.

• Berry's phase for a cyclic adiabatic process vanishes if the space of environmental parameters that are varied is one dimensional. In this case,

$$\gamma_n = \oint_C \langle\psi_n|\nabla\psi_n\rangle\cdot dl \tag{103}$$

is a line integral along a curve that simply retraces itself backwards, so $\gamma_n = 0$. For Berry's phase to be non-trivial, we need at least two environmental parameters to be varied in a cyclic adiabatic process. In particular γ_n vanishes for an SHO whose frequency is adiabatically increased and decreased to its original value.

• The last two remarks partly explain why Berry's phase was not discovered till long after the formulation of quantum mechanics. The other reason is that it was perhaps thought that these phases could be absorbed into a redefinition of the instantaneous eigenstates and therefore could not have any observable consequences. This turns out to be false for a cyclic adiabatic process.

• Berry's phase for a cyclic adiabatic process cannot be changed (modulo 2π) by a redefinition of the phases of instantaneous energy eigenfunctions. In particular, Berry's phase cannot be eliminated by such a redefinition. To see why this is so, suppose we redefine the phases of instantaneous eigenfunctions by choosing a new set of eigenfunctions

$$\phi_n(t) = e^{i\delta_n(t)}\psi_n(t), \quad \text{satisfying} \quad H(t)\phi_n(t) = E_n(t)\phi_n(t). \tag{104}$$

For a cyclic adiabatic process, $l_i(0) = l_i(T)$ so that $H(0) = H(T)$. For consistency, the instantaneous eigenfunctions must be single-valued, we must use the same set of eigenfunctions for the same hamiltonian: $\phi_n(0) = \phi_n(T)$ which implies

$$e^{i\delta_n(0)} = e^{i\delta_n(T)} \quad \text{or} \quad \delta_n(T) - \delta_n(0) = 2\pi k \quad \text{for some} \quad k\in\mathbb{Z}. \tag{105}$$

So what ever choice of phases we make for the instantaneous eigenfunctions, they must return to their initial values modulo 2π after a cyclic process[4]. Under such a redefinition of phases,

[4]In particular, we cannot in general redefine the phases by choosing $\delta_n(t) = \gamma_n(t) = i\int_0^t\langle\psi_n|\dot{\psi}_n\rangle dt'$. Such a choice would be consistent only if $\gamma_n(T) = \gamma_n(0)$ modulo 2π. But $\gamma_n(0) = 0$, so this choice would be consistent

how does Berry's phase change? Let us denote the old and new Berry phases by

$$\gamma_n = i\int_0^T \langle\psi_n(t)|\dot{\psi}_n(t)\rangle dt \quad \text{and} \quad \tilde{\gamma}_n = i\int_0^T \langle\phi_n(t)|\dot{\phi}_n(t)\rangle dt \tag{106}$$

We note that

$$\dot{\phi}_n = e^{i\delta_n}\dot{\psi}_n + i\dot{\delta}_n\phi_n \quad \Rightarrow \quad \langle\phi_n|\dot{\phi}_n\rangle = \langle\psi_n|\dot{\psi}_n\rangle + i\dot{\delta}_n\langle\psi_n|\psi_n\rangle \tag{107}$$

so that

$$\tilde{\gamma}_n = i\int_0^T \langle\psi_n|\dot{\psi}_n\rangle dt + ii\int_0^T \dot{\delta}_n(t)dt = \gamma_n - (\delta_n(T) - \delta_n(0)) \;\Rightarrow\; \tilde{\gamma}_n = \gamma_n - 2\pi k \tag{108}$$

So Berry's phase is unaltered by a consistent change in phase of instantaneous eigenfunctions.

• The semi-classical approximation and the adiabatic approximation bear some resemblance. The slow spatial variation of a potential is replaced by a slow time-dependence of the hamiltonian. The condition $\lambda_{dB}/L \gg 1$ is replaced by $T_{Bohr}/\tau \ll 1$. Here L is the length scale over which the potential changes appreciably while τ is the time scale over which the adiabatic change happens. λ_{dB} plays the same role as the 'internal' time scale, the Bohr time period $T_{Bohr} = 2\pi/\omega_{fi}$. For a constant potential, the wave function is a plane wave of a definite constant momentum. For a slowly varying potential, the momentum in a sense becomes position dependent $p(x) = \sqrt{2m(E - V(x))}$. Similarly, for a time-independent hamiltonian, the energy eigenvalues are time-independent. For an adiabatically varied hamiltonian, the energy eigenvalues $E_n(t)$ of instantaneous eigenstates become time-dependent. The phase of the wave function $\psi(x) \sim e^{\frac{i}{\hbar}\int_0^x p(x')dx'}$ in the semi-classical approximation is to be compared with the dynamical phase $e^{-\frac{i}{\hbar}\int_0^t E(t')dt'}$ in the adiabatic approximation. Periodic classical orbits in a slowly varying potential are like cyclic adiabatic processes. The single-valuedness of the semi-classical wave function is like the consistency in the choice of instantaneous eigenstates. The Bohr-quantization condition coming from periodic classical orbits is to be compared with the requirement that the choice of phases of instantaneous eigenstates must be single-valued for a cyclic adiabatic process.

• The effects of the Pancharatnam phase (dynamical plus geometric phase) as well as Berry's phase are physically observable via interference experiments. The overall phase of a single wavefunction at a particular time is arbitrary in the sense that two wave functions $\psi, e^{i\theta}\psi$ that differ by a multiplicative phase describe the same physical state in isolation at that time. However, the relative phase between two state vectors at a particular time can be observed via an interference experiment since $|\psi(t)+e^{i\theta}\psi(t)| = |\psi|^2(2+2\cos\theta)$. As an oversimplified thought experiment, suppose we consider two spin magnetic moments $1, 2$. At $t = 0$ both are in an up spin state with respect to a magnetic field, so we can take $\psi_1(0) = \psi_2(0) = \psi_+(0)$. Now we keep the magnetic field fixed for the first spin, so that its state vector evolves very simply to $\psi_+(0)e^{-iE_+T/\hbar}$ after a time T. The second spin is subjected to a magnetic field with adiabatic time dependence, say a magnetic field that is slowly rotated in direction and brought back to

only if Berry's phase $\gamma_n(T)$ is a multiple of 2π. But we have calculated Berry's phase in the case of a spin in a time-dependent magnetic field and found that it is not simply a multiple of 2π, but rather equal to minus half the solid angle enclosed by the path in the space of $\vec{B}$ fields. This solid angle can be continuously varied by changing the opening angle of the cone of magnetic fields, and clearly isn't always a multiple of 2π. Of course, there are problems where Berry's phase is simply zero, as when the instantaneous eigenstates are real or when only one environmental parameter is varied. In those problems, we are of course free to choose $\delta_n(t) = \gamma_n(t)$.

its initial direction at time T. So its state vector is $\psi_+(T)e^{i\theta_+^D(T)}e^{i\theta_+^G(T)} = \psi_+(0)e^{i\theta(T)}$ at time T due to the cyclicity of the process, where we have defined $\theta(T)$ as the sum of dynamical and geometric phases. $\theta(T)$ depends on the time T as well as on the geometry of the path traversed through the space of environmental parameters. Now if the two amplitudes are allowed to interfere at time T, we will find constructive and destructive interference depending on the value of the relative phase $\theta(T) + E_+T/\hbar$, due to the cosine term above. By changing T and changing the path through environmental parameter space, we can try to determine how θ depends on them. So the Pancharatnam phase has observable consequences.

2 Time evolution operator for Schrödinger equation

2.1 Uniqueness of Schrödinger evolution

• Even if the external magnetic field is varied in time, we expect that the *total* probability of finding the spin in *some* state at any give time should be one. So time dependence of $H(t)$ should not violate the preservation of probabilities under Schrödinger evolution, provided the hamiltonian remains hermitian at all times. This is easy to show using the SE and its adjoint

$$i\hbar\frac{\partial}{\partial t}||\psi(t)||^2 = i\hbar\frac{\partial}{\partial t}\langle\psi(t)|\psi(t)\rangle = i\hbar\langle\dot{\psi}|\psi\rangle + i\hbar\langle\psi|\dot{\psi}\rangle = -\langle\psi|H^\dagger|\psi\rangle + \langle\psi|H|\psi\rangle = \langle\psi(t)|H(t) - H(t)^\dagger|\psi(t)\rangle$$

Thus the time derivative of the norm vanishes provided $H(t) = H(t)^\dagger$. A similar argument shows that inner products are preserved in time (homework).

• We often say that classical mechanics is deterministic: once we fix the initial state of a particle, Newton's/Hamilton's equations uniquely determine its subsequent state (i.e. trajectory) as a function of time. There cannot be two distinct trajectories with the same initial conditions[5]. This can be established for some simple systems, though for more complicated ones like a fluid it is not known how to do so due to the non-linearity of the equations of motion, though there is a lot of evidence that it is true.

• Surprisingly, the situation is simpler in QM, owing to the linearity of the SE. Schrödinger time evolution is deterministic in the sense that if the initial state $\psi(0)$ is known then the state at any subsequent time is uniquely fixed by Schrödinger evolution. To show this we suppose that $\psi(t)$ and $\phi(t)$ are two solutions of the Schrödinger initial value problem for the same hamiltonian $H(t)$ with the same initial state $\psi(0) = \phi(0) = f$ of norm one. We will show that $\psi(t) = \phi(t)$.

• To do so, we consider the vector $v(t) = \psi(t) - \phi(t)$ and hope to show it is the zero vector. To do this, it suffices to show its norm is zero $||v(t)||^2 = 0$. First, we notice that due to linearity of SE, $v(t)$ itself satisfies the SE $i\hbar\dot{v} = H(t)v(t)$ with the initial condition $v(0) = 0$. Now we showed above that SE preserves norms, so in particular $||v(t)|| = ||v(0)|| = 0$. Thus $v(t)$ must be the zero vector. We have shown Schrödinger time-evolution is unique. Of course, none of this depended on whether the hamiltonian is time-dependent or not. Nor did it depend on the details of the system, number of particles or type of forces. On the other hand, showing the uniqueness of Newtonian evolution even for simple forces and a few particles is much more complicated.

[5]This leaves open the possibility that the dependence on the initial cond. is quite sensitive, leading to the phenomenona of chaos.

2.2 Time evolution operator

• Though we know that Schrödinger evolution is unique, is there always a solution for a given initial condition? This is the question of existence. We will show that the answer is yes by explicitly constructing a solution with prescribed initial condition $\psi(t_0)$. To do so, we make the ansatz

$$\psi(t) = U(t, t_0)\psi(t_0) \tag{109}$$

for some linear operator $U(t, t_0)$ called the time evolution operator, which is assumed *independent* of $\psi(0)$ This ansatz satisfies the initial condition provided $U(t_0, t_0) = I$. This ansatz is linear in the initial condition, which is what we have found in all our explicit solutions of the SE so far (e.g. for stationary states of time independent hamiltonians). This is a reasonable ansatz owing to the linearity of the SE. If the initial state is doubled, we expect $\psi(t)$ to be doubled and similarly for linear combinations of initial states. The linearity in $\psi(0)$ is also approximately true for small t: $\psi(t) \approx \left(1 + \frac{1}{i\hbar}H(0)t\right)\psi(0)$.

• We are of course free to look for solutions of the SE that are possibly non-linear in the initial state, $\psi(t) = W(t, t_0, \psi(0))\psi(0)$ while satisfying the given initial condition $W(t_0, t_0, \psi(0)) = I$. But suppose we have already found one solution of the SE with initial condition $\psi(0)$, say in the form of the above ansatz $\psi(t) = U(t, t_0)\psi(t_0)$. Then by uniqueness, we know there cannot be any distinct solution with the same initial condition. Therefore we need not consider the non-linear ansatz $\psi(t) = W(t, t_0, \psi(0))\psi(0)$.

• On the other hand, consider Newton's equation even for a free particle $m\ddot{x}(t) = 0, x(0) = x_0, \dot{x}(0) = v$. The state at time t is not proportional to the state at time zero $\begin{pmatrix} x(t) \\ p(t) \end{pmatrix} = \begin{pmatrix} x_0 + vt \\ mv \end{pmatrix}$. In general it does not even make sense to ask for the solution of Newton's equation to be linear in the initial conditions, as the space of classical states is not necessarily a linear space, e.g.: a particle moving on a circular ring.

• For simplicity we take $t_0 = 0$ and denote $U(t, t_0) = U(t)$. We will find an explicit formula for $U(t)$ in terms of the hamiltonians $H(t')$ for $0 \le t' \le t$. We begin with simple cases.

• Recall that for a time-independent hamiltonian H we could write the solution to the Schrödinger initial value problem (SIVP) $i\hbar\dot{\psi} = H\psi$ in terms of the time-evolution operator

$$\psi(t) = U(t, t_0)\psi(t_0) \quad \text{where} \quad U(t, t_0) = e^{-iH(t-t_0)/\hbar} \tag{110}$$

Recall further that the time evolution operator was unitary and preserved inner products (and total probabilities). Taking $t_0 = 0$ for simplicity, $U(t)$ had the expansion

$$U(t) = e^{-iHt/\hbar} = \sum_{n=0}^{\infty} \left(\frac{1}{i\hbar}\right)^n \frac{t^n H^n}{n!}. \tag{111}$$

What are the analogous statements for a time-dependent hamiltonian?

• The preservation of inner products shows $U(t)^\dagger U(t) = I$, since for any pair of initial states $\psi(0), \phi(0)$,

$$\langle\psi(0)|\phi(0)\rangle = \langle\psi(t)|\phi(t)\rangle = \langle\psi(0)|U(t)^\dagger U(t)|\phi(0)\rangle \quad \Rightarrow \quad U(t)^\dagger U(t) = I. \tag{112}$$

• Interestingly, the time-evolution operator itself satisfies the SE. Differentiating (109) in time, we find

$$i\hbar\frac{\partial U(t,t_0)}{\partial t}\psi(t_0) = H(t)\psi(t_0). \tag{113}$$

As this is true for any initial state, we find that $U(t,t_0)$ must itself satisfy the SE

$$i\hbar\frac{\partial U(t,t_0)}{\partial t} = H(t)U(t,t_0) \quad \text{with initial condition} \quad U(t_0,t_0) = I. \tag{114}$$

Our aim is to solve this equation $i\hbar\dot{U} = H(t)U(t)$ for the operator $U(t)$.

2.3 Separation of variables for a separable hamiltonian

• First, let us try separation of variables (SOV) and point out its limitations. Suppose we want to solve the SIVP $i\hbar\dot{\Psi}(t) = H(t)\Psi(t)$. We look for a solution of the form $\Psi(x,t) = \psi(x)T(t)$ and find

$$i\hbar\psi(x)\dot{T}(t) = \left(H(t)\psi\right)(x)\, T(t). \tag{115}$$

Upon dividing by $T(t)\psi(x)$ we obtain

$$i\hbar\frac{\dot{T}(t)}{T(t)} = \frac{\left(H(t)\psi\right)(x)}{\psi(x)}. \tag{116}$$

Now, $H(t)$ (e.g. $H(t) = \frac{p^2}{2m} + \frac{1}{2}m\omega(t)^2x^2$) is typically a differential operator in x which depends parametrically on time. So though x apparantly appears only on the rhs, both lhs and rhs depend on t. A complete separation may be effected if the hamiltonian itself is separable, $H(t) = h(t)H$ as the product of some real function of time $h(t)$, and a time-independent hermitian operator H that acts on $\psi(x)$[6]. Such time-dependence is usually too simple to be interesting, but there are examples, such as a free particle whose mass is changing with time $H(t) = \frac{1}{2m(t)}p^2$. Under these circumstances, SOV gives

$$\frac{i\hbar\dot{T}(t)}{h(t)T(t)} = \frac{(H\psi)(x)}{\psi(x)} = E \tag{117}$$

where E is a separation constant. Thus

$$T(t) = \exp\left[-\frac{i}{\hbar}E\int_0^t h(t')dt'\right]T(0) \tag{118}$$

and $\psi(x)$ must be an eigenstate of the time-independent operator H. Suppose $\psi_n(x)$ are the orthonormal eigenstates of H with eigenvalues E_n, i.e., $H\psi_n(x) = E_n\psi_n(x)$. Note that $H(t)\psi_n(x) = h(t)E_n\psi_n(x)$, so the instantaneous eigenstates are time-independent, though the instantaneous energies $h(t)E_n$ change with time.

• We use linearity of the SE and the above results to synthesize the general solution of the SIVP for a separable hamiltonian. If the initial state is $\psi(x,0) = \sum_n c_n\psi_n(x)$, then

$$\psi(x,t) = \sum_n e^{-\frac{i}{\hbar}E_n\int_0^t h(t')dt'}c_n\psi_n(x). \tag{119}$$

[6]The property of being separable is basis-independent $H(t) = h(t)H \;\Rightarrow\; (S^{-1}H(t)S) = h(t)(S^{-1}HS)$. It can be show that if $H(t)$ is hermitian at all times and is separable as a product of a complex function of time $h(t)$ and a time-independent operator H, then we can always choose $h(t)$ to be real and H to be hermitian.

From this we extract the time-evolution operator, which is defined as the operator that expresses $\psi(t) = U(t)\psi(0)$ in terms of $\psi(0)$

$$\psi(t) = \sum_n e^{-\frac{i}{\hbar}E_n \int_0^t h(t')dt'} c_n \psi_n = U(t)\psi(0) = U(t)\sum_n c_n \psi_n \tag{120}$$

The above formula says that the time evolution operator is *diagonal* in the basis of eigenstates of H, indeed by taking $c_n = \delta_{nm}$ we find

$$U(t)\psi_m = e^{-\frac{i}{\hbar}E_m \int_0^t h(t')dt'} \psi_m \tag{121}$$

and taking an inner product with ψ_n we obtain the matrix elements of $U(t)$ in the energy basis

$$\langle \psi_n | U(t) | \psi_m \rangle = \delta_{nm} e^{-\frac{i}{\hbar}E_n \int_0^t h(t')dt'} \tag{122}$$

Since $U(t)$ is diagonal in the energy basis for a separable hamiltonian $H(t) = h(t)H(x)$ we may write

$$U(t) = e^{-\frac{i}{\hbar}\int_0^t H(t')dt'}. \tag{123}$$

Notice that such separable hamiltonians commute at distinct times $[H(t), H(t')] = h(t)h(t')[H, H] = 0$ and that the above $U(t)$ commutes with each of them. However, most interesting time-dependent hamiltonians are not separable and nor do they have the property of commuting at distinct times $[H(t), H(t')] \neq 0$. In such situations, the above formula ceases to be valid and we need other ways to think about the time-evolution operator.

2.4 Time-ordered exponential

• We turn to the problem of finding the time evolution operator by solving the Schrödinger initial value problem $i\hbar\dot{U} = H(t)U(t)$, $U(0) = I$.

• It is tempting to simply divide by U, or more precisely right multiply by its inverse and write the equation as $i\hbar\dot{U}(t)U(t)^{-1} = H(t)$. In general $\dot{U}(t)$ and $U(t)$ may not commute. Moreover, since they are operators, it is not clear whether we can write the lhs as the time-derivative of the logarithm of $U(t)$. At the very least, we would need to define the logarithm of $U(t)$ in such a way that it gives $\dot{U}U^{-1}$ upon differentiation. Glossing over these difficulties, we may just guess that the time evolution operator is

$$V(t) = e^{\frac{1}{i\hbar}\int_0^t H(t')dt'} \tag{124}$$

At first, this guess is quite promising since it reduces to the correct time-evolution operator when H is time-independent or separable. However, examples show that $V(t)$ does not always satisfy the SE! The problem lies in the fact that hamiltonians at distinct times do not commute in general. $H(t)$ and $\int_0^t H(t')\,dt'$ also do not commute in general and the formula for the time derivative of $V(t)$ is

$$i\hbar\dot{V} = \sum_1^\infty \frac{1}{(i\hbar)^2}\frac{1}{n!} \sum_{p+q+1=n} \left(\int_0^t H(t')dt'\right)^p H(t) \left(\int_0^t H(t')dt'\right)^q \tag{125}$$

It is only on very rare occasions, such as when $[H(t), H(t')] = 0$, that we can write the rhs as $H(t)V(t)$.

• Instead of going down this path, it is advantageous to write the SE with initial condition $U(0) = I$ as an integral equation by integrating from 0 to t:

$$U(t) - I = \frac{1}{i\hbar} \int_0^t H(t')U(t')\, dt' \tag{126}$$

The unknown operator appears on both sides, but as with the Born series, we may obtain an explicit solution by iteration:

$$U(t) = I + \frac{1}{i\hbar} \int_0^t dt'\, H(t') \left(I + \frac{1}{i\hbar} \int_0^{t'} dt''\, H(t'')U(t'') \right) \tag{127}$$

Proceeding in this manner, we get the infinite series

$$\begin{aligned} U(t) &= I + \frac{1}{i\hbar} \int_0^t dt_1\, H(t_1) + \frac{1}{(i\hbar)^2} \int_0^t dt_1\, H(t_1) \int_0^{t_1} dt_2\, H(t_2) + \cdots \\ &= I + \sum_1^\infty \frac{1}{(i\hbar)^n} \iiint_{0<t_n<\cdots<t_n<t} dt_1 \ldots dt_n\, H(t_1)H(t_2)\cdots H(t_n). \end{aligned} \tag{128}$$

Each term is called an iterated integral. For $n \geq 2$ notice that the region of integration is not the hyper cube $[0, t]^n$, but rather the simplex defined by $0 < t_n < \cdots < t_2 < t$. Notice also, that the product of hamiltonians appears in a time-ordered fashion, in increasing order of 'age' (t_i) from the right: younger ones to the right. The order is important, as hamiltonians at distinct times *do not* commute in general.

• By analogy with the case of a time-independent hamiltonian, we'd like to think of the time-evolution operator as some sort of exponential of the hamiltonian. However, the above series is not an exponential series since there is no $n!$ in the denominator and individual terms are not simply powers of $\int_0^t H(t')dt'$. But remarkably, it can be written nearly as an exponential series.

• To do so, we notice that the integration is only over a region defined by one particular ordering of the times. There are a total of $n!$ possible ways of sequentially ordering the times $t_1, \cdots, t_n$. Each of these defines an n-dimensional polyhedron called a simplex. The hypercube $[0, t]^n$ is a disjoint union of these $n!$ simplices. The strategy is to extend the integration over all these simplices, in such a way that they all contribute equally. This expansion of the integration region will result in over estimating the iterated integral by a factor of $n!$, which we must then divide by. In this manner we will write $U(t)$ more like an exponential series. We begin by noting the identity

$$\int_{t_1>t_2} dt_1 dt_2 H(t_1)H(t_2) = \int_{t_2>t_1} dt_1 dt_2\, H(t_2)H(t_1). \tag{129}$$

obtained by changing the variables of integration $t_1 \leftrightarrow t_2$. Now we define the time-ordered product (T-product) of operators by positioning the younger operator to the right

$$T\left(H(t_1)H(t_2)\right) = \begin{cases} H(t_1)H(t_2) & \text{if } t_1 \geq t_2 \\ H(t_2)H(t_1) & \text{if } t_2 \geq t_1 \end{cases}. \tag{130}$$

In terms of the T-product this identity is

$$\int_{t>t_1>t_2>0} dt_1 dt_2 T\left(H(t_1)H(t_2)\right) = \int_{t>t_2>t_1>0} dt_1 dt_2 T\left(H(t_1)H(t_2)\right). \tag{131}$$

In other words, the integral of the *time-ordered* product over the two triangles making up the square $[0,t]^2$ are equal.

• More generally, we can show that the integral of the time-ordered product over each of the $n!$ distinct simplices constituting the hypercube $[0,t]^n$ are equal. Thus we can write the iterated integral appearing in the time-evolution operator as

$$\iiint_{0<t_n<\cdots<t_2<t} dt_1 \dots dt_n H(t_1)H(t_2)\cdots H(t_n) = \frac{1}{n!}\int_{[0,t]^n} dt_1\cdots dt_n T\left(H(t_1)\cdots H(t_n)\right) \quad (132)$$

So we have another way of writing the time evolution operator

$$U(t) = \sum_0^\infty \frac{1}{(i\hbar)^n}\frac{1}{n!}\int_0^t dt_1\cdots dt_n\, T\left(H(t_1)\cdots H(t_n)\right) \quad (133)$$

This looks a lot more like the exponential series, except for the time-ordering. So we *define* the *time-ordered exponential* by this series

$$U(t) = \mathrm{Texp}\left[-\frac{i}{\hbar}\int_0^t H(t')\,dt'\right] \equiv \sum_0^\infty \frac{1}{(i\hbar)^n}\frac{1}{n!}\int_0^t dt_1\cdots dt_n\, T\left(H(t_1)\cdots H(t_n)\right) \quad (134)$$

Loosely, we say that the time evolution operator is simply the time-ordered exponential of the hamiltonian. We showed earlier that $U(t)^\dagger U(t) = I$, a fact that is tedious to show using this infinite series.

• Note that the time ordering has to be performed before the integration, otherwise there will be nothing to order. The time-ordered exponential is a *new* function, it is not the composition of time ordering with the ordinary exponential function. You can think of Texp as a new 'special function' that arises from solving the operator differential equation $i\hbar\dot{U} = H(t)U(t)$. For each t, the time-ordered exponential is an operator-valued function of the whole chain of hamiltonian operators $\{H(t')\}_{0\le t'\le t}$.

• Notice that for a time-independent hamiltonian, the time-ordered exponential reduces to the ordinary exponential since the time-ordering does not play any role in that case.

2.5 Failure of naive guess for time-evolution operator

• It is instructive to see how the 'naive' guess for the time-evolution operator, which is simply the exponential of the integral of the hamiltonian differs from the time-ordered exponential.

$$\begin{aligned} V(t) &= e^{\frac{1}{i\hbar}\int_0^t H(t')dt'} = I + \frac{1}{i\hbar}\int_0^t H(t')\,dt' + \frac{1}{(i\hbar)^2}\frac{1}{2!}\int_0^t dt'dt''H(t')H(t'') + \cdots \\ U(t) &= Te^{\frac{1}{i\hbar}\int_0^t H(t')dt'} = I + \frac{1}{i\hbar}\int_0^t H(t')\,dt' + \frac{1}{(i\hbar)^2}\frac{1}{2!}\int_0^t dt'dt''T(H(t')H(t'')) + \cdots \end{aligned} \quad (135)$$

First, both reduce to the time evolution operation for a time-independent hamiltonian. Additionally, they both satisfy the initial condition. Now we compare their series expansions in the hamiltonian given above[7]. The zeroth and first order terms are identical, but a difference arises

[7] We could work with $gH(t)$ instead, and consider U, V as functions of g and compare their series expansions around $g = 0$.

at second order due to the time-ordering in U. The coefficients of $\frac{1}{2!(i\hbar)^2}$ are

$$U_2 = \int_{t_1>t_2} H(t_1)H(t_2)\,dt_1\,dt_2 + \int_{t_2>t_1} H(t_2)H(t_1)\,dt_1\,dt_2$$
$$V_2 = \int_{t_1>t_2} H(t_1)H(t_2)\,dt_1\,dt_2 + \int_{t_2>t_1} H(t_1)H(t_2)\,dt_1\,dt_2 \tag{136}$$

We see that their difference is given by the integral of the commutator over a simplex

$$U_2 - V_2 = \int_{t>t_2>t_1>0} [H(t_2), H(t_1)]\,dt_1\,dt_2. \tag{137}$$

In general, this commutator is non-vanishing and so is the integral. In the case of an SHO with time dependent frequency, $H(t) = \frac{1}{2m}p^2 + \frac{1}{2}m\omega(t)^2x^2$ one finds the hamiltonians do not commute

$$[H(t_2), H(t_1)] = \frac{i\hbar}{2}\left[\omega(t_2)^2 - \omega(t_1)^2\right](xp + px) \tag{138}$$

and the difference of second order terms is

$$U_2 - V_2 = \frac{i\hbar}{2}(xp + px)\int_{t>t_2>t_1>0} \left[\omega(t_2)^2 - \omega(t_1)^2\right]\,dt_1\,dt_2 \tag{139}$$

This integral can be non-zero, e.g., if $\omega(t)$ is increasing with time. So we have exhibited an example where the naive formula $V(t)$ for time evolution simply disagrees with the time-ordered exponential.

2.6 Finite evolution from infinitesimal evolution: infinite product form of $U(t, t_0)$

• Recall that the exponential function can also be defined as the limit of an infinite product $e^{ht} = \lim_{n\to\infty}(1+\frac{ht}{n})^n$. We would like to find an analogue of this for the time evolution operator.

• For infinitesimal evolution from t to $t + \Delta t$ we can approximate the solution of the SIVP by

$$\psi(t + \Delta t) \approx \psi(t) - \frac{i\Delta t}{\hbar}H(t)\psi(t) = \left(I - \frac{i\Delta t}{\hbar}H(t)\right)\psi(t). \tag{140}$$

This gives us an infinitesimal time evolution operator for small Δt

$$U(t + \Delta t, t) \approx \left(I - \frac{i\Delta t}{\hbar}H(t)\right) \tag{141}$$

By composing several successive infinitesimal evolutions, we can get evolution over a finite time. Let us break up the time interval $[0, t]$ into n equal steps of size $\Delta t = t/n$ with the sequence of times $t_j = jt/n$ for $0 \le j \le n$. Then we have an infinite product for the time evolution operator

$$U(t, 0) = \lim_{n\to\infty}\left(I - \frac{i\Delta t}{\hbar}H(t_{n-1})\right)\left(I - \frac{i\Delta t}{\hbar}H(t_{n-2})\right)\cdots\left(I - \frac{i\Delta t}{\hbar}H(t_1)\right)\left(I - \frac{i\Delta t}{\hbar}H(t_0)\right). \tag{142}$$

In general, the hamiltonians at distinct times do not commute. The chronological ordering of times with the earliest to the right mirrors what we obtained for the time-ordered exponential.

By multiplying out the factors, we can show that the product representation gives the path ordered exponential in the limit $n \to \infty$. The first few terms are

$$\begin{aligned} U(t,0) &= I + \lim_{n\to\infty} \sum_{j=0}^{n-1} \frac{1}{i\hbar} H(t_j) + \sum_{n>i>j\geq 0} \frac{1}{(i\hbar)^2} (\Delta t)^2 H(t_i) H(t_j) + \cdots \\ &= I + \int_0^t \frac{1}{i\hbar} H(t)\, dt + \int_0^t dt_1 \int_{t_0}^{t_1} dt_2 \frac{1}{(i\hbar)^2} H(t_1) H(t_2) + \cdots = \text{Texp}\left[\frac{1}{i\hbar}\int_0^t H(t')dt'\right] \end{aligned} \quad (143)$$

• The above infinite product form of the time-evolution operator is the generalization of the formula

$$e^{-iHt/\hbar} = \lim_{n\to\infty} \left(I - \frac{iHt}{n\hbar}\right)^n. \quad (144)$$

for the time evolution operator when H is time-independent.

2.7 Fundamental solution of the Schrödinger equation and the time evolution operator

• Finding the time-evolution operator is equivalent to finding the solution of the SE for an *arbitrary* initial condition, for it gives us the solution as $\psi(t) = U(t)\psi(0)$. Suppose we have found $U(t)$ by solving $i\hbar\dot{U}(t) = H(t)U(t)$. Then the columns of $U(t)$ are themselves solutions of SE. For illustration, suppose the Hilbert space is finite (n) dimensional. Denote the columns of $U(t)$ by the column vectors $(u_1(t), u_2(t) \cdots, u_n(t))$. Then the columns of the matrix $H(t)U(t)$ are $(Hu_1, Hu_2, \cdots, Hu_n)$ (work out the 2×2 case). Thus the SE for $U(t)$ is

$$i\hbar \begin{pmatrix} \dot{u}_1(t) & \dot{u}_2(t) & \cdots & \dot{u}_n(t) \end{pmatrix} = \begin{pmatrix} H(t)u_1(t) & H(t)u_2(t) & \cdots & H(t)u_n(t) \end{pmatrix}. \quad (145)$$

So $i\hbar\dot{u}_j(t) = H(t)u_j(t)$ and the columns of $U(t)$ are solutions of the SE. Moreover, unitarity $U(t)^\dagger U(t) = I$ means the columns of $U(t)$ are orthonormal at *every* instant of time $t \geq 0$. Further, $U(0) = I$. Thus by finding the time evolution operator we have in effect found n linearly independent (in fact orthonormal) solutions of the time-dependent SE, satisfying a 'unit' initial condition. Such a collection of linearly independent solutions with 'unit' initial condition is called the (principal) fundamental solution of the system of ODEs $i\hbar\dot{\psi} = H(t)\psi(t)$[8]. The solution of the SE for an arbitrary initial condition can be obtained by taking an appropriate linear combination of the columns of $U(t)$ as specified by the initial condition:

$$\psi(0) = \sum_1^n \psi_i u_i(0) \quad \Rightarrow \quad \psi(t) = \sum_1^n \psi_i u_i(t). \quad (146)$$

which is the same as

$$\psi(t) = U(t)\psi(0) \quad \text{where} \quad U(t) = \begin{pmatrix} u_1(t) & \cdots & u_n(t) \end{pmatrix} \quad \text{and} \quad \psi(0) = \begin{pmatrix} \psi_1 \\ \vdots \\ \psi_n \end{pmatrix} \quad (147)$$

[8]This is a system of first order ODEs for the various components of the vector ψ (which are usually labelled by x).

2.8 Example: time evolution operator for spin in a rotating $\vec{B}$ field

• In general, finding the time evolution operator explicitly by summing the above time-ordered exponential series is quite hard, though the first few terms provide an approximation. On rare occasions, when we know the general solution of the Schrödinger IVP, we may be able to write $U(t)$ in closed form.

• E.g.: Let us find $U(t)$ from our general solution (homework) of the Schrödinger IVP for a spin in a magnetic field B rotating at angular speed ω with opening angle θ w.r.to the z-axis. We choose to write $U(t)$ in the standard basis of up and down spin eigenstates of S_z. Then $U(t) = \left(\psi^{(1)}(t)\ \psi^{(2)}(t)\right)$ where the first column of $U(t)$ is the solution of the IVP with the initial condition $\psi^{(1)}(0) = \begin{pmatrix}1\\0\end{pmatrix} = \psi_+(0)$. We already determined this solution in the homework

$$\psi^{(1)}(t) = c_+ e^{i\theta_+}\psi_+ + c_- e^{i\theta_-}\psi_- \tag{148}$$

where $c_+(0) = 1, c_-(0) = 0$ with their time-dependence given by

$$c_+(t) = e^{i\phi/2}\left[\cos\left(\frac{\lambda t}{2}\right) + \frac{i}{\lambda}(\omega\cos\theta - \omega_l)\sin\left(\frac{\lambda t}{2}\right)\right] \quad \text{and} \quad c_-(t) = \frac{i\omega}{\lambda}e^{-i\phi/2}\sin\left(\frac{\lambda t}{2}\right)\sin\theta. \tag{149}$$

Recall that the dynamical phases are $\theta_\pm = \mp\omega_l t/2$ and the instantaneous eigenstates are

$$\psi_+(t) = \begin{pmatrix}\cos(\theta/2)\\ e^{i\omega t}\sin(\theta/2)\end{pmatrix} \quad \text{and} \quad \psi_-(t) = \begin{pmatrix}e^{-i\omega t}\sin(\theta/2)\\ -\cos(\theta/2)\end{pmatrix}. \tag{150}$$

The second column of $U(t)$ is the solution with initial condition $\psi^{(2)}(0) = \begin{pmatrix}0\\1\end{pmatrix} = -\psi_-(0)$. We find it by a similar method and express it in terms of the same coefficients $c_\pm(t)$[9]

$$\psi^{(2)}(t) = c_-^* e^{i\theta_+}\psi_+ - c_+^* e^{i\theta_-}\psi_-. \tag{151}$$

By stacking these as its columns, we get the 2×2 time evolution operator $U(t) = (\psi^{(1)}(t),\ \psi^{(2)}(t))$.

2.9 Reproducing property / composition law for $U(t, t_0)$

• $U(t, t_0)$ satisfies a composition law which we already used in obtaining its infinite product representation. This is simply the statement that one can evolve directly from t_0 to $t_2 > t_0$ or in two steps from $t_0 \to t_1$ and then from $t_1 \to t_2$. Thus composing two time evolution operators *whose initial and final times coincide*, reproduces another time evolution operator:

$$U(t_2, t_0) = U(t_2, t_1)U(t_1, t_0) \quad \text{for} \quad t_2 \geq t_1 \geq t_0. \tag{152}$$

• In the case of a time independent hamiltonian the composition law says that

$$e^{-iH(t-t_0)/\hbar} = e^{-iH(t-t_1)/\hbar}e^{-iH(t_1-t_0)/\hbar} \tag{153}$$

[9] We write $\psi^{(2)} = c_+^{(2)}\psi_+ e^{i\theta_+} + c_-^{(2)}\psi_- e^{i\theta_-}$ with $c_+^{(2)}(0) = 0, c_-^{(2)}(0) = -1$. In this case $f(0) = S^{-1}c^{(2)}(0) \Rightarrow f_\pm(0) = \mp 1/2\lambda$ and one finds the coefficients $c_+^{(2)} = c_-^*$ and $c_-^{(2)} = -c_+^*$.

In this case, $U(t,t_0)$ is only a function of the time difference and we may denote the reduced time-evolution operator $\tilde{U}(t) = e^{-iHt/\hbar}$. Then we have $\tilde{U}(t+s) = \tilde{U}(t)\tilde{U}(s)$. In this case, the composition law is commutative $\tilde{U}(t)\tilde{U}(s) = \tilde{U}(s)\tilde{U}(t)$. $\tilde{U}(0) = I$ and $\tilde{U}(-t)\tilde{U}(t) = I$ defines the inverse with $U(-t) = U(t)^\dagger$. Thus the reduced time evolution operators of a system with time-independent hamiltonian may be used to obtain a unitary representation of the abelian group of rotations $\mathrm{U}(1)$.

• For a time-dependent hamiltonian, $U(t,t')$ is generally not just a function of the time difference as time-translation invariance is broken, so we cannot write $U(t,t') = \tilde{U}(t-t')$. The $U(t,t')$ do not form a group since in general we cannot compose two of them to produce another time-evolution operator, this is possible only if the final time of the right factor matches the initial time of the left factor.

• The reproducing property is important. It can be used to define the time-evolution operator, and thereby serve as an alternative to the Schrödinger equation.

2.10 Time evolution operator in the position basis

• The time evolution operator $U(t,t_0)$ can be expressed in any basis. For a time-independent Hamiltonian, it is simplest in the energy basis. If $H|n\rangle = E_n|n\rangle$, then

$$\langle n|U(t,0)|m\rangle = \langle n|e^{-iHt/\hbar}|m\rangle = e^{-iE_nt/\hbar}\delta_{nm}. \tag{154}$$

• To work our way to the path integral formulation, it is instructive to consider the time evolution operator in a basis of position eigenstates $|x'\rangle$. In the position basis, if we denote $\langle x|U(t,t')|x'\rangle = U(xt;x't')$, then

$$\psi(x,t) = \langle x|\psi(t)\rangle = \langle x|U(t,t')|\psi(t')\rangle = \int dx'\ \langle x|U(t,t')|x'\rangle\langle x'|\psi(t')\rangle = \int dx' U(xt;x't')\psi(x',t'), \tag{155}$$

In a sense, $U(x't';xt)$ propagates the initial wave function to the final wave function. So the time evolution operator in the position basis is also called the *propagator*. In particular, if the initial state was delta localized at the point x_0, then $\psi(x,t) = U(xt;x_0t_0)$[10]. So the matrix elements of the propagator give the amplitude for finding the particle at x' at time t' given that it was at location x_0 at time t_0.

• The reproducing property can be expressed in any basis. For example, in the position basis we get

$$\langle x_2|U(t_2,t_0)|x_0\rangle = \int dx_1\ \langle x_2|U(t_2,t_1)|x_1\rangle\langle x_1|U(t_1,t_0)|x_0\rangle \tag{156}$$

or $U(x''t'';x,t) = \int dx'\ U(x''t'';x't')\ U(x't';xt)$.

• Most often we do not directly know the time evolution operator in the position basis. But suppose we know the energy levels and eigenfunctions, then we can get an expression for the propagator $U(x'\,t';x\,t)$. Suppose the energy levels are discrete $H\psi_n = E_n\psi_n$ then

$$\langle x_f|U(t_f,t_i)|x_i\rangle \;=\; \sum_{nn'}\langle x_f|n\rangle\langle n|U(t_f,t_i)|n'\rangle\langle n'|x_i\rangle = \sum_{nn'}\psi_n(x_f)\langle n|e^{-\frac{i}{\hbar}H(t_f-t_i)}|n'\rangle\psi^*_{n'}(x_i)$$

[10]Strictly, $\psi(x,t_0) = \delta(x-x_0)$ is not a good initial state, it isn't normalizable. Indeed, it is a plane wave in momentum space $\tilde{\psi}(k) = e^{-ikx_0}$, and we know that plane waves are orthogonal but not normalizable. In a more careful treatment, we would have to take say a gaussian wave packet for the initial state localized around x_0, instead of a delta-localized initial wave function.

$$= \sum_n \psi_n(x_f) e^{-\frac{i}{\hbar}E_n(t_f-t_i)} \psi_n^*(x_i). \tag{157}$$

To better understand the propagator, we find the free particle propagator using our knowledge of free particle energies and eigenfunctions.

2.11 Free particle propagator

• The free particle hamiltonian $H = p^2/2m$ is diagonal in the basis of momentum eigenstates $H|k\rangle = \frac{\hbar^2 k^2}{2m}|k\rangle$, and so is the time evolution operator $U(t,t') = e^{-\frac{i}{\hbar}H(t-t')}$

$$U(t,t')|k\rangle = e^{-\frac{i}{\hbar}\frac{\hbar^2k^2}{2m}(t-t')}|k\rangle \quad \Rightarrow \quad \langle k|U(t,t')|k'\rangle = 2\pi\delta(k-k')e^{-\frac{i\hbar k^2}{2m}(t-t')} \tag{158}$$

In the basis of position eigenstates $\langle k|x\rangle = e^{-ikx}$ we have

$$\langle x|U(t,t')|x'\rangle = \int [dk][dk']\, \langle x|k\rangle\, \langle k|U(t,t')|k'\rangle\, \langle k'|x'\rangle = \int [dk]\, e^{-\frac{i\hbar k^2(t-t')}{2m}+ik(x-x')} \tag{159}$$

The 'gaussian integral'[11] is done by completing the square $-ak^2+bk = -a(k-b/2a)^2 + b^2/4a$ where

$$a = \frac{i\hbar}{2m}(t-t'), \quad b = i(x-x') \;\; \Rightarrow \;\; U = \int [dk] e^{-ak^2+bk} = \frac{1}{2\pi} e^{b^2/4a}\sqrt{\frac{\pi}{a}} \tag{160}$$

Thus the propagator is

$$U(x\,t; x'\,t') = \left(\frac{m}{ih(t-t')}\right)^{\frac{1}{2}} \exp\left[\frac{i}{\hbar}\frac{m}{2}\frac{(x-x')^2}{(t-t')}\right]. \tag{161}$$

Similarly in three dimensions we have

$$U(\vec{r}\,t; \vec{r}'\,t') = \left(\frac{m}{ih(t-t')}\right)^{\frac{3}{2}} \exp\left[\frac{i}{\hbar}\frac{m}{2}\frac{|\vec{r}-\vec{r}'|^2}{(t-t')}\right]. \tag{162}$$

Since H is time-independent, U depends only on the difference $t-t'$. As H is translation invariant, U only depends on the difference $\vec{r}-\vec{r}'$ and furthermore only on the magnitude of the difference on account of rotation invariance.

• The propagator is a gaussian in $(x-x')$ with a (complex) standard deviation σ

$$U(x\,t; x'\,t') = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{(x-x')^2}{2\sigma^2}} \quad \text{where} \quad \sigma = \sqrt{\frac{i\hbar(t-t')}{m}} \tag{163}$$

Since $\sigma \propto \sqrt{t-t'}$, the 'width' $|\sigma|$ of the gaussian grows with time. This is an indication of the dispersive broadening of the probability amplitude as time passes. To properly understand this phenomenon, we must use this propagator to evolve, say, a gaussian wave packet forward in time and see it broaden out. We already did this by a different method two semesters ago by decomposing the initial state in the energy basis and evolving the energy eigenstates forward in time. Both methods can be shown to give the same answer. The advantage of having an explicit

[11] This is not an ordinary real gaussian integral, but an oscillatory integral as the exponent is imaginary. More care is needed to justify the answer obtained below than we provide here.

formula for the propagator is that it can be used to evolve *any* state forward in time, not just a gaussian wave packet.

• Since the limit of gaussians as the width tends to zero is

$$\lim_{\sigma\to 0}\frac{1}{\sqrt{2\pi}\sigma}e^{-x^2/2\sigma^2}=\delta(x), \tag{164}$$

the propagator satisfies the unit initial condition representing a particle initially localized at x'

$$\lim_{t\to t'}U(x,t;x',t')=\delta(x-x'). \tag{165}$$

• The free particle propagator (161) may be written in terms of the classical action of the straight line path $x(t)=x_i+\frac{x_f-x_i}{t_f-t_i}(t-t_i)$ traversed by a classical particle in going from $x_i\to x_f$ as time runs from $t_i\to t_f$. The velocity is constant, and so is the Lagrangian $L(t)=\frac{1}{2}m\dot{x}^2=\frac{1}{2}m\frac{(x_f-x_i)^2}{(t_f-t_i)^2}$ along such a straight line trajectory, so the classical action for this trajectory is

$$S(x_f(t_f),x_i(t_i))=\int_{t_i}^{t_f}L\,dt=\frac{m}{2}\frac{(x_f-x_i)^2}{(t_f-t_i)}. \tag{166}$$

Thus (U is dimensionless, but its matrix elements in the position basis have dimension 1/length)

$$U(x_f\,t_f;x_i\,t_i)=\left(\frac{m}{ih(t_f-t_i)}\right)^{\frac{1}{2}}\exp\left[\frac{i}{\hbar}S\left(x_f(t_f),x_i(t_i)\right)\right]. \tag{167}$$

Thus the amplitude for the free particle to be found at x_f at t_f given that it was at x_i at t_i is proportional to the exponential of $(i/\hbar)\times$ the action for the classical trajectory between those two points. A similar formula holds in 3d with the exponent of the pre-factor 1/2 replaced by 3/2. We emphasize that this formula for the paopagator is special to a free particle and does not generally hold for a particle in a potential.

2.12 Feynman path integral for a free particle

• Since the time evolution operator satisfies the reproducing property, we can write the free particle propagator as a product of time evolution operators. Let us divide the time interval $[t_i,t_f]$ into n subintervals $t_i=t_0<t_1<\cdots<t_{n-1}<t_n=t_f$ (say equally spaced $t_{j+1}-t_j=\Delta t$, for simplicity). Then

$$U(t_f;t_i)=U(t_n,t_{n-1})U(t_{n-1},t_{n-2})\cdots U(t_1,t_0). \tag{168}$$

The amplitude for the free particle to go from $x_0=x_i(t_i)$ to $x_n=x_f(t_f)$ is

$$\langle x_f|U(t_f,t_i)|x_i\rangle=\int dx_{n-1}\cdots dx_1\,\langle x_n|U(t_n,t_{n-1})|x_{n-1}\rangle\cdots\langle x_1|U(t_1,t_0)|x_0\rangle. \tag{169}$$

Written in terms of the classical action, we have an exact formula for each n:

$$U(x_n,t_n;x_0,t_0)=\left(\frac{m}{ih\Delta t}\right)^{\frac{n}{2}}\int dx_1\cdots dx_{n-1}\,e^{(i/\hbar)\{S[x(t_n),x(t_{n-1})]+S[x(t_{n-1}),x(t_{n-2})]+\cdots+S[x(t_1),x(t_0)]\}}. \tag{170}$$

So the propagator is an integral over all piecewise straight line paths going from $x_0(t_0) \to x_n(t_n)$, each comprising n segments. This is best illustrated by a figure. Each segment is a classical trajectory and contributes a phase factor equal to $(i/\hbar)\times$ its classical action. Though each segment is a classical trajectory, when joined together, the resulting piecewise linear paths are typically not classical trajectories. Now if we let $n \to \infty$, formally we find that the free particle propagator is proportional to an integral over all the paths connecting the initial and final locations, each weighted by a phase proportional to the classical action for the path. Absorbing the pre-factor (and its dimensions) into a pre-factor C and formally denoting the integration element on the space of paths by $\mathrm{D}[x]$,

$$\langle x_f|U(t_f,t_i)|x_i\rangle = C\int_{x(t_i)=x_i}^{x(t_f)=x_f} \mathrm{D}[x]\; e^{\frac{i}{\hbar}S[x]} = C\int_{x(t_i)=x_i}^{x(t_f)=x_f} \mathrm{D}[x]\; e^{\frac{i}{\hbar}\int_{t_i}^{t_f}\frac{1}{2}m\dot{x}^2\,dt}. \tag{171}$$

This representation of the free particle propagator is called the Feynman path integral. The integral is over the space of paths connecting x_i and x_f. This is an infinite dimensional space, and it is not easy to define integration over such an infinite dimensional space. However (170) is a completely well-defined and exact formula that involves integration over a finite $(n-1)$ dimensional space[12]. A similar path integral representation is available for a particle moving in a potential $V(x)$. In that case, the weights for the individual paths are given by the exponential of the classical action $S[x] = \int_{t_i}^{t_f} dt\,\left(\frac{1}{2}m\dot{x}^2 - V(x)\right)$. Though we do not have an explicit formula like (167) for the propagator of a particle moving in an arbitrary potential $V(x)$, it can be shown that the above path integral representation for the time-evolution operator continues to hold.

• Classically the particle follows a trajectory that solves Newton's equation. The principle of stationary action says that a classical trajectory between $x_i(t_i)$ and $x_f(t_f)$ is one for which the classical action functional is extremal. Quantum mechanically, the above formula says that one way to compute the propagator, is to evaluate a sum over paths. This does not mean that the particle travels along all these paths, nor does it imply that the particle has *any* well-defined trajectory. However, we sometimes loosely say that in QM, the particle samples all paths including the classical trajectory.

• The Feynman path integral reformulates the problem of solving the SE for the time evolution operator on a Hilbert space. Rather than work with operators and Hilbert spaces, it says that we may compute the sum of phases contributed by various paths, each weighted by its classical action. So the problem of quantum evolution is couched in terms of some classical concepts. However, QM has *not* been reduced to classical mechanics. No where in CM do we admit paths for particles that are not classical trajectories.

• We can recover the principle of extremal action from the Feynman path integral by appropriately considering the limit $\hbar \to 0$. Each path $x(t)$ contributes a phase $(i/\hbar)S[x]$ to the sum over paths. Now consider two adjacent paths $x(t)$ and $x(t)+\delta x(t)$ with $\delta x(t_i) = \delta x(t_f) = 0$. Suppose further that $S'[x] \neq 0$. In the semi-classical limit, the difference in their actions $S[x] - S[x+\delta x]$ will typically be quite large compared to $\hbar$. So they contribute with rather different phases $e^{\frac{i}{\hbar}S}$. In this manner, the amplitudes of nearby paths contribute 'random' (i.e. not all correlated and pointing in one direction) phases which destructively interfere and cancel out. Thus these paths do not contribute significantly to the propagator in the semi-classical approximation. However,

[12] So we use integration over a finite dimensional space to approximate integration over an infinite dimensional space. This is analogous to how we use finite Riemann sums to approximate integration over the infinite set of points in an interval.

there is occasionally a path $x_{cl}(t)$ in whose vicinity all paths contribute constructively to the sum. This happens if the action is stationary, which is precisely the case for the classical trajectory $S'[x_{cl}] = 0$. In other words, paths in the neighborhood of the classical trajectory have roughly the same classical action and therefore contribute roughly the same phase $e^{(i/\hbar)S[x]}$ to the sum over paths. This constructive interference in the neighborhood of the classical trajectory explains why we may approximate quantum dynamics by motion along the classical trajectory in the classical limit. All the other paths in the Feynman path integral contribute negligibly to the propagator when $\hbar \to 0$.

• Note that we are not taking the $\hbar \to 0$ limit of the propagator $U(t, t')$. We are only discussing the relative contributions of various paths to the path integral in the $\hbar \to 0$ limit. We already know from the semiclassical WKB analysis that the wave function does not have a good $\hbar \to 0$ limit, as it has an essential singularity at $\hbar = 0$. Similarly, the time-evolution operator does not have a good classical limit. However, as is evident from (167), the logarithm of the time evolution operator (times $-i\hbar$) has a good classical limit, indeed, it is the classical action of the classical trajectory in that case[13].

• We can interpret interference and diffraction phenomena for matter waves (e.g. electrons) in terms of the Feynman path integral. In the absence of any obstacles, the amplitude for the particle to go from $x_i(t_i)$ to $x_f(t_f)$ is given by a sum over all paths connecting these locations. If an obstacle is introduced, certain paths are forbidden, but there are still many paths that 'go around' the obstacle, though they are not classical trajectories. These are the paths that contribute to 'diffraction around an obstacle'. In double slit interference, the amplitude at a point $x_f(t_f)$ on the screen is given by a sum over paths. These include piecewise straight line paths ('classical trajectories') that go through either one of the slits S_1 or S_2. But there are other paths that go through S_1, come out of S_2 and go back out through S_1 before reaching the screen. We must sum over all these paths. The contributions of most of these paths cancel out due to destructive interference with nearby paths since the action is not stationary around them. In the semi-classical limit, it is the two piecewise straight-line paths around which the action is stationary, that contribute maximally to the amplitude. Thus it is sufficient to consider the interference between these two paths to get the interference pattern on the screen to first approximation.

2.13 Path integral for a particle in a potential

• Consider a particle in a potential with hamiltonian $H = \frac{\hat{p}^2}{2m} + V(\hat{x})$. We wish to find a path integral representation for the propagator. Here, unlike for the free particle we do not have an explicit formula for U since we do not know the energy levels and eigenfunctions of H. Nevertheless, we wish to write the propagator in terms of classical quantities like the Lagrangian/Hamiltonian/action. Recall that $U(t, t') = e^{-\frac{i}{\hbar}H(t-t')}$. Let us begin by expressing the matrix elements of H in term of the classical hamiltonian. $\hat{H}$ in the position basis is a differential operator and in the momentum basis is also a differential operator. But interestingly,

[13] Though the limits $t \to t'$ and $\hbar \to 0$ look formally the same, a more careful treatment of (161) shows that they are not the same. In a sense the limit $t \to t'$ needs to be taken via real gaussians while the limit $\hbar \to 0$ is the naive one. This is to be expected on physical grounds, the propagator must tend to the identity at $t = t'$ and must have an essential singularity as $\hbar \to 0$

the mixed matrix elements $\langle p|\hat{H}|x\rangle$ are directly related to the classical hamiltonian

$$\langle k|\hat{H}|x\rangle = \langle k|x\rangle H(x,p) = e^{-ikx}H(x,p) \tag{172}$$

To see this, note that $\hat{x}|x\rangle = x|x\rangle$, $\langle k|\hat{p} = \langle k|p$ where $p = \hbar k$ and x, p are real numbers, not operators. So $\langle k|\hat{x}|x\rangle = x\langle k|x\rangle$ and $\langle k|\hat{p}|x\rangle = p\langle k|x\rangle$. Thus

$$\begin{aligned}
\hat{H}|x\rangle &= \left(\frac{\hat{p}^2}{2m} + V(\hat{x})\right)|x\rangle = \left(\frac{\hat{p}^2}{2m} + V(x)\right)|x\rangle \quad \Rightarrow \\
\langle k|\hat{H}|x\rangle &= \langle k|\left(\frac{p^2}{2m} + V(x)\right)|x\rangle = \left(\frac{p^2}{2m} + V(x)\right)\langle k|x\rangle = e^{-ikx}\left(\frac{p^2}{2m} + V(x)\right) = e^{-ikx}H(x,p)
\end{aligned}$$

However, since $\hat{x}$ and $\hat{p}$ do not commute, for a non-constant potential,

$$\langle k|e^{-\frac{i}{\hbar}(\frac{\hat{p}^2}{2m}+V(\hat{x}))(t-t')}|x\rangle \neq e^{-\frac{i}{\hbar}\left(\frac{p^2}{2m}+V(x)\right)(t-t')}e^{-ikx}. \tag{173}$$

Nevertheless, they are approximately equal if $t - t' = \Delta t$ is small. As a consequence, the mixed matrix elements of the infinitesimal time evolution operator may also be expressed in terms of the classical hamiltonian. For small Δt, $U(\Delta t) \approx I - \frac{i}{\hbar}H\Delta t$, so

$$\langle k|U(\Delta t)|x\rangle \approx \langle k|I - \frac{i}{\hbar}\hat{H}\Delta t|x\rangle = \left(1 - \frac{i}{\hbar}H(x,p)\Delta t\right)e^{-ikx} \approx e^{-\frac{i}{\hbar}H(x,p)\Delta t}e^{-ikx} \tag{174}$$

Unlike the case of a free particle where we had an exact formula (167) for $\langle x|U(\Delta t)|x'\rangle$ in terms of the classical action, here we only have an approximate formula for $\langle k|U(\Delta t)|x\rangle$ in terms of the classical hamiltonian. However, this is adequate to derive a Feynman path integral representation, since we are going to let $\Delta t \to 0$ eventually.

• We can use these mixed matrix elements to evaluate the propagator in the position basis. As before, we sub-divide the time $t_f - t_i = n\Delta t$ into n equal steps $t_j = t_i + j\Delta t$ for $0 \leq j \leq n$ and denote $x_i = x_0, x_f = x_n$. Using the reproducing property we have

$$\langle x_f|U(t_f,t_i)|x_i\rangle = \int dx_1 \cdots dx_{n-1}\langle x_n|U(t_n,t_{n-1})|x_{n-1}\rangle\langle x_{n-1}|U(t_{n-1},t_{n-2})|x_{n-2}\rangle \cdots \langle x_1|U(t_1,t_0)|x_0\rangle \tag{175}$$

In order to exploit our formula for the mixed matrix elements of U, we insert complete sets of momentum eigenstates in n places. Thus

$$\begin{aligned}
U(x_f t_f, x_i t_i) &= \int dx_1 \cdots dx_{n-1}[dk_0 \cdots dk_{n-1}]\ \langle x_n|k_{n-1}\rangle\langle k_{n-1}|U(t_n,t_{n-1})|x_{n-1}\rangle\langle x_{n-1}|k_{n-2}\rangle \\
&\quad \langle k_{n-2}|U(t_{n-1},t_{n-2})|x_{n-2}\rangle \cdots \langle k_1|U(t_2,t_1)|x_1\rangle\langle x_1|k_0\rangle\langle k_0|U(t_1,t_0)|x_0\rangle \\
&\approx \int dx_1 \cdots dx_{n-1}[dk_0 \cdots dk_{n-1}]\ \exp\left[i\sum_{j=0}^{n-1}k_j(x_{j+1}-x_j) - \frac{i}{\hbar}\sum_{j=0}^{n-1}H(x_j,p_j)\Delta t\right] \\
&= \int dx_1 \cdots dx_{n-1}[dk_0 \cdots dk_{n-1}]\ \exp\left[\frac{i}{\hbar}\sum_{j=0}^{n-1}\Delta t\left(p_j\frac{(x_{j+1}-x_j)}{\Delta t} - H(x_j,p_j)\right)\right]
\end{aligned}$$

Now as $n \to \infty$ the exponent tends to $\frac{i}{\hbar}\int_{t_i}^{t_f}(p\dot{x} - H(x,p))\,dt$, a formula familiar from classical mechanics. The first term is the abbreviated action we came across in the the semiclassical

approximation. We write formally (absorbing the numerical factors of $1/2\pi\hbar$ into a pre-factor C)

$$U(x_f t_f, x_i t_i) = C \int_{x(t_i)=x_i}^{x(t_f)=x_f} \mathrm{D}[x]\, \mathrm{D}[p]\; e^{\frac{i}{\hbar}\int_{t_i}^{t_f}(p\dot{x}-H(x,p))\,dt} \tag{176}$$

This is called a phase space path integral, as we integrate over paths in phase space $(x(t), p(t))$. Notice however, that the initial and final momenta are unconstrained, unlike the initial and final positions. To get the configuration space path integral, we perform the gaussian integral over the momenta. This is possible since $H(x,p) = p^2/2m + V(x)$ is quadratic in the momenta. Returning to the finite n formula, let us consider one of the p integrals

$$I_j = \int \frac{dp_j}{h} e^{\frac{i}{\hbar}\left(p_j(x_{j+1}-x_j)-\frac{p_j^2}{2m}\right)\Delta t} = \sqrt{\frac{m}{ih\Delta t}} \exp\left[\frac{i}{\hbar}\frac{m}{2}\frac{(x_{j+1}-x_j)^2}{\Delta t}\right] \tag{177}$$

Thus we have an expression for $U(x_f t_f, x_i t_i)$ which becomes increasingly accurate as $n \to \infty$:

$$U(x_f t_f, x_i t_i) \approx \left(\frac{m}{ih\Delta t}\right)^{n/2} \int dx_1 \cdots dx_{n-1} \exp\left[\frac{i}{\hbar}\sum_{j=0}^{n-1}\left(\frac{1}{2}m\frac{(x_{j+1}-x_j)^2}{(\Delta t)^2} - V(x_j)\right)\Delta t\right] \tag{178}$$

In the limit $n \to \infty$ we see that the exponent becomes the classical action for the path $x(t)$. We write the propagator formally as a path integral

$$U(x_f t_f, x_i t_i) = C \int \mathrm{D}[x]\; e^{\frac{i}{\hbar}\int_{t_i}^{t_f}\left[\frac{1}{2}m\dot{x}^2 - V(x)\right]dt} \tag{179}$$

where some (dimensional) factors have been absorbed into the pre-factor C. We are not in a position to give a direct mathematically precise definition for such a path integral. What is more, C, $D[x]$, $D[p]$ in all likelihood cannot be given a meaning in isolation. However, it is likely that the integral as a whole can be given a mathematically precise meaning. In any case, the finite n version above gives a sequence of calculable approximants which can be improved by making n larger, just as we can improve our calculation of the area of a region of the plane by using a finer square grid. We may also profitably regard the path integral as a short-hand notation for the previous multiple integral as n is made large. This is similar to the way we regard the expression $\int_a^b f(x)dx$ as a short-hand notation for the process of taking Riemann sums. Just as we first learned to integrate polynomials and trigonometric functions before attempting to define the integral of an arbitrary function, it is necessary to understand the path integral and its physical implications for simple quantum mechanical systems before attempting to give a mathematically precise definition of the path integral.

3 Aharonov-Bohm effect

• An uncharged infinite current carrying solenoid ($N \gg 1$ turns per unit length of current I) produces no electric field but produces a uniform magnetic field pointing along its axis on the inside and zero magnetic field outside.

• Classically, if a charged particle traverses a path along which the electric and magnetic fields are zero, then it feels no electromagnetic (Lorentz) forces. This continues to be true even if its

path encircles a solenoid. On the other hand, if a charged quantum mechanical particle goes round a solenoid, its wave function picks up a phase proportional to the magnetic flux enclosed by the path. This is despite the fact that it never encounters a non-zero electric/magnetic field. The effects of this phase have been measured by interference experiments. This striking phenomenon was emphasized by Aharonov and Bohm (1959). It may be interpreted as an example of Berry's phase.

• Recall that the electric and magnetic fields can be expressed in terms of scalar and vector potentials $\vec{E} = -\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t}$ and $\vec{B} = \vec{\nabla} \times \vec{A}$. The fields are directly measurable in classical electromagnetism by the forces they exert on charges. But the potentials are not uniquely determined by the fields. Indeed $\vec{E}, \vec{B}$ are unaltered by a *gauge* transformation of the potentials by an arbitrary scalar function $\chi(\vec{r}, t)$

$$\vec{A} \to A + \nabla\chi, \quad \phi \to \phi - \frac{\partial \chi}{\partial t}. \tag{180}$$

• A gauge transformation in classical mechanics only acts on the EM potentials and does not affect the position or momentum coordinate of a particle. The equations for the state of a classical particle interacting with electromagnetic fields are unchanged by a gauge transformation. We say classical EM is gauge invariant. We might suppose the same to be true in quantum mechanics. However, in QM, there is more room to maneuver. The quantum state of a particle defines its wave function only up to a phase. So it is possible that under a gauge transformation, not only $\vec{A}, \phi$ are transformed, but the wave function is also altered by a phase, while leaving the equation as a whole invariant.

• In classical E & M the gauge potentials $\vec{A}, \phi$ do not play an essential role since the equations of motion, Maxwell's equations and the Lorentz force law can be formulated entirely in terms of the fields $\vec{E}, \vec{B}$.

• In quantum mechanics, the gauge potentials A, ϕ play a more crucial role since the hamiltonian of a particle of charge e in an electromagnetic field is expressed in terms of them

$$H = \frac{1}{2m}\left(\vec{p} - e\vec{A}\right)^2 + e\phi = \frac{1}{2m}\left(p^2 + e^2A^2 - ep \cdot A - eA \cdot p\right) + e\phi. \tag{181}$$

One can show that if the wave function is transformed to $\psi(x) \to e^{ie\chi/\hbar}\psi(x)$ then the Schrödinger equation is invariant under the above gauge transformations. We say that the equations for a quantum mechanical particle interacting with electromagnetic fields is gauge invariant. Despite this, it is not possible to express H directly in terms of $\vec{E}$ and $\vec{B}$ in any simple way.

• Let us begin by finding a vector potential for the magnetic field due to a solenoid. Consider a solenoid of radius a with axis pointing along $\hat{z}$ with N turns per unit length of a wire carrying a current I. We use cylindrical coordinates z, r, θ. As it is uncharged, $\vec{E} = 0, \phi = 0$. The magnetic field can be determined using cylindrical symmetry and Ampere's law[14]

$$\oint_C \vec{B} \cdot d\vec{l} = \mu_0 I_{\text{enc}} \tag{182}$$

[14]Since $\vec{J}$ is cylindrically symmetric, $\vec{B}$ must be symmetric under rotations about the z-axis and translations along the z axis. So $\vec{B}$ can only depend on r, not z or θ. If it has a radial component B_r, $B_r\hat{r}$ must point radially outward everywhere or inward everywhere by cylindrical symmetry. $\vec{B}$ would reverse sign under $I \to -I$, but that is the same as looking at the configuration upside down (or turning the solenoid upside down), which should not change whether the radial component of the magnetic field points inwards or outwards. Thus $B_r = 0$. We can find the azimuthal component B_θ by using a horizontal circular loop centered on the z-axis, we have $B_\theta 2\pi r = \mu_0 I_{enc} = 0$ since there is very little current (I) passing up wards, though there is a large current per

One finds that $\vec{B} = \mu_0 NI\hat{z}$ inside the solenoid ($r < a$) and $\vec{B} = 0$ outside. To find the hamiltonian, we need a vector potential corresponding to this magnetic field. Consider a horizontal circular loop of radius $r > a$. If S is the disc whose boundary is C, by Stokes' theorem, the magnetic flux through the disc is

$$\Phi = \mu_0 NI\pi a^2 = \int_S \vec{B}\cdot\vec{ds} = \oint_C \vec{A}\cdot dl \tag{183}$$

Since the flux is non-zero, the vector potential $\vec{A}$ cannot be identically zero outside the solenoid, even though $\vec{B} = 0$ for $r > a$. There are many vector potentials that satisfy this equation, they differ by gauge transformations $A \to A + \nabla\Lambda$, since the $\nabla\Lambda$ term does not contribute to the line integral over a closed loop. One convenient solution is obtained by *assuming* that $\vec{A} = A_\theta\hat{\theta}$ is azimuthal and that A_θ depends only on r. Then one finds $A_\theta 2\pi r = \Phi$. Thus $\vec{A} = \frac{\Phi}{2\pi r}\hat{\theta}$ for $r > a$. Similarly, for $r < a$ one finds $\vec{A} = \frac{\Phi r}{2\pi a^2}\hat{\theta}$. It is easily checked that $\nabla\times\vec{A}$ reproduces the magnetic field

$$\vec{A} = \begin{cases} \frac{\Phi}{2\pi r}\hat{\theta} & \text{if } r > a \\ \frac{\Phi r}{2\pi a^2}\hat{\theta} & \text{if } r < a \end{cases} \quad\Rightarrow\quad \nabla\times A_\theta(r)\hat{\theta} = \frac{1}{r}\frac{\partial\left(rA_\theta(r)\right)}{\partial r}\hat{z} = \mu_0 NI\;\Theta(r<a)\;\hat{z}. \tag{184}$$

We emphasize that this is simply one possible vector potential that gives the above magnetic field $\vec{B}$. It is convenient because $\nabla\cdot A = \frac{1}{r}\partial_r(rA_r) + \frac{1}{r}\partial_\theta A_\theta + \partial_z A_z = 0$ so that the $\vec{p}\cdot\vec{A}$ term in the hamiltonian may be written $\vec{A}\cdot\vec{p}$:

$$H = \frac{1}{2m}\left(p^2 - 2eA\cdot P + e^2A^2\right) \tag{185}$$

3.1 Effect on energy spectrum

To illustrate the effect of the solenoid on the quantum mechanics of a charged particle, let us consider for simplicity, a charge e *constrained* to move on a horizontal circular ring of radius $b > a$ centered on the z-axis (see Griffiths). $\vec{p} = -\frac{i\hbar}{b}\hat{\theta}\frac{\partial}{\partial\theta}$ and the wave function $\psi(\theta)$ can only depend on the azimuthal coordinate as the particle is on the ring. The Schrödinger eigenvalue problem becomes

$$H\psi = \frac{1}{2m}\left(-\frac{\hbar^2}{b^2}\frac{\partial}{\partial\theta^2} + \left(\frac{e\Phi}{2\pi b}\right)^2 + \frac{ie\hbar\Phi}{\pi b^2}\frac{\partial}{\partial\theta}\right)\psi(\theta) = E\psi(\theta) \tag{186}$$

Recall from the Landau level problem that $\Phi_0 = h/e$ has the dimensions of magnetic flux. It may be regarded as a quantum of magnetic flux appropriate to a particle of charge e. So it makes sense to measure the flux Φ through the horizontal disc in units of Φ_0 and define

$$\nu = \Phi/\Phi_0 = e\Phi/h = e\Phi/2\pi\hbar > 0 \quad \text{(generically } \nu \text{ is } \textit{not} \text{ an integer!)}. \tag{187}$$

unit vertical distance (NI) going circumferentially round the solenoid as $N \gg 1$. Thus $B_\theta = 0$. So $\vec{B} = B_z(r)\hat{z}$. To find $B_z(r)$ we consider a rectangular loop lying in a plane of constant azimuthal angle, with vertical height L. If both vertical sides are outside the solenoid at radial distances r_1, r_2, we use the fact that the loop does not enclose any current to show that $B_z(r_1)L - B_z(r_2)L = 0$, and thus B_z is independent of r. But $B_z(\infty) = 0$, so $\vec{B} = 0$ outside the solenoid. If just one side is inside the solenoid we find $B_z L = \mu_0 NIL$. So $\vec{B} = \mu_0 NI\hat{z}$ inside the solenoid.

Then the eigenvalue problem becomes

$$-\psi'' + 2i\nu\psi' = \left(\frac{2mEb^2}{\hbar^2} - \nu^2\right)\psi. \tag{188}$$

We solve this linear ODE with constant coefficients by making the ansatz $\psi \propto e^{i\lambda\theta}$ and obtain a quadratic equation for λ

$$\lambda^2 - 2\nu\lambda + \left(\nu^2 - \frac{2mEb^2}{\hbar^2}\right) = 0 \tag{189}$$

whose solutions are

$$\lambda_\pm = \nu \pm \frac{b\sqrt{2mE}}{\hbar}. \tag{190}$$

Thus the general eigenfunction is $\psi(\theta) = c_+ e^{i\lambda_+(E)\theta} + c_- e^{i\lambda_-(E)\theta}$ with eigenenergy E. However, most of these eigenfunctions are unphysical. Note that $\theta = 0, 2\pi, -2\pi, \ldots$ represent the same physical point. We seek solutions $\psi(\theta)$ of the Schrödinger eigenvalue problem that are continuous around the circle, since the potential (coefficients) are smooth. This requirement that ψ be single-valued is satisfied if $\psi(0) = \psi(2\pi)$, i.e., if $\lambda_\pm$ are integers

$$\lambda_\pm = \nu \pm \frac{b\sqrt{2mE}}{\hbar} = n_\pm \tag{191}$$

Note that $\nu > 0$ and $E \geq 0$ since the hamiltonian $H \propto (p - eA)(p - eA)^\dagger$ is a positive operator. So $\lambda_+ = n_+ > 0$ must be a positive integer. The smallest possible value of n_+ may be quite large if the flux through the solenoid ν is large in units of the flux quantum h/e. On the other hand $\lambda_- < \lambda_+$, so $\lambda_- = n_-$ can be any integer less than the smallest possible value of n_+. Combining, n_- and n_+ together run over all integral values n. So the energies corresponding to continuous eigenfunctions are[15]

$$E_n = \frac{\hbar^2}{2mb^2}(n - \nu)^2, \quad \psi_n(\theta) = \frac{1}{\sqrt{2\pi}} e^{in\theta} \quad \text{for} \quad n \in \mathbb{Z} \quad \text{and} \quad \nu = \frac{e\Phi}{h}. \tag{192}$$

The energy eigenvalues are generically non-degenerate unlike the doubly degenerate spectrum ($n \to -n$) of the free particle moving on the same circular ring. The latter case is obtained in the limit of zero flux $\nu \to 0$, when the current in the solenoid is turned off. But for $\nu \neq 0$, ψ_n has a lower energy compared to ψ_{-n}, the counter-clockwise moving stationary state $e^{in\theta - iE_n t/\hbar}$ has a lower energy compared to the stationary state $e^{-in\theta - iE_{-n}t/\hbar}$ that moves in the direction opposite to the current in the solenoid.

[15] Prior to imposing continuity, for each value of E we had two values of λ, $\lambda_\pm$ and the eigenfunctions were doubly degenerate. After imposing single-valuedness of ψ, as long as ν isn't itself an integer or half-odd integer (which are non generic), $e^{i\lambda_\pm\theta}$ are non-degenerate in energy and to be an eigenfunction we must take one of $c_\pm = 0$. In other words we go through each value of $E \geq 0$, all of which were allowed prior to imposing continuity. For each value of E there are two values of λ, λ_+ and λ_-. Now we select those values of E for which at least one from among $\lambda_\pm$ is integral. Most values of E do not satisfy this requirement, there is only a discrete set of E's for which either λ_+ or λ_- is an integer. Moreover, (for generic currents I), if $\lambda_+(E)$ is an integer, $\lambda_-(E)$ for the same value of E will not be an integer. It is possible to physically force ν to be an integer, by either turning off the current or taking the ring on which the charged particle moves to be a superconducting ring. Due to compensation from super-currents, the flux enclosed $\nu = \Phi/\Phi_0$ must be an integer in that case, and the degeneracy of energy levels is restored though in a shifted manner, i.e. it is not that $E_n = E_{-n}$ but that $E_{n_1} = E_{n_2}$ where $n_1 + n_2 = 2\nu$.

• We conclude that though the particle classically never feels a non-zero magnetic field, its quantum mechanical energy spectrum has been affected by the magnetic field inside the solenoid, an effect that can be detected by varying the current in the solenoid.

• So far we considered stationary states, and saw that their energies are affected by the current in the solenoid even if the magnetic field is zero on the ring. Now we consider the dynamical problem of a particle moving around such a solenoid and show that its wave function is affected by the flux enclosed.

3.2 Effect on time-evolution

• Aharonov and Bohm proposed an experiment where we have an infinite current carrying solenoid with vertical axis. A horizontal beam of electrons approaches radially and is split at r_i into two and passed on either side of the solenoid. The two beams are combined and an interference pattern is produced on a screen beyond the solenoid. The beams do not encounter a non-zero magnetic field. Yet, when the current in the solenoid is varied, it is found that the interference pattern is shifted. Let us try to explain this phenomenon.

• The SE for a charged particle moving in a vector potential $\vec{A}(\vec{r})$ reads

$$i\hbar\frac{\partial\psi}{\partial t} = \left[\frac{1}{2m}\left(p - eA\right)^2 + V\right]\psi \tag{193}$$

Here $V = e\phi + U$ where ϕ is the electric potential and U a potential due to any other forces of non-electromagnetic origin. Now suppose we consider a (simply-connected) region outside the solenoid, where $B = \nabla \times A = 0$. Remarkably, we can absorb the effect of the vector potential in this region onto a redefinition of the wave function by a phase, i.e., we can 'map' this problem to one of the same particle moving in the absence of any vector potential by making a gauge transformation $\vec{A}' = \vec{A} + \nabla\chi$ in a subregion exterior to the solenoid. Let us pick χ carefully so that $A' = 0$. A choice that seems to do the job is $\chi(\vec{r},\gamma) = -\int_{r_0}^{r}\vec{A}\cdot dl$ where $\vec{r}_0$ is some reference point, say where the beams are split and the integral is along some (open) contour γ connecting $\vec{r}_0$ to $\vec{r}$ that lies entirely outside the solenoid. Under this gauge transformation, the new vector potential in this region outside the solenoid is

$$\vec{A}'(\vec{r}) = \vec{A} + \nabla\chi = \vec{A}(r) - \vec{A}(r) = 0. \tag{194}$$

and the new wave function is

$$\psi'(\vec{r},t) = e^{\frac{ie\chi}{\hbar}}\psi(r,t) \quad \text{where} \quad \chi(\vec{r},\gamma) = -\int_{\gamma,r_0}^{r}\vec{A}\cdot dl \tag{195}$$

Here we assume the gauge transformation is performed only in a simply connected region exterior to the solenoid. So the contour γ is entirely in a region where $B = 0$. This ensures that the line integral is in fact independent of γ so that $\chi(\vec{r},\gamma) = -\int_{r_0}^{r}\vec{A}\cdot dl$ depends only on the end points $\vec{r}_0, \vec{r}$ and not the whole contour γ. For, if we change to a new contour γ', the difference $\int_\gamma A\cdot dl - \int_{\gamma'} A\cdot dl$ is the line integral around a *closed* contour (which can be regarded as the boundary of a surface lying entirely in the zero field region) $\oint_{\gamma-\gamma'} A\cdot dl = \int_S(\nabla\times A)\cdot dS$. The latter integral vanishes since $\nabla\times A = 0$ on this surface. So we have the path independence of χ if we restrict to a simply connected region outside the solenoid.

• This gauge transformation *cannot* be extended to include the region of the solenoid. $\chi(\vec{r},\gamma)$ *would depend* on the curve γ if the point $\vec{r}$ lay within the solenoid. We say the above gauge transformation is a *singular* gauge transformation since it can be defined only locally, not globally.

• Since $\chi(r)$ is independent of time, the scalar potential is unchanged. Due to the gauge invariance of the SE, in the new variables we have

$$i\hbar\frac{\partial\psi'(r,t)}{\partial t} = H'\psi' = \left[\frac{p^2}{2m} + V\right]\psi'(r,t) \tag{196}$$

So all we have to do is solve the SE for ψ' with $\vec{A}' = 0$ and multiply the resulting wave function by the phase $e^{-ie\chi/\hbar}$ to get the original unprimed wave function $\psi(\vec{r},t)$.

• In the Aharonov-Bohm set up, let us assume that the two beams of electrons experience the same potential V while traveling along symmetrical beam pipes (clockwise and anti-clockwise, along and opposite the direction of the current) on either side of the solenoid. Then the primed wave functions for the clockwise and anti-clockwise beams $\psi'_c(r_f,t_f) = \psi'_a(r_f,t_f)$ are the same, as the potentials are the same. But the original (unprimed) wave functions have different phases $e^{\frac{ie}{\hbar}\int A\cdot dl}$. In fact, the phase difference is proportional to the line integral of the vector potential around a closed loop enclosing the solenoid, i.e., proportional to the flux through the solenoid

$$\text{phase difference between two amplitudes} = \frac{e}{\hbar}\oint A\cdot dl = \frac{e\Phi}{\hbar} = 2\pi\frac{\Phi}{\Phi_0}. \tag{197}$$

If the flux through the solenoid is an integer multiple of the flux unit $\Phi_0 = h/e$, then this phase difference is undetectable. But generically, this phase difference is not an integer multiple of 2π and can be varied by changing the current in the solenoid. The effect has been experimentally confirmed via a shift in the interference pattern on the screen as the current is varied.

3.3 Path integral approach to Aharonov-Bohm effect

• We briefly discuss the Aharonov-Bohm effect via path integrals. We need to know the classical Lagrangian $L(\vec{r},\dot{\vec{r}})$ for a particle in a magnetic vector potential $\vec{A}$. In terms of the Lagrangian, the probability amplitude for a particle to go from r_i,t_i to r_f,t_f is given by an integral over all paths

$$U(r_i,t_i;r_ft_f) = C\int_{r(t_i)=r_i}^{r(t_f)=r_f} \mathrm{D}[\vec{r}]\, e^{\frac{i}{\hbar}\int_{t_i}^{t_f} L(r,\dot{r})\,dt} \tag{198}$$

Let us guess the Lagrangian first. When $\vec{A} = 0$ we know the Lagrangian in the presence of a potential (which could include an electric as well as non-electromagnetic contributions)

$$L_0(\vec{r},\dot{r}) = \frac{1}{2}m\dot{r}^2 - V(r) \quad \text{where} \quad V(r) = U(r) + e\phi. \tag{199}$$

We saw above that the probability amplitude in the presence of a vector potential is simply the amplitude in the absence of a vector potential times the phase $e^{\frac{ie}{\hbar}\int A\cdot dl}$. Up to the factor $i/\hbar$, this line integral can be written as

$$S_A = e\int_{t_i}^{t_f} \vec{A}(\vec{r})\cdot\dot{\vec{r}}(t)\,dt. \tag{200}$$

So we guess that the full Lagrangian is just the sum

$$L(r,\dot{r}) = L_0 + L_A = \frac{1}{2}m\dot{\vec{r}}(t)^2 - V(r) + e\vec{A}(\vec{r})\cdot\dot{\vec{r}}(t). \tag{201}$$

It can be checked that the Euler-Lagrange equations $\frac{d}{dt}\frac{\partial L}{\partial \dot{\vec{r}}} = \frac{\partial L}{\partial \vec{r}}$ for this L give Newton's second law with the Lorentz force (use $(v\times B)_i = (\partial_i A_j - \partial_j A_i)\dot{r}_j$)

$$\begin{aligned} \frac{d}{dt}\frac{\partial L}{\partial \dot{r}_i} &= m\ddot{r}_i - e\left(\frac{\partial A_i}{\partial t} + \frac{\partial A_i}{\partial r_j}\frac{dr_j}{dt}\right), \quad \frac{\partial L}{\partial r_i} = -e\partial_i\phi - \partial_i U + e\dot{r}_j\frac{\partial A_j}{\partial r_i}. \\ \Rightarrow \qquad & m\ddot{r}_i = -\partial_i U - eE_i + e\left(\partial_i A_j - \partial_j A_i\right)\dot{r}_j \quad \Rightarrow \quad m\ddot{\vec{r}} = -\vec{\nabla}U + e\vec{E}(r) + e\dot{\vec{r}}\times\vec{B} \end{aligned} \tag{202}$$

Thus the path integral for the propagator becomes

$$U(r_i,t_i;r_f t_f) = C\int_{r(t_i)=r_i}^{r(t_f)=r_f} \mathrm{D}[\vec{r}]\; e^{\frac{i}{\hbar}\int_{t_i}^{t_f} L_0(r,\dot{r})\,dt} \times e^{\frac{ie}{\hbar}\int_{t_i}^{t_f} A(\vec{r}',t)\cdot\dot{\vec{r}}'dt} \tag{203}$$

In the Feynman path integral formulation, there are no operators left, the classical action is just a real number and the exponential of a sum of two actions is just the product of exponentials! So the contribution to the propagator (transition amplitude) due to a path that goes clockwise around the solenoid differs from that of an anti-clockwise path by a phase equal to the magnetic flux through the solenoid, which is proportional to the current. It is this phase difference that is responsible for the Aharonov-Bohm effect and shift of interference fringes as the current is varied.

• We check that the above Lagrangian leads to the familiar hamiltonian upon Legendre transformation.

$$H(r,p) = \mathrm{ext}_{\dot{r}}\left(p\dot{r} - L(r,\dot{r})\right) \;\Rightarrow\; p_i = \frac{\partial L}{\partial \dot{r}_i} = m\dot{r}_i + eA_i \;\Rightarrow\; \dot{r}_i = \frac{1}{m}\left(p_i - eA_i\right) \;\Rightarrow\; H = \frac{(p-eA)^2}{2m} + e\phi$$

4 A second look at the harmonic oscillator

4.1 Coherent states of the harmonic oscillator

• We have seen that the highly excited stationary states $|n\rangle$ of the harmonic oscillator have a probability distribution of locations that is time-independent and approaches the classical distribution of times spent by an oscillating particle at various locations along its trajectory. However, the time-dependence of a highly excited stationary state certainly does not mimic the oscillatory motion of a classical spring. Indeed, in the n^{th} stationary state $\langle n|x|n\rangle$ is simply zero and by Ehrenfest's principle $\langle p\rangle = m\frac{\partial\langle x\rangle}{\partial t} = 0$ is also zero. What is more, the uncertainty product $(\Delta x\Delta p)_n = \hbar(n+\frac{1}{2})$ in a highly excited stationary state is not small, it grows with n[16].

• Following Schrödinger (1926), we seek quantum states (not necessarily stationary) of the SHO that display semi-classical behavior in a dynamical sense. We want *localized* states whose mean position and momentum oscillate with time, just like a classical particle attached to a spring does.

[16] This is a consequence of the Virial theorem $\langle T\rangle_n = \langle V\rangle_n = \frac{1}{2}\langle H\rangle_n = \frac{1}{2}\hbar\omega\left(n+\frac{1}{2}\right)$

• We are also interested in states that are semi-classical in the sense that the uncertainty product is small (in units of $\hbar$). After all, in classical mechanics, the uncertainty product is zero. But the Heisenberg principle tells us that $\Delta x \Delta p$ is minorized by $\hbar/2$. So we are interested in states for which $\Delta x \Delta p = \hbar/2$ or as small as possible.

• Remarkably, both these requirements are satisfied by certain states called *coherent states*.

• We already know one state that has these features, the g.s. It minimizes the uncertainty product. It is localized around $x = 0$ with $\langle x \rangle_0 = 0$ independent of time, which is a lot like a classical particle at the bottom of a quadratic potential well (it does not oscillate). We seek appropriate generalizations of this state. Since a gaussian wave packet minimizes the uncertainty product, we might expect coherent states to be gaussian wave packets. But they need not be at rest, indeed, their mean location could oscillate just like a classical particle attached to a spring. Let us start with static properties of coherent states before studying their dynamics.

• Recall the SHO and creation-annihilation operators

$$\begin{aligned} H &= \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 = \frac{\hbar\omega}{2}(\xi^2 + \mathtt{p}^2) = \hbar\omega(a^\dagger a + \frac{1}{2}) \quad \text{where} \quad \xi = \beta x,\ \mathtt{p} = -i\frac{\partial}{\partial\xi} = \frac{i}{\beta}\frac{\partial}{\partial x} = \frac{p}{\hbar\beta}, \\ a &= \frac{\xi + i\mathtt{p}}{\sqrt{2}} = \frac{1}{\sqrt{2}}\left(\xi + \frac{\partial}{\partial\xi}\right),\ a^\dagger = \frac{\xi - i\mathtt{p}}{\sqrt{2}} = \frac{1}{\sqrt{2}}\left(\xi - \frac{\partial}{\partial\xi}\right), \quad [a, a^\dagger] = 1, \quad \beta = \sqrt{\frac{m\omega}{\hbar}}. \end{aligned} \tag{204}$$

The g.s. of the SHO was the state annihilated by the annihilation operator $a\psi_0 = 0$ i.e.,

$$\frac{1}{\sqrt{2}}\left(\xi\psi_0 + \psi_0'\right) = 0\,\psi_0 \quad \Rightarrow \quad \psi_0'/\psi_0 = -\xi \quad \Rightarrow \quad \psi_0 = Ae^{-\xi^2/2}. \tag{205}$$

So the g.s. gaussian wave packet is the eigenstate of a with eigenvalue zero. Interestingly, we would get a gaussian no matter what the eigenvalue was. Indeed, let us find the other eigenfunctions of a. As it isn't a hermitian operator, we don't expect its eigenvalues to all be real, so let us denote them by z. The eigenvalue problem $a\psi = z\psi$ becomes

$$\frac{1}{\sqrt{2}}\left(\xi\psi + \psi'\right) = z\psi \quad \Rightarrow \quad \psi'/\psi = \sqrt{2}z - \xi \quad \Rightarrow \quad \psi = \tilde{N}e^{-\frac{1}{2}\xi^2 + \sqrt{2}z\xi}. \tag{206}$$

We can write this eigenfunction more elegantly by completing the square

$$-\left(\frac{1}{2}\xi^2 - \sqrt{2}z\xi\right) = -\frac{1}{2}\left[(\xi - \sqrt{2}z)^2 - 2z^2\right] \quad \Rightarrow \quad \psi_z(\xi) = N(z)e^{-(\xi - \sqrt{2}z)^2/2} \tag{207}$$

So the annihilation operator has a normalizable eigenfunction, (indeed a gaussian) for each eigenvalue z, which can be an arbitrary complex number. $N(z)$ is a normalization constant. [17]

• $\psi_z(\xi)$ is in general complex. Let us denote $z = u + iv$. In order that they be normalized $||\psi_z(\xi)||^2 = 1$, we can pick (the phase e^{iuv} is for later convenience.)

$$N(z) = \pi^{-1/4}e^{-v^2}e^{iuv}. \tag{208}$$

• Another convention is $||\psi_z(\xi)||^2 = e^{zz^*}$ by picking $N(z) = \pi^{-1/4}e^{-v^2}e^{iuv}e^{zz^*/2}$. We do not use it here.

[17] By contrast the creation operator $a^\dagger$ has no non-trivial normalizable right-eigenstates.

• The corresponding probability density is a gaussian representing a particle most likely to be found at the location $\xi = \sqrt{2}\Re z$.

$$|\psi_z(\xi)|^2 = \frac{1}{\sqrt{\pi}} e^{-\left(\xi - \sqrt{2}u\right)^2} \quad \text{where} \quad z = u + iv. \tag{209}$$

• It is convenient to label these eigenfunctions by the corresponding eigenvalue $|z\rangle$. Then

$$a|z\rangle = z|z\rangle, \quad \langle z|a^\dagger = \langle z|z^*, \quad \langle \xi|z\rangle = \psi_z(\xi) = N(z)\, e^{-(\xi - \sqrt{2}z)^2/2}, \quad \langle z|z\rangle = 1. \tag{210}$$

The state $|z\rangle$ is called a (symmetric) coherent state with label z. There is precisely one for each label (complex eigenvalue) z[18].

• We will show that the uncertainty product $\Delta x \Delta p = \hbar/2$ is minimal in coherent states. They are symmetric in the sense that $\Delta x = \Delta p$ or $\Delta\xi = \Delta\mathtt{p}$ for these coherent states. It turns out there are additional coherent states with $\Delta x \Delta p = \hbar/2$ which are asymmetric $\Delta x \neq \Delta p$. They are called squeezed coherent states. Coherent states have numerous attractive physical features and remarkable mathematical properties and find applications in many areas of physics, e.g. quantum optics.

• Since $\xi = \beta x$ and $\mathtt{p} = \frac{1}{\beta\hbar} p$, we must have $\Delta\xi\Delta\mathtt{p} = \frac{\Delta x \Delta p}{\hbar}$. So the Heisenberg uncertainty inequality is $\Delta\xi\Delta\mathtt{p} \geq \frac{1}{2}$ in these dimensionless variables.

• Let us calculate the uncertainty product in the coherent state $|z\rangle$ using creation-annihilation operators $\xi = (a + a^\dagger)/\sqrt{2}$ and $\mathtt{p} = (a - a^\dagger)/(i\sqrt{2})$. We find

$$\langle z|\xi|z\rangle = \sqrt{2}u, \quad \langle z|\xi^2|z\rangle = \frac{1}{2} + 2u^2, \quad \langle z|\mathtt{p}|z\rangle = \sqrt{2}v, \quad \langle z|\mathtt{p}^2|z\rangle = \frac{1}{2} + 2v^2, \tag{211}$$

Thus $(\Delta\xi)^2 = (\Delta\mathtt{p})^2 = \frac{1}{2}$ so that the coherent states saturate the uncertainty bound $\Delta\mathtt{p}\Delta\xi = \frac{1}{2}$. In particular, all coherent states $\psi_z(\xi)$ have the same 'shape' but different 'locations' in phase space.

• Another consequence is that upto a numerical factor $\sqrt{2}$, the real part of the coherent state label z gives the mean location of the particle, while its imaginary part gives the mean momentum of the particle (in dimensionless units). Thus, there is a $1-1$ correspondence between coherent states and points in phase space $|z\rangle \leftrightarrow (\sqrt{2}\Re z, \sqrt{2}\Im z)$.

• For $z = 0$ we get the g.s. For $z \neq 0$ these states are not stationary (not energy eigenstates), so we might expect them to 'move around' (i.e. $\frac{\partial\langle x\rangle}{\partial t} \neq 0$) if we let them evolve via the SE. But before studying their dynamics, let us understand more of their static properties.

• Since the energy eigenstates $|n\rangle = \frac{1}{\sqrt{n!}}(a^\dagger)^n|0\rangle$ form a complete set of states, we can expand the coherent states as a linear combination of them. To do so, we compute the projection of $|z\rangle$ on $|n\rangle$. The simplest case is $z = 0$ where $|z = 0\rangle$ is the same as the g.s. $|n = 0\rangle$ and their inner product is 1. For $z \neq 0$ we use $a|z\rangle = z|z\rangle$ to write

$$\langle n|z\rangle = \frac{1}{z}\langle n|a|z\rangle \;\; \Rightarrow \;\; \langle 1|z\rangle = z\langle 0|z\rangle, \;\; \langle 2|z\rangle = \frac{z^2}{\sqrt{2}}\langle 0|z\rangle, \ldots \Rightarrow \;\; \langle n|z\rangle = \frac{z^n}{\sqrt{n!}}\langle 0|z\rangle. \tag{212}$$

[18]Note that $|2z\rangle$ is the coherent state with label $2z$ and in general $|2z\rangle \neq 2|z\rangle$. Similarly $|2\xi'\rangle$ is the position eigenstate localized at the position $\xi = 2\xi'$, in general (i.e. except when $\xi' = 0$), it is *not* twice the position eigenstate localized at $\xi = \xi'$.

The projection on the g.s. is calculated explicitly

$$\langle 0|z\rangle = \int d\xi\ \psi_0^*(\xi)\psi_z(\xi) = e^{-|z|^2/2}. \tag{213}$$

Thus we have our expansion of the coherent state as a linear combination of energy eigenstates[19]

$$|z\rangle = e^{-zz^*/2}\sum_{n=0}^{\infty}\frac{z^n}{\sqrt{n!}}|n\rangle. \tag{214}$$

If we make measurements of energy on an ensemble of particles in a coherent state $|z\rangle$ then the energies obtained will be $E_n = \hbar\omega(n+\frac{1}{2})$ where n follows the Poisson distribution with parameter zz^*, since $P(n) = |\langle n|z\rangle|^2 = e^{-|z|^2}\frac{|z|^{2n}}{n!}$. Suitably interpreted, this has applications in modeling coherent laser light, the probability of detecting n photons in a coherent state of laser light follows this Poisson distribution.

• Classical Limit: What happens to a coherent state as $\hbar \to 0$? First consider $z = 0$, i.e., the g.s. $|\psi_0(x)|^2\,dx = \frac{\beta}{\sqrt{\pi}}e^{-\beta^2x^2/2}\,dx$, which is a gaussian centered at $x = 0$ with standard deviation $\propto \sqrt{\hbar}$ since $\beta^2 = m\omega/\hbar$. As $\hbar \to 0$, the density tends to a delta function representing a particle located at $x = 0$. Similarly, for the coherent state with label $z = u+iv$, $|\psi_z(x)|^2\,dx = \frac{\beta}{\sqrt{\pi}}e^{-\beta^2\left(x-\sqrt{2}u/\beta\right)^2}\,dx$ is a gaussian centered at $x = \sqrt{2}u/\beta = \sqrt{2}\Re z/\beta$ with standard deviation $\propto \sqrt{\hbar}$. So if we suppose that z/β remains finite as $\hbar \to 0$ then in the limit $\hbar \to 0$, we get a delta-localized probability density concentrated at $x = \sqrt{2}u$. So coherent states in the classical limit tend to point-like particles with definite position and momentum given by $x_{cl} = \lim_{\hbar\to 0}\sqrt{2}u\beta$ and $p_{cl} = \lim_{\hbar\to 0}\sqrt{2}v\beta$.

• Inner products: The coherent states are normalized to one, but aren't orthogonal. We should not expect two gaussian wave packets to be orthogonal. To begin with, $\langle 0|z\rangle = e^{-zz^*/2} \neq 0$ says that the coherent state with eigenvalue z has a non-zero overlap with the one with eigenvalue $z = 0$, their inner product vanishes only if $|z| \to \infty$. This is a general feature, coherent states with labels w, z become orthogonal only as $|z-w| \to \infty$. We see this by expanding each in the energy basis,

$$\langle w|z\rangle = \sum_{mn} e^{-\frac{1}{2}\left(|z|^2+|w|^2\right)}\frac{z^n(w^*)^m}{\sqrt{n!m!}}\langle m|n\rangle = e^{-\frac{1}{2}\left\{|z|^2+|w|^2-2w^*z\right\}}.$$

This implies

$$|\langle w|z\rangle|^2 = e^{-\left[|z|^2+|w|^2-w^*z-wz^*\right]} = e^{-|z-w|^2}. \tag{215}$$

• Completeness: Coherent states are a complete set of states for the SHO Hilbert space. They satisfy the completeness relation

$$\frac{1}{\pi}\int |z\rangle\langle z|\ du\,dv = I \quad \text{where} \quad z = u+iv. \tag{216}$$

To show this we expand the coherent states in the energy basis (r, θ are polar coords in the u-v plane)

$$\int |z\rangle\langle z|\ \frac{du\,dv}{\pi} \;=\; \sum_{mn}\frac{|n\rangle\langle m|}{\sqrt{n!m!}}\int\frac{du\,dv}{\pi}z^n(z^*)^m e^{-|z|^2}$$

[19] One can check using $[a, a^\dagger] = 1$ and $|n\rangle = \frac{1}{\sqrt{n!}}(a^\dagger)^n|0\rangle$ that $a|z\rangle = z|z\rangle$.

$$= \frac{1}{\pi}\sum_{mn}\frac{|n\rangle\langle m|}{\sqrt{n!m!}}\int_0^\infty r^{m+n+1}e^{-r^2}\,dr\int_0^{2\pi}e^{i(n-m)\theta}d\theta$$
$$= \sum_n\frac{|n\rangle\langle n|}{n!}\int_0^\infty t^n e^{-t}\,dt = \sum_n|n\rangle\langle n|\frac{\Gamma(n+1)}{n!} = \sum_n|n\rangle\langle n| = I. \quad (217)$$

So any state can be decomposed as an integral over coherent states[20]

$$|\phi\rangle = \frac{1}{\pi}\int|z\rangle\langle z|\phi\rangle\,du\,dv \quad (218)$$

• We can write the n^{th} stationary state in of the SHO $|n\rangle$ in the coherent state representation

$$\phi_n(z) = \langle z|n\rangle = \frac{(z^*)^n}{\sqrt{n!}}e^{-\frac{1}{2}zz^*}. \quad (219)$$

The stationary state wave functions in the coherent state representation are much simpler than in the coordinate representation $\phi_n(x)$, where we need the Hermite polynomials.

• CREATING $|z\rangle$: We use the decomposition of coherent states in the energy basis to construct a 'creation operator' that makes a coherent state from the vacuum (the g.s. $|0\rangle$ is also called the vacuum state)

$$|z\rangle = e^{-|z|^2/2}\sum_0^\infty\frac{z^n(a^\dagger)^n}{n!}|0\rangle = e^{-|z|^2/2}e^{za^\dagger}|0\rangle. \quad (220)$$

So up to a normalization factor $e^{a^\dagger z}$ is a creation operator for a coherent state. However, this 'creation operator' is not unitary even though it preserves the unit norm of the vacuum.

• DISPLACEMENT OPERATOR: There is a much nicer way of creating a coherent state from the vacuum. Notice that in essence, the coherent state with label z is obtained from the coherent state with label 0 by a displacement of the gaussian wave packet, the mean position and momentum are displaced $(\langle\xi\rangle, \langle\mathfrak{p}\rangle) = (0,0) \to \sqrt{2}(\Re z, \Im z)$ while maintaining the unit norm of the state $\langle z|z\rangle = \langle 0|0\rangle = 1$. There is a unitary operator, the so-called displacement operator that does this job. Notice that the above creation operator can equally well be written

$$|z\rangle = e^{-\frac{1}{2}|z|^2}e^{za^\dagger}e^{-z^*a}|0\rangle \equiv D_z|0\rangle. \quad (221)$$

The operator we introduced on the right (e^{-z^*a}) acts as the identity on $|0\rangle$. This is because $a|0\rangle = 0$ so $e^{-z^*a}|0\rangle = (I - z^*a + \cdots)|0\rangle = |0\rangle$. But now we can use the identity

$$e^Xe^Y = e^{X+Y+\frac{1}{2}[X,Y]} \quad \text{if } [X,Y] \text{ commutes with } X \text{ and } Y \quad (222)$$

to write the displacement operator as

$$D_z = e^{za^\dagger - z^*a} \quad \text{where we put } X = za^\dagger \text{ and } Y = -z^*a \text{ so that } [X,Y] = |z|^2[a,a^\dagger] = |z|^2 \quad (223)$$

[20] However, the coherent states are not a basis in the usual sense. They are labeled by the uncountable set of complex numbers unlike the countable set of energy eigenstates. One suspects there are 'too many' coherent states. This is true, they form a so-called 'over complete basis', they aren't linearly independent. One can remove a coherent state and they would still be complete in the sense that any vector can be approximated arbitrarily well as a finite linear combination of the remaining coherent states.

D_z is the exponential of an anti-hermitian operator $A(z) = za^\dagger - z^* a$ (just as the time evolution operator is the exponential of the anti-hermitian operator $iHt/\hbar$), so D_z is unitary and

$$D_z^\dagger = D_z^{-1} = e^{-A(z)} = e^{A(-z)} = D_{-z}. \tag{224}$$

The name displacement operator is justified by the fact that D_z displaces the label of a coherent state. It produces a displaced coherent state up to a phase

$$D_z|w\rangle = e^{i\Im(zw^*)}|z+w\rangle \tag{225}$$

To see this we use the fact that $[A(z), A(w)] = zw^* - z^*w$ commutes with both $A(z)$ and $A(w)$ to write

$$D_z|w\rangle = D_z D_w|0\rangle = e^{A(z)}e^{A(w)}|0\rangle = e^{A(z)+A(w)+\frac{1}{2}[A(z),A(w)]}|0\rangle = e^{i\Im(zw^*)}D_{z+w}|0\rangle = e^{i\Im(zw^*)}|z+w\rangle. \tag{226}$$

To further justify the name *displacement*, we can show that $D_z^\dagger a D_z = (a+z)$ by using $e^A B e^{-A} = B + [A, B]$ if A, B commute with their commutator (see problem set 7).

• Time evolution of coherent states: Suppose the initial state is a coherent state with label $z = z(0)$. To evolve it forward in time we expand it in the energy basis $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$

$$\begin{aligned} U(t)|z(0)\rangle &= e^{-iHt/\hbar}|z(0)\rangle = e^{-|z|^2/2}\sum_{n=0}^{\infty}\frac{z^n}{\sqrt{n!}}e^{-iHt/\hbar}|n\rangle = e^{-|z|^2/2}\sum_{n=0}^{\infty}\frac{z^n}{\sqrt{n!}}e^{-i\omega t/2}e^{-i\omega nt}|n\rangle \\ &= e^{-i\omega t/2}e^{-|z|^2/2}\sum_{0}^{\infty}\frac{\left(ze^{-i\omega t}\right)^n}{\sqrt{n!}}|n\rangle = e^{-i\omega t/2}|z(t)\rangle \quad \text{where} \quad z(t) = z(0)e^{-i\omega t}. \end{aligned} \tag{227}$$

Note that $|z(t)|^2 = |z(0)|^2 = |z|^2$. So under time evolution, a coherent state with initial label $z(0)$ evolves (up to the phase $e^{-i\omega t/2}$ which arises because the g.s. energy of the SHO is not 0 but $\hbar\omega/2$) into a coherent state with label $z(t) = e^{-i\omega t}z(0)$. In particular, the wave packet retains its shape, though it moves around. This is truly remarkable, most initial states do not display this property. In fact, the coherent state label traces out a circle in the clockwise direction. This means the mean position and mean momentum of the wave packet oscillate with time. Explicitly, let us denote the expectation values of position and momentum (in dimensionless variables) by

$$\xi(t) = \langle\hat{\xi}\rangle_t = \sqrt{2}\Re z(t), \quad \text{and} \quad \mathtt{p}(t) = \langle\mathtt{p}\rangle_t = \sqrt{2}\Im z(t). \tag{228}$$

and start in an initial coherent state with label

$$z(0) = \frac{1}{\sqrt{2}}\left[\xi(0) + i\mathtt{p}(0)\right]. \tag{229}$$

Then we find the time development of mean position and momentum (using $z(t) = e^{-i\omega t}z(0)$)

$$\xi(t) = \xi(0)\cos\omega t + \mathtt{p}(0)\sin\omega t \quad \text{and} \quad \mathtt{p}(t) = \mathtt{p}(0)\cos\omega t - \xi(0)\sin\omega t. \tag{230}$$

It is easily checked that the mean location of the coherent state wave packet satisfies Newton's equation $\ddot{\xi}(t) = -\omega^2\xi(t)$ for a simple harmonic oscillator. The fact that quantum mechanical expectation values satisfy classical equations of motion is not in itself surprising. This is a consequence of Ehrenfest's theorem and is true for any initial state, not just for a coherent initial state. What is remarkable is that coherent states remain coherent and localized in time like a classical particle, and have minimal uncertainty product. This is the reason for the

descriptor 'coherent'. A generic wave packet under Schrödinger evolution is unlikely to remain localized, due to the dispersive behavior of matter waves. We have already seen that a free particle gaussian wave packet suffers dispersive broadening. In a sense, the harmonic oscillator potential perfectly counters this dispersive broadening of the gaussian wave packet, ensuring that it retains its shape while allowing it to oscillate like a classical particle. Thus, coherent states fulfill our objective of finding *localized minimum uncertainty* wave packets whose *dynamics mimics that of a classical particle* in an SHO potential.

• The sense in which coherent states display behavior akin to that of classical point-like particles (minimal uncertainty product, preservation of localization under time evolution and expectation values obeying classical equations of motion) is different from the sense in which highly excited stationary states display semi-classical behavior. Notice that we made no approximations in our treatment of coherent states. Coherent quantum states provide an exact 1-1 correspondence with points in classical phase space, and the dynamics of a point in phase space is reflected in the time evolution of the corresponding coherent state.

4.2 Harmonic oscillator propagator by path integral

• It was reasonably easy to find the energy levels of the SHO by solving the Schrödinger eigenvalue problem using creation-annihilation operators. We could use the spectrum of energies E_n and eigenfunctions $\psi_n(x) = \langle x|n\rangle$ (Hermite polynomial times gaussian) to find the propagator by summing the series

$$\langle x_f|U(t_f,t_i)|x_i\rangle = \sum_n e^{-iE_n(t_f-t_i)/\hbar}\psi_n(x_f)\psi_n^*(x_i). \tag{231}$$

The path integral gives a different way of finding the SHO propagator. In fact, we can even find the energy spectrum from the propagator. Recall the path integral representation

$$U(x_f,t_f;x_i,t_i) = C\int_{x(t_i)=x_i}^{x(t_f)=x_f} \mathrm{D}[x]\; e^{\frac{i}{\hbar}\int_{t_i}^{t_f}\left[\frac{1}{2}m\dot{x}(t)^2-\frac{1}{2}m\omega^2x(t)^2\right]dt}. \tag{232}$$

The main problem is to give a meaning to this path integral by defining it as the limit of appropriate multi-dimensional integrals. In particular, we haven't tried to define the integration element on paths $\mathrm{D}[x]$ by taking a limit of time-sliced integrals $dx_1\cdots dx_{N-1}$ nor the factor C by taking the limit of $C_N = (m/ih\Delta t)^{N/2}$ since these may not be individually meaningful. Indeed C_N tends to infinity. However, the pre-factor C_N will be multiplied by certain other factors arising from evaluation of the integral $\int \mathrm{D}[x]\cdots$, these other factors will tend to zero, so that the product has a finite limit. Moreover, all these factors will be seen to be independent of ω, x_i and x_f and can be fixed by requiring that the SHO propagator reduce to the free particle propagator in the limit $\omega \to 0$.

• Since U is only a function of the difference $t_f - t_i$, we may without loss of generality take $t_i = 0$ and write $T = t_f$. We will evaluate this integral over paths in the generic case where ωT isn't an integer multiple of π. We have already seen that there is a unique classical trajectory joining x_i, t_i and x_f, t_f in this case. The exceptional cases $\omega T = n\pi$ are more subtle since there are either none or infinitely many classical trajectories joining x_i to x_f if $T\omega$ is an integer multiple of π.

• The Lagrangian is quadratic in $x(t)$, so the above path integral looks like an (infinite dimensional) gaussian integral. To exploit this feature, let x_{cl} be the unique classical trajectory satisfying the above boundary conditions and let us write the path $x(t)$ as $x(t) = x_{cl}(t) + \delta x(t)$ where $\delta x(t)$ is an arbitrary (not necessarily small) variation in the path satisfying $\delta x(0) = \delta x(T) = 0$. Then S is extremal at x_{cl} and we may write the path integral as an integral over the variations δx

$$\begin{aligned} U &= Ce^{\frac{i}{\hbar}S[x_{cl}]} \int_{\delta x(t_i)=0}^{\delta x(t_f)=0} \mathrm{D}[\delta x] \exp\left\{ \frac{i}{\hbar} \int_{t_i}^{t_f} \left[\frac{1}{2} m\, \delta\dot{x}^2 - \frac{1}{2} m\omega^2 \delta x^2 \right] dt \right\} \\ &= Ce^{\frac{i}{\hbar}S[x_{cl}]} \int_{\delta x(t_i)=0}^{\delta x(t_f)=0} \mathrm{D}[\delta x] \exp \frac{i}{\hbar} \int_0^T \delta x(t)\, A\, \delta x(t)\, dt \quad \text{where} \quad A = -\frac{m}{2}\left(\frac{d^2}{dt^2} + \omega^2 \right) \end{aligned} \tag{233}$$

The exponent is quadratic in the variables of integration $\delta x(t)$, so this is an infinite dimensional analogue of a gaussian integral[21]. We give meaning to it as a limit of finite dimensional discretized integrals. There are many ways of discretizing the integral. Rather than time-slice the interval (which is how we arrived at the path integral in the first place), let us follow the somewhat more elegant method of Fourier monomials, which are an eigenbasis for the hessian operator A (second variation of the action). $\delta x(t)$ is a function that vanishes at the end points of the interval $[0, T]$. The Fourier sine monomials $\phi_n(t) = \sin \frac{n\pi t}{T}$ are a complete orthogonal set of eigenfunctions of A in the Hilbert space of square-integrable functions on $[0, T]$ vanishing at the end points. ϕ_n have non-zero eigenvalues as long as $\omega T \neq n\pi$:

$$\text{for } n = 1, 2, \ldots, \quad A\phi_n = -\frac{1}{2} m \left(\frac{d^2}{dt^2} + \omega^2 \right) \sin \frac{n\pi t}{T} = \lambda_n \sin \frac{n\pi t}{T} \quad \text{where} \quad \lambda_n = \frac{m}{2}\left(\frac{n^2\pi^2}{T^2} - \omega^2 \right) \neq 0.$$

So we should expect the gaussian integral to simplify in the Fourier sine basis, which in effect is a convenient basis to compute the determinant of A. We may expand $\delta x(t)$ in a Fourier sine series

$$\delta x(t) = \sum_{n=1}^{\infty} c_n \sin \frac{n\pi t}{T}, \quad \text{where} \quad c_n \in \mathbb{R}. \tag{234}$$

The information in $\delta x(t)$ is contained in the Fourier coefficients, so an integration over all paths may be replaced by an integration over all possible Fourier coefficients, any Jacobian from the change in integration element will be absorbed into the pre factor C. To make it a finite dimensional integral, we restrict to Fourier polynomials of degree N and eventually let $N \to \infty$. First we write the integrand in terms of the Fourier coefficients. Using orthogonality of $\sin \frac{n\pi t}{T}$, we have

$$\int_0^T \left[\frac{1}{2} m\delta\dot{x}^2 - \frac{1}{2} m\omega^2 \delta x^2 \right] = \frac{m}{2}\frac{T}{2} \sum_1^{\infty} c_n^2 \left(\frac{n^2\pi^2}{T^2} - \omega^2 \right) \tag{235}$$

There are no cross terms $c_n c_m$ for $n \neq m$ as A is diagonal in the Fourier sine basis. Thus the N^{th} approximant to the propagator is a product of gaussian integrals

$$U_N(x_f, T; x_i, 0) = C_N e^{\frac{i}{\hbar}S[x_{cl}]} \int_{-\infty}^{\infty} \left(\prod_{n=1}^{N} dc_n \right) \exp\left\{ -\frac{mT}{4i\hbar} \sum_1^N c_n^2 \left(\frac{n^2\pi^2}{T^2} - \omega^2 \right) \right\}$$

[21] E.g. A finite dimensional gaussian integral over $x_1, \cdots, x_N$: $I = \int e^{-x^t A x} \prod_i dx_i$ for a real symmetric matrix A. It may be evaluated by going to a basis in which A is diagonal, one gets $I = \int e^{-\sum_n a_n y_n^2} \prod_n dy_n = \pi^{N/2}(a_1 \cdots a_N)^{-1/2} = \pi^{N/2}/\sqrt{\det A}$

$$= C_N e^{\frac{i}{\hbar}S[x_{cl}]} \prod_1^N \left[\int_{-\infty}^{\infty} e^{-\alpha_n c_n^2}\, dc_n \right]$$

$$\text{where } \alpha_n = \frac{mT}{4i\hbar}\left(\frac{n^2\pi^2}{T^2} - \omega^2\right) = \frac{m\pi^2 n^2}{4i\hbar T}\left(1 - \frac{\omega^2 T^2}{n^2\pi^2}\right).$$

The gaussian integrals are evaluated and one gets

$$U_N = \frac{C_N \pi^{N/2}}{\sqrt{\prod_1^N \frac{m\pi^2 n^2}{4i\hbar T}}} e^{\frac{i}{\hbar}S[x_{cl}]} \prod_1^N \left(1 - \frac{\omega^2 T^2}{n^2\pi^2}\right)^{-1/2} = \tilde{C}_N(h,m,T)\; e^{\frac{i}{\hbar}S[x_{cl}]} \left[\prod_{n=1}^N \left(1 - \frac{\omega^2 T^2}{n^2\pi^2}\right)\right]^{-1/2}. \tag{236}$$

Both $C_N \pi^{N/2}$ as well as the denominator $\sqrt{\prod_1^N \frac{m\pi^2 n^2}{4i\hbar T}}$ are divergent as $N \to \infty$, but the limit is taken in such a way that the quotient $\tilde{C}_N$ has a finite limit. Note that the new pre-factor $\tilde{C}_N$ is independent of ω, x_i and x_f. So let us denote $\tilde{C}(h,m,T) = \lim_{N\to\infty} \tilde{C}_N$. As for the ω-dependent product (see homework),

$$\lim_{N\to\infty} \prod_{n=1}^N \left(1 - \frac{\omega^2 T^2}{n^2\pi^2}\right) = \frac{\sin \omega T}{\omega T}. \tag{237}$$

Thus the SHO propagator is

$$U^{\rm SHO}(x_f, T; x_i, 0) = \tilde{C}(h,m,T)\, \sqrt{\frac{\omega T}{\sin \omega T}} \exp\left\{\frac{i}{\hbar} S[x_{cl}]\right\} \tag{238}$$

The factor $\tilde{C}$ is fixed by comparing with the free particle propagator

$$\lim_{\omega\to 0} U^{\rm SHO} = U^{\text{free particle}} = \sqrt{\frac{m}{ihT}} e^{\frac{i}{\hbar}S[x_{cl}]} \;\; \Rightarrow \;\; \tilde{C} = \sqrt{\frac{m}{ihT}} \tag{239}$$

So the SHO propagator (also known as the Mehler kernel) when $\omega T \neq n\pi$ is

$$U(x_f, T; x_i, 0) = \sqrt{\frac{m\omega}{ih \sin \omega T}} \exp\left\{\frac{i}{\hbar} S[x_{cl}]\right\}. \tag{240}$$

where $x_{cl}(t)$ is the unique classical trajectory satisfying $x(0) = x_i$ and $x(T) = x_f$ and

$$S[x_{cl}] = \frac{m\omega}{2 \sin \omega T} \left[(x_i^2 + x_f^2)\cos \omega T - 2 x_i x_f\right]. \tag{241}$$

4.3 Harmonic oscillator spectrum from path integral

Now that we have evaluated the SHO propagator by path integrals, we put it to use to obtain the SHO energy levels. This provides an alternate route to the SHO spectrum without any need to solve the Schrödinger eigenvalue problem. The main idea is to exploit the relation

$$U(T) = U(T,0) = e^{-iHT/\hbar} = \sum_{nn'} |n\rangle\langle n| e^{-iHT/\hbar} |n'\rangle\langle n'| = \sum_n e^{-iE_n T/\hbar} |n\rangle\langle n| \tag{242}$$

To concentrate on the energy spectrum, we evaluate the trace of U. U is diagonal in the energy basis, so its trace is easily expressed in terms of the energy levels.

$$\text{tr } U(T) = \sum_n e^{-iE_nT/\hbar} \tag{243}$$

The trace is basis independent, so we will compute it in the position basis using our formula (240) for the propagator, assuming $\omega T \neq n\pi$. By comparing the answer with the previous expression, we aim to extract the energy levels. Recall that the SHO propagator is

$$U(x_f, T; x_i, 0) = \sqrt{\frac{m\omega}{ih \sin \omega T}} \exp\left\{\frac{i}{\hbar} S[x_{cl}]\right\} \tag{244}$$

For $t_f - t_i = T \neq n\pi/\omega$, the unique classical trajectory joining x_i to x_f is (denote $\cos \omega t_i = c_i$ etc)

$$x(t) = a \cos \omega t + b \sin \omega t \quad \text{where} \quad a = \frac{s_f x_i - s_i x_f}{s_{f-i}} \quad \text{and} \quad b = \frac{c_i x_f - c_f x_i}{s_{f-i}}. \tag{245}$$

The Lagrangian for this trajectory $L = \frac{1}{2}m\dot{x}^2 - \frac{1}{2}m\omega^2 x^2$ is (denote $s = \sin \omega t, c = \cos \omega t$)

$$L = \frac{1}{2}m\omega^2 \left[a^2\left(s^2 - c^2\right) + b^2\left(c^2 - s^2\right) - 4absc\right] = \frac{1}{2}m\omega^2 \left[\left(b^2 - a^2\right)\cos 2\omega t - 2ab \sin 2\omega t\right]. \tag{246}$$

Without loss of generality, we take $t_i = 0, t_f = T$ and the action for this path is

$$S[x] = \int_0^T L\, dt = \frac{m\omega}{2}\left[\frac{\left(b^2 - a^2\right)}{2} \sin 2\omega T - 2\, ab \sin^2 \omega T\right] = \frac{m\omega}{2 \sin \omega T}\left[\left(x_i^2 + x_f^2\right)\cos \omega T - 2x_i x_f\right]$$

where $a = x_i$ and $b = \frac{x_f - x_i c_f}{s_f}$. To evaluate the trace of the propagator,

$$\text{tr } U(T) = \int_{-\infty}^{\infty} \langle x \mid U(T) \mid x\rangle dx, \tag{247}$$

we need the action of the classical trajectory $x(t)$ with $x_i = x_f = x$ for $0 \leq t \leq T$. In this case, one finds[22]

$$a = x, \quad b = x \tan \frac{\omega T}{2}, \quad x(t) = x[\cos \omega t + \tan \frac{\omega T}{2} \sin \omega t] \text{ and } S[x, T; x, 0] = -m\,\omega\, x^2 \tan\left(\frac{\omega T}{2}\right)$$

[22]This trajectory makes sense as long as $T \neq (2n+1)\pi/\omega$ which is ensured by our assumption that $\omega T \neq n\pi$. It is checked that $x(0) = x(T) = x$. Note that for this trajectory, the particle returns to the point x after a time T that has nothing to do with the period of oscillation $T^* = 2\pi/\omega$. This is because, when the particle returns to x, its velocity is reversed in sign. The time it takes for this need not be a half period, nor have any relation to the period. To visualize this, imagine a point x near the maximal extension of an oscillating spring. The tip of the spring passes through x on its way out and returns to x on its way in, and the time elapsed T has nothing to do with the period of oscillation. To drive home this point, move x closer to the maximal extension point. Then T will decrease, while the period of oscillation T^* is unaltered. Of course, there are exceptional points x to which a particle can return only after a time equal to a multiple of a half-period $T^*/2$. These are the points of maximal extension and the point $x = 0$. These exceptional cases are mostly omitted via the assumption $T \neq n\pi/\omega$. The exceptional case $x = 0$ is included via the trajectory $x(t) \equiv 0$, which returns to $x = 0$ after *any* time T and has zero action.

Thus the trace of the propagator has been reduced to a gaussian integral which we evaluate

$$\text{tr } U(T) = \int_{-\infty}^{\infty} U(x,T;x,0)dx = \sqrt{\frac{m\omega}{ih\sin\omega T}}\int_{-\infty}^{\infty}\exp\left[-\frac{i}{\hbar}m\omega x^2\tan\frac{\omega T}{2}\right]\,dx = \left(2i\sin\frac{\omega T}{2}\right)^{-1} \tag{248}$$

We can now use this remarkably simple formula for the trace of the propagator to recover the SHO spectrum. We wish to write $\text{tr } U$ as a sum of phases each proportional to the time T, and compare with the expression $\text{tr } U = \sum_n e^{-iE_nT/\hbar}$ to read off the energies

$$\text{tr } U = \frac{1}{e^{i\omega T/2}-e^{-i\omega T/2}} = \frac{e^{-i\omega T/2}}{1-e^{-i\omega T}} = \sum_0^\infty \exp\left[-\frac{iT}{\hbar}\hbar\omega\left(n+\frac{1}{2}\right)\right] \tag{249}$$

From this we infer the spectrum of energies of the SHO, $E_n = \hbar\omega\left(n+\frac{1}{2}\right)$.

5 Variational principle for Schrodinger eigenvalue problem

• The concept of a variational principle is among the most fruitful ideas in all of theoretical physics. It is the idea that an equation may be fruitfully viewed as the condition that a certain functional be extremal. For example, Newton's equations are the condition for the action to be extremal. One advantage of this viewpoint is that it facilitates a passage to the quantum theory where we are interested not just in extrema of the action but a sum over all paths with weights determined by their actions. The hamiltonian formulation gives another variational formulation of classical mechanics which was crucial to the development of the Schrödinger equation of QM as well as the development of statistical mechanics. Variational principles appear in other areas such as electromagnetic theory, statistical physics and gravitation. Variational principles also lead to approximation methods, as already discussed in QM1.

• In QM1 we showed that the task of finding the ground state of a quantum system with time-independent hamiltonian H could be formulated as the variational problem of minimizing $\langle\psi|H|\psi\rangle$ over all states of unit norm. The g.s. energy is

$$E_0 = \min_{||\psi||^2=1}\langle\psi|H|\psi\rangle = \min_\psi \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}. \tag{250}$$

The g.s. wave function ψ_0 is the one that minimizes this expectation value. What about the other stationary states besides the g.s.? In classical mechanics, the static solutions of Hamilton's equations for $H = \frac{p^2}{2m}+V(x)$ are given by $p=0$ and x a local extremum of $V(x)$. So we might expect a relation between the extrema of $\langle H\rangle$ and the stationary states (ones where the probability distribution of every observable is constant in time, i.e., energy eigenstates). In other words, we seek a variational reformulation of the Schrödinger eigenvalue problem $H\psi = E\psi$.

• The obvious idea is to look for the extrema of $\langle\psi|H|\psi\rangle$ as ψ is varied over all wave functions. However, this problem is nearly always uninteresting[23]. A physical manifestation of this problem is that it is possible to change $\langle\psi|H|\psi\rangle$, say by halving ψ whence $\langle\psi|H|\psi\rangle \to \frac{1}{4}\langle\psi|H|\psi\rangle$ *without*

[23] A small change $\psi\to(1+\epsilon)\psi$ will produce a change in $\langle\psi|H|\psi\rangle$ that is generically again *of the same order* $\langle\psi|H|\psi\rangle \to \langle\psi|H|\psi\rangle + (\epsilon+\epsilon^*)\langle\psi|H|\psi\rangle + \mathcal{O}(\epsilon^2)$. In other words, $\langle\psi|H|\psi\rangle$ generically has no local extrema. The only situation where $\langle\psi|H|\psi\rangle$ has a local extremum is when there is a state annihilated by H. But even in this situation, extremizing $\langle\psi|H|\psi\rangle$ will only produce the zero energy eigenstate and not any of the other eigenstates.

even changing the physical state. To avoid this problem, we look for extrema of $\langle\psi|H|\psi\rangle$ subject to the normalization constraint $\langle\psi|\psi\rangle = 1$. After all, this is the idea that worked for the ground state. The local extrema of a function occur at points where the gradient vanishes. But how do we extremize a function subject to a constraint? The method of Lagrange multipliers is helpful in doing so.

• Suppose we wish to extremize the 'energy' function $E(\vec{x})$ subject to the constraint $C(\vec{x}) = 0$ for $\vec{x} \in \mathbb{R}^n$. E.g., keep $n = 2$ in mind, $E = x^2 + y^2$ and $C(x, y) = (x-2)^2 + y^2 - 1$. In other words, we want to find extrema of E among points that lie on the constraint 'curve/surface' S defined by $C(\vec{x}) = 0$. The unconstrained extrema of E, i.e., points where $\nabla E = 0$ will generically not lie on S. S is a surface of dimension $n-1$ in $\mathbb{R}^n$. Recall from calculus that the gradient of a function is a vector that points in the direction in which the function increases fastest. But C does not change on the constraint surface, it is always zero. If ∇C had a component along the constraint surface, then we could increase C by traveling in that direction along the surface, which contradicts $C \equiv 0$ on S. *So the gradient of C must point orthogonal to the constraint surface.* So any normal vector to the surface S is a multiple of ∇C.

• Now we wish to minimize (similar argument applies to maximize/extremize) E holding $C = 0$ fixed. ∇E points in the direction of steepest increase of E. Consider ∇E at all points of the constraint surface S. At most points, ∇E is likely to have a component tangential to the surface. Imagine starting at such a point $\vec{x}$ on S where $-\nabla E$ has a non-zero component along S. This means we can reduce E by taking a small step along the direction of this component of $-\nabla E$, while remaining on S. On the other hand, if the gradient of E has no component along the constraint surface, then the only way of decreasing E is to fly off the surface. In other words, if ∇E is normal to S, then E attains a local extremum at that point of S. But normal vectors to S are of the form $\lambda\nabla C$ for any scalar $\lambda \in \mathbb{R}$. So extrema of E on S occur at points satisfying $\nabla E = \lambda\nabla C$ or $\nabla(E - \lambda C) = 0$. In other words, extremizing E subject to the constraint $C = 0$ is the same as extremizing $E - \lambda C$ where λ is a priori unknown[24].

• Let us apply the method of Lagrange multipliers to a toy quantum system with a real symmetric hamiltonian on a finite dimensional real Hilbert space. We try to extremize $v^t H v$ subject to the constraint $v^t v - 1 = 0$. This is equivalent to extremizing $G(v) = v^t H v - \lambda v^t v = H_{ij} v_i v_j - \lambda v_i v_i - \lambda$. Differentiating in v_k we get

$$\frac{\partial G}{\partial v_k} = H_{kj} v_j + H_{ik} v_i - 2\lambda v_k = 0 \quad \Rightarrow \quad (Hv)_k = \lambda v_k \tag{251}$$

which is the Schrödinger eigenvalue problem. The complex version is an exercise.

• In general, we have the following variational formulation of the Schrödinger eigenvalue problem. ψ is an eigenfunction of H with eigenenergy E iff the functional $\langle\psi|H|\psi\rangle - E\langle\psi|\psi\rangle$ is extremal:

$$H\psi = E\psi \quad \Leftrightarrow \quad \langle\psi|H|\psi\rangle - E\langle\psi|\psi\rangle \text{ is extremal.} \tag{252}$$

• We are not bound to use the method of Lagrange multipliers. We could instead have extremized the expectation value of the real symmetric hamiltonian

$$\langle H\rangle \equiv \frac{v_k H_{kl} v_l}{v_j v_j}. \tag{253}$$

[24]The parameter λ is called a Lagrange multiplier. At each such extremum of E on S, the Lagrange multiplier will be seen to take a particular value.

The condition for an extremum is readily seen to reproduce Schrödinger's eigenvalue problem

$$\begin{aligned}\frac{\partial\langle H\rangle}{\partial v_i} &= \frac{\langle v|v\rangle\,(H_{il}v_l + v_k H_{ki}) - \langle v|H|v\rangle 2v_i}{\langle v|v\rangle^2} = 0 \quad \Rightarrow \\ 2Hv &= 2\frac{\langle v|H|v\rangle}{\langle v|v\rangle}v \;\; \Rightarrow Hv = Ev \;\text{ where }\; E = \frac{\langle v|H|v\rangle}{\langle v|v\rangle}.\end{aligned} \tag{254}$$

6 Schrödinger-Pauli equation for spin half electron

• We saw that a spin half non-relativistic particle (electron) is described by a wave function $\psi_\pm(x)$ which gives the probability amplitude of finding the particle at x with spin projection $S_z = \pm\frac{1}{2}\hbar$. This wave function lives in the Hilbert space $L^2(\mathbb{R}^3)\otimes\mathbb{C}^2$. The hamiltonian for such a particle in a potential V is $H = (\frac{p^2}{2m} + V(x))\otimes I$ and is proportional to the identity in spin space. Now if such a particle has charge e and is in a magnetic field, by analogy with the classical dipole interaction, we add the spin magnetic dipole moment energy

$$H_{md} = -g\frac{e}{2m}\vec{S}\cdot\vec{B} = -\frac{ge\hbar}{4m}\vec{\sigma}\cdot\vec{B} \approx \frac{e\hbar}{2m}\sigma\cdot B. \tag{255}$$

The spin gyromagnetic ratio is $g \approx 2$ for the electron, based on experiment.

• On the other hand, we know that the interaction of a charged (spin zero) particle with electromagnetic fields is given by replacing $\vec{p}\to\vec{p} - e\vec{A}$ and $E \to E - e\phi$ in the hamiltonian $H = p^2/2m + V$

$$\left(\frac{p^2}{2m} + V\right)\psi = \hat{E}\psi \longrightarrow \left(\frac{(p-eA)^2}{2m} + V + e\phi\right)\psi = \hat{E}\psi = i\hbar\frac{\partial\psi}{\partial t} \tag{256}$$

Now we wish to generalize this hamiltonian to the case of a spin half particle. The hamiltonian cannot simply be proportional to the identity in spin space as that would not give rise to a magnetic moment interaction, which we expect to arise as a consequence.

• Notice that for a free particle, the hamiltonian $H = I\otimes\frac{p^2}{2m}$ could equally well be written $H = \frac{1}{2m}(\vec{\sigma}\cdot\vec{p})^2$ on account of $\sigma_i\sigma_j = \delta_{ij} + \sqrt{-1}\epsilon_{ijk}\sigma_k$. This suggests a hamiltonian for a spin-half charged particle in an electromagnetic field, acting on two-component spinor wave functions

$$H = \frac{1}{2m}(\sigma\cdot(p-eA))^2 + e\; I\otimes\phi. \tag{257}$$

The corresponding Schrödinger equation for this hamiltonian is called the Pauli equation (1927). Of course, it is just a guess for the appropriate hamiltonian. But it is a good guess. To see why, we use the above identity in the form $(\sigma\cdot A)(\sigma\cdot B) = A\cdot B + i\sigma\cdot(A\times B)$ to write (show this!)

$$H = \frac{1}{2m}(p-eA)^2 + \frac{i}{2m}\sigma\cdot(p-eA)\times(p-eA) + e\phi = \frac{1}{2m}(p-eA)^2 - \frac{e\hbar}{2m}\sigma\cdot B + e\phi. \tag{258}$$

In addition to the usual (spin-independent) electromagnetic interactions we also get the expected spin magnetic moment coupling with the approximately correct gyromagnetic ratio $g = 2$ for the electron.

7 Relativistic quantum mechanics

• The Schrödinger and Schrödinger-Pauli equations *with the above hamiltonians* can be used to describe non-relativistic particles of spin zero (no internal degrees of freedom) and half. Schrodinger in 1926 looked for a wave equation that was appropriate to a particle that might travel at speeds approaching that of light. Though he had an electron in mind, he did not consider its spin as that concept was still being developed. He obtained a relativistic wave equation now called the Klein-Gordan (KG) equation; it is of some relevance to a spin zero particle like a pion. A relativistic wave equation relevant to a spin half particle was subsequently discovered by Dirac (1928).

• In hindsight, both the KG and Dirac relativistic wave equations are flawed in that they cannot provide a self-consistent description of a single relativistic particle. The number of particles is not a conserved quantity in a relativistic setting, due to the processes of particle production and annihilation. Despite their inconsistencies, these equations are approximately valid when appropriately interpreted in the context of many-particle quantum mechanics. They also lead to many correct physical predictions, such as the existence of anti-particles and relativistic corrections to the hydrogen spectrum.

7.1 Klein-Gordon equation

• Recall that the Schrödinger equation could be obtained by the so-called correspondence rule of replacing $E \to i\hbar\frac{\partial}{\partial t}$, $\vec{p} \to -i\hbar\nabla$ and $x \to \hat{x}$ in the hamiltonian of a non-relativistic particle and asking that the wave function be annihilated by the corresponding differential operator

$$E = \frac{p^2}{2m} + V(x) \quad \longrightarrow \quad i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V(x)\psi(x). \tag{259}$$

We want to do the same thing for a free massive relativistic particle, whose energy is given by $E = \sqrt{p^2c^2 + m^2c^4}$. The resulting differential equation is

$$i\hbar\frac{\partial\psi}{\partial t} = \sqrt{-\hbar^2c^2\nabla^2 + m^2c^4}\ \psi \tag{260}$$

To make sense of the operator on the rhs, we could expand in inverse powers of m

$$i\hbar\frac{\partial\psi}{\partial t} = mc^2\left[1 - \frac{\hbar^2\nabla^2}{2m^2c^2} - \frac{\hbar^4\nabla^4}{8m^4c^4} + \ldots\right]\psi \tag{261}$$

At leading order we get the non-relativistic SE where the hamiltonian includes an additive constant coming from the rest energy. However, this new equation is first order in time but of infinite order in space derivatives. It is not a differential equation in the usual sense, making it a bit hard to work with. Moreover, relativistic covariance is not manifest since space and time derivatives appear very differently. The above equation could be useful in working out relativistic corrections to the SE by truncating the series. But due to the difficulties in dealing with a differential operator of infinite order, and lack of manifest relativistic covariance a simpler relativistic wave equation was investigated.

• The relativistic energy momentum relation can also be written $E^2 = p^2c^2 + m^2c^4$, though this includes negative energy solutions which are not admissible in classical physics. But we set

aside this objection for now and work with this form due to its simplicity, largely on aesthetic grounds. Applying the correspondence rule, we get the Schrödinger relativistic wave equation or (massive) Klein-Gordon equation

$$-\hbar^2\frac{\partial^2\psi}{\partial t^2} = -\hbar^2c^2\nabla^2\psi + m^2c^4\psi \quad \text{or} \quad \left(\hbar^2\Box + m^2c^2\right)\psi = 0. \tag{262}$$

$\Box = \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \hbar^2\nabla^2$ is the d'Alembert or wave operator. Notice that the KG equation is 2^{nd} order in both space and time derivatives unlike the SE which is first order in time. Notice that the KG equation admits every solution of (260) as a solution. So even if our aim was to exclusively study (260), it could be technically easier to do so by solving the KG equation first and then discarding the 'unwanted' solutions. But we wish to study the KG equation in its own right for now, even if only for *aesthetic* reasons.

• To decide whether KG is a physically correct equation and what it might physically describe, we need to study its features. With the benefit of hindsight, we can say that suitably interpreted, the predictions of KG are in *better* agreement with experimental findings concerning relativistic spin-less particles, than the equation (260). Ultimately, this is the *physical* justification to study it.

7.1.1 Plane wave solutions of KG

• To get a feeling for what the KG equation describes, let us look for separable solutions $\Psi(r,t) = \psi(\vec{r})T(t)$. We find

$$-\hbar^2\frac{\ddot{T}}{T} = \frac{m^2c^4\psi - \hbar^2c^2\nabla^2\psi}{\psi} = E^2 \tag{263}$$

where we introduced a separation constant E^2 independent of both $\vec{r}$ and t and have dimensions of energy-squared. $\psi(\vec{r})$ must be an eigenfunction of the Laplacian (i.e., satisfy the Helmholtz equation)

$$\left(-\hbar^2c^2\nabla^2 + m^2c^4\right)\psi = E^2\psi. \tag{264}$$

The operator $-\hbar^2c^2\nabla^2 + m^2c^4$ is mathematically the same as the hamiltonian of a non-relativistic particle in a constant potential. It is a positive operator. So the separation constant E^2 must be positive, which justifies the notation E^2 with E real. This then guarantees that the solutions be oscillatory in time, for if we denote by E either the positive or negative square-root of E^2, then we have

$$T(t) = Ae^{iEt/\hbar} + Be^{-iEt/\hbar} \tag{265}$$

Let us for convenience of notation denote the quantity $E^2 - m^2c^4$ by p^2c^2 for some positive number p^2. We of course recognize that this Helmholtz equation arises from the relativistic energy-momentum dispersion relation $E^2 - m^2c^4 = \vec{p}^2c^2$ upon use of the correspondence rule $\vec{p} \to -i\hbar\nabla$. The general solution of the Helmholtz equation is a linear combination

$$\psi(\vec{r}) = Fe^{i\vec{p}\cdot\vec{r}/\hbar} + Ge^{-i\vec{p}\cdot\vec{r}/\hbar} \tag{266}$$

where $\vec{p}$ is *any* 'momentum' vector that satisfies the so-called mass-shell condition $c^2\vec{p}^2 = E^2 - m^2c^4$. Thus, separable solutions of the KG equation take the form

$$\Psi(\vec{r},t) = \left(Fe^{i\vec{p}\cdot\vec{r}/\hbar} + Ge^{-i\vec{p}\cdot\vec{r}/\hbar}\right)\left(Ae^{iEt/\hbar} + Be^{-iEt/\hbar}\right) \tag{267}$$

These solutions are bounded over all of space at all times, and to that extent, could potentially describe the amplitude of some disturbance. But a peculiar feature is that for a fixed momentum vector $\vec{p}$, there can be both a right moving and a left moving plane wave. This is at variance with our experience from classical mechanics as well as non-relativistic quantum mechanics. It is a reflection of the fact that we started with $E^2 - \vec{p}^2c^2 = m^2c^4$, which includes both positive and negative energies for a given momentum vector. This problem did not arise for the Schrödinger equation as it is first order in time, while the KG equation is second order in time.

• We can synthesize the general solution of the KG equation by taking an arbitrary linear combination of separable solutions.

• Another way of looking at this: The KG equation admits plane wave solutions $e^{i(\vec{k}\cdot\vec{r}-Et/\hbar)}$ where $\vec{k} = \vec{p}/\hbar$ is an arbitrary wave vector and

$$E = \pm\sqrt{m^2c^2 + \hbar^2c^2\vec{k}^2}. \tag{268}$$

It is checked by explicit substitution that this is a solution of KG. E is called energy for obvious reasons. The mode with $E > 0$ or $\omega = E/\hbar > 0$ is called a positive energy/frequency mode and one with $\omega < 0$ a negative energy mode. So the spectrum of energies of the massive KG equation is continuous and comes in two disjoint pieces $(-\infty, -mc^2] \cup [mc^2, \infty)$. In other words, the energy spectrum is not bounded below, there is no ground state.

• One attractive option is to simply disallow the negative energy solutions as possible initial conditions. We might implement this idea by saying that the initial conditions always be chosen so that the particle starts out in a positive energy state (or a linear combination thereof). This is seemingly ok, since the particle will then remain in that stationary state for ever. However, under the influence of external perturbations, the particle could make a transition to a lower energy state. And since there is no ground state, the particle could keep dropping down in energy while emitting radiation. The system is unstable to perturbations as it does not have a ground state. This is problematic since we could extract an infinite amount of energy from such a particle as it makes transitions to states of arbitrarily negative energy.

7.1.2 Lorentz invariance

The principles of relativity say that there is no way of physically distinguishing between different frames of reference related by Lorentz transformations. A way of ensuring this is for the differential equations describing the laws of physics to take the same form in all such frames i.e., to be Lorentz invariant. Negative energy solutions are in a sense the price we have to pay for manifest Lorentz invariance. To discuss the Lorentz invariance of KG, we introduce the Minkowski metric $\eta_{\mu\nu} = \text{diag}(1, -1, -1, -1)$ and the 4-vector coordinate and gradient

$$x^\mu = (x^0, \vec{x}) = (ct, \vec{x}), \quad \partial_\mu = \frac{\partial}{\partial x^\mu} = \left(\frac{1}{c}\frac{\partial}{\partial t}, \nabla\right). \tag{269}$$

A Lorentz transformation[25] $x' = \Lambda x$ is one that preserves inner products $\langle x, y\rangle = x^t\eta y$ of 4-vectors: $\langle x, y\rangle = \langle x', y'\rangle$. This is the condition that for any 4-vectors x, y

$$x^t\Lambda^t\eta\Lambda y = x^t\eta y. \tag{270}$$

[25]For example, a Lorentz boost in the x direction leads to $x' = \gamma(x - vt), t' = \gamma(t - xv/c^2), y' = y, z' = z$ and $E' = \gamma(E - p_xv), p'_x = \gamma(p_x - vE/c^2), p'_y = p_y, p'_z = p_z$. The nontrivial part of the corresponding transformation,

In other words, the Lorentz transformation matrix must satisfy $\Lambda^t \eta \Lambda = \eta$. In components, this reads

$$x'^\mu = \Lambda^\mu_\nu x^\nu \quad \text{and} \quad \Lambda^\mu_\nu \, \eta_{\mu\rho} \, \Lambda^\rho_\sigma = \eta_{\nu\sigma}. \tag{271}$$

We say that the Lorentz transformation preserves the metric.

• x^μ is called a contravariant vector or the contravariant components of the position and ∂_μ is a covariant vector or covariant components of the gradient. The terminology is because of the way they behave under a Lorentz transformation (transforming via Λ and Λ^t):

$$x'^\mu = \Lambda^\mu_\nu x^\nu \quad \text{and} \quad \partial'_\mu = \Lambda^\nu_\mu \partial_\nu \tag{272}$$

Indices are raised by the Minkowski metric $\eta^{\mu\nu} = \text{diag}(1, -1, -1, -1)$ and lowered by its inverse $\eta_{\mu\nu} = \text{diag}(1, -1, -1, -1)$. The vectors with raised/lowered indices are denoted by the same symbols

$$x_\mu = \eta_{\mu\nu} x^\nu = (ct, -\vec{x}), \quad \partial^\mu = \frac{\partial}{\partial x_\mu} = \left(\frac{1}{c} \frac{\partial}{\partial t}, -\nabla \right) \tag{273}$$

Then it is seen that the wave operator is $\Box = \partial_\mu \partial^\mu$. The wave operator is Lorentz invariant. This is because under a Lorentz transformation Λ, c is unchanged and any expression where the space-time indices are contracted is Lorentz invariant, e.g. $x'^\mu x'_\mu = x^\mu x_\mu$. So $\Box_x = \Box_{x'}$. Thus, the KG equation $(\hbar^2 \Box_x + m^2 c^2)\psi(x) = 0$ is Lorentz invariant as long as $\psi(x)$ transforms as a scalar under Lorentz transformations $\psi'(x') = \psi(x)$. Since we have not considered any internal (spin) degrees of freedom, the KG equation may be of relevance to spin zero scalar particles, such as pions.

7.1.3 Non-relativistic limit

It is possible to obtain the Schrödinger equation in a non-relativistic limit of the KG equation. However, one cannot do this by simply putting $c = \infty$ in the KG equation. Classically, a non-relativistic situation is one where the energy is mostly rest energy $E = mc^2 + KE \approx mc^2 + \frac{p^2}{2m}$. In this case, the primary time dependence of a plane wave $\psi(x,t) = e^{i(\vec{k}\cdot x - Et/\hbar)}$ is given by putting $E \approx mc^2$. Of course, there would be some residual time dependence due to the remaining energy. So to facilitate taking the non-relativistic limit, let us change variables to a new wave function $\phi(r,t)$

$$\psi(r,t) = e^{-imc^2 t/\hbar} \phi(r,t) \tag{274}$$

We have in mind that the factor $e^{-imc^2 t/\hbar}$ takes care of the fast time dependence (high frequency) and $\phi(r,t)$ only has a residual slow time dependence. Putting this form in KG, one finds that ϕ satisfies

$$i\hbar \dot{\phi} - \frac{\hbar^2}{2mc^2} \ddot{\phi} = -\frac{\hbar^2}{2m} \nabla^2 \phi. \tag{275}$$

So far we have made no approximation. Now we may take a non-relativistic limit by letting $c \to \infty$, the term second order in time derivatives drops out (ϕ has slow time dependence) and we get the usual free particle SE. An energy eigenstate is then of the form $\phi(r,t) = e^{i(\vec{k}\cdot r - E_{nr} t/\hbar)}$

in matrix form, is $\begin{pmatrix} ct' \\ x' \end{pmatrix} = \gamma \begin{pmatrix} 1 & -\beta \\ -\beta & 1 \end{pmatrix} \begin{pmatrix} ct \\ x \end{pmatrix}$ and $\begin{pmatrix} E'/c \\ p' \end{pmatrix} = \gamma \begin{pmatrix} 1 & -\beta \\ -\beta & 1 \end{pmatrix} \begin{pmatrix} E/c \\ p \end{pmatrix}$ so that $\Lambda = \gamma \begin{pmatrix} 1 & -\beta \\ -\beta & 1 \end{pmatrix}$ where $\gamma = (1-\beta^2)^{-1/2}$ and $\beta = v/c$. A Lorentz transformation matrix is symmetric for a boost but not for a rotation.

where $E_{nr} = \hbar^2\vec{k}^2/2m$. Thus the original wave function is $\psi(r,t) \approx e^{i\vec{k}\cdot\vec{r}-iEt/\hbar}$ where $E = mc^2 + E_{nr}$.

7.1.4 Coupling to electromagnetic field

We can study the KG equation in the presence of an electromagnetic field defined by the scalar and vector potential $\phi, \vec{A}$ in the same way as we did for the Schrödinger equation. We apply the 'minimal coupling' prescription

$$E \to E - e\phi \quad \text{and} \quad \vec{p} \to \vec{p} - e\vec{A}. \tag{276}$$

to the relativistic energy momentum dispersion relation $E^2 = \vec{p}^2c^2 + m^2c^4$. This is a sensible thing to do since it is shown in electrodynamics that $A_\mu = (\phi/c, -\vec{A})$ transform in the same manner as $p_\mu = (E/c, -\vec{p}) = i\hbar\partial_\mu$, i.e. as the covariant components of a 4-vector. Thus $\pi_\mu = p_\mu - eA_\mu$ is a covariant 4-vector under Lorentz transformations.

• To get a wave equation we then use the correspondence rule $E \to i\hbar\frac{\partial}{\partial t}, \vec{p} \to -i\hbar\nabla$ and treat $\vec{A}$ and ϕ as multiplication operators on the wave function $\psi(x,t)$. The resulting wave equation is

$$\left(i\hbar\frac{\partial}{\partial t} - e\phi\right)^2 \psi = c^2\left(-i\hbar\nabla - e\vec{A}\right)^2 \psi + m^2c^4\psi. \tag{277}$$

7.1.5 Local conservation law and physical interpretation

• Recall that a key feature of the SE that made it acceptable as a quantum mechanical wave equation is its physical probability interpretation: the presence of a positive probability density and a current which together satisfy a local conservation law (continuity equation) $\frac{\partial P}{\partial t} + \nabla\cdot j = 0$. We seek a probability density $P(x,t)$ and current $j(x,t)$ for the KG equation that satisfy a continuity equation and reduce to the known non-relativistic quantities in the appropriate limit. Since the non-relativistic probability density and current

$$P_{nr}(x,t) = |\psi(x,t)|^2 \quad \text{and} \quad j_{nr}(x,t) = \frac{\hbar}{2mi}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right) \tag{278}$$

are bilinear, it is simplest to look for a local conservation law bilinear in ψ. We multiply the KG equation $-\hbar^2\ddot{\psi} = -\hbar^2c^2\nabla^2\psi + m^2c^4\psi$ by ψ^* and the complex conjugate equation by ψ and subtract the two to get

$$\frac{\partial}{\partial t}\left(\psi^*\dot{\psi} - \psi\dot{\psi}^*\right) = c^2\nabla\cdot\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right). \tag{279}$$

To match the Schrodinger probability current, if we define

$$P(x,t) = \frac{i\hbar}{2mc^2}\left(\psi^*\dot{\psi} - \psi\dot{\psi}^*\right) \quad \text{and} \quad j(x,t) = \frac{\hbar}{2mi}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right) \tag{280}$$

then $\partial_t P(x,t) + \nabla\cdot j(x,t) = 0$ is a local conservation law for the KG equation.

• What is more, this continuity equation is Lorentz invariant. Let us define the current density

$$j^\mu = \left(cP, \vec{j}\right) = -\frac{\hbar}{m}\Im\left(\psi^*\frac{1}{c}\frac{\partial\psi}{\partial t}, -\psi^*\nabla\psi\right) \tag{281}$$

Since ψ is a scalar under Lorentz transformations, j^μ transforms in the same manner as the 4-vector $\partial^\mu = \left(\frac{1}{c}\frac{\partial}{\partial t}, -\nabla\right)$. So j^μ are the contravariant components of a 4-vector. Contracting with the covariant 4-divergence, $\partial_\mu j^\mu$ is a Lorentz invariant quantity, which by the continuity equation must vanish $\partial_\mu j^\mu = 0$.

• We check via the substitution $\psi = e^{-imc^2 t/\hbar}\phi$ that

$$P = \frac{i\hbar}{2mc^2}\left(-\frac{2imc^2}{\hbar}|\phi|^2 + \phi^*\dot{\phi} - \phi\dot{\phi}^*\right) \to |\phi|^2 = P_{nr} \quad \text{and} \quad \vec{j} = \vec{j}_{nr} \tag{282}$$

in the non-relativistic limit $c \to \infty$ where ϕ solves the non-relativistic SE.

• So we have a Lorentz-invariant local conservation law for the KG equation, with the correct non-relativistic limit! But can $P(x,t)$ be interpreted as a probability density? No, since it can be negative. Notice that $P = -\frac{\hbar}{mc^2}\Im\psi^*\dot{\psi}$. Since KG is second order in time, both $\psi(x,0)$ and $\dot{\psi}(x,0)$ may be freely specified as initial conditions. E.g., we could take $\psi(x,0) \in \mathbb{R}$ and $\Im\dot{\psi}(x,0) > 0$. Then $P(x,0)$ would be negative. As another example, let us calculate P for a plane wave solution of KG

$$\psi(x,t) = e^{i(\vec{k}\cdot r - \omega t)} \quad \text{where} \quad \hbar\omega = \pm\sqrt{c^2\hbar^2\vec{k}^2 + m^2c^4}. \tag{283}$$

We find $P(x,t)$ is positive for positive energy plane waves and negative for negative energy plane waves:

$$P(x,t) = \frac{\hbar\omega}{mc^2} = \pm\sqrt{1 + \frac{p^2}{m^2c^2}}. \tag{284}$$

Thus we may not interpret $P(x,t)$ as a probability density.

• What is more, $P(x,t)$ is identically zero at all times if the initial conditions $\phi(x,0)$ and $\dot{\phi}(x,0)$ are chosen to be real. A real initial condition is a perfectly legitimate initial condition, and one checks that a real initial wave function remains real at all times under Klein-Gordon evolution. It is hard to understand why the KG equation assigns zero 'probability' to such a wave function.

• The lack of a non-negative P and thus the absence of a probability interpretation arises from the fact that the KG equation is second order in time, unlike the SE which is first order in time. Thus, the KG equation cannot be interpreted as a quantum mechanical wave equation for one relativistic particle in the same way as the SE is a qm wave equation for one non-relativistic particle. For this reason, as well as due to the spectrum being unbounded below, the KG equation was discarded as a consistent description of a single relativistic spin zero particle.

• In retrospect, it was unreasonable to expect to find a consistent quantum mechanical relativistic wave equation for one particle (or even any fixed number of such particles). This is because it was found experimentally that if a particle is accelerated to an energy significantly in excess of its rest energy, then by the process of particle production and destruction, an indefinite number of additional particles are produced. The number of particles is not fixed in time. However, even in such a situation, one finds that total electric charge is conserved.

• Later, the Klein-Gordon equation was resurrected by Pauli and Weisskopf (1934), who interpreted P as proportional to electric charge density and j as proportional to charge current and the negative energy solutions could be interpreted in terms of particles of opposite charge. However, in its new incarnation, the KG equation for a complex-valued wave function $\psi(x,t)$

was not a quantum mechanical wave equation at all, but rather an equation for some sort of charged relativistic fluid. A situation in which $\phi(x,t)$ is real is then interpreted as an uncharged fluid! Looked at this way, the KG equation could be incorporated as an ingredient in a larger framework of quantum fields, applicable to the relativistic quantum mechanics of an indefinite number of spin-0 particles, rather than to a single spin-0 particle.

7.2 Dirac equation

• Some of the difficulties with the KG equation (esp the lack of a positive locally conserved probability density) stem from the fact that it is second order in time. Dirac (1928) looked for a relativistic wave equation that is first order in time and admits a non-negative conserved density which could be interpreted as a probability. The simplest first order equation, which follows by applying the correspondence rule to $E = \sqrt{p^2c^2 + m^2c^4}$, is however not manifestly Lorentz invariant. Indeed it is not of finite order in space-derivatives though it is first order in time. Dirac looked for some other way of 'taking this square-root' so that the equation is first order in space derivatives. This would make it easier to ensure Lorentz invariance. He found a remarkable solution to this problem. However, there is a necessary condition for the consistency of any relativistic wave equation: the wave function must satisfy the KG equation. This would ensure that wave packet solutions in the classical limit obey the energy momentum dispersion relation $E^2 = p^2c^2 + m^2c^4$ which must hold for any relativistic particle in classical mechanics. We will use this consistency condition to obtain Dirac's relativistic wave equation for the spin-half electron. Recall that the Pauli equation for a non-relativistic electron was for a two component wave function. So we expect to need at least a two component wave function to account for two linearly independent spin projections. We seek a wave equation of the form

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi \quad \text{for} \quad H \quad \text{hermitian} \tag{285}$$

and linear in momenta. For a free particle, any such linear hamiltonian can be written

$$H = c\vec{\alpha}\cdot\vec{p} + \beta mc^2 = -i\hbar c\vec{\alpha}\cdot\nabla + \beta mc^2 \tag{286}$$

where $\vec{\alpha}$ and β are dimensionless and independent of x, t, p, E. Dimensional analysis implies the constant term must be linear in mass and also fixes the factors of $\hbar$ and c. H is called the Dirac hamiltonian or the Dirac operator. We expect ψ to have at least $N = 2$ components, so $\vec{\alpha}$ and β must be constant $N \times N$ hermitian matrices[26]. Such matrices already appeared in the hamiltonian of the Pauli equation

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{1}{2m}(\vec{\sigma}\cdot\vec{p})^2\psi. \tag{287}$$

• A solution of the Dirac equation automatically satisfies the second order equation

$$-\hbar^2\frac{\partial^2\psi}{\partial t^2} = H^2\psi = \left[-\hbar^2c^2\alpha_i\alpha_j\partial_i\partial_j + \beta^2m^2c^4 + mc^3(\alpha_i\beta + \beta\alpha_i)p_i\right]\psi. \tag{288}$$

Comparing with the KG equation

$$-\hbar^2\frac{\partial^2\psi}{\partial t^2} = \left[-\hbar^2c^2\partial_i\partial_i + m^2c^4\right]\psi \tag{289}$$

[26] If $N = 1$, the hamiltonian wouldn't be rotation-invariant as there would be a preferred vector $\vec{\alpha}$ involved in its specification.

we find the consistency conditions for Dirac's matrices

$$\alpha_i^2 = \beta^2 = I, \;\; [\alpha_i, \beta]_+ = 0 \quad \text{and} \quad [\alpha_i, \alpha_j]_+ = 0. \tag{290}$$

In other words, the hermitian α and β matrices must square to the identity and anti-commute in pairs. So their eigenvalues must be ± 1. What is more, we can show that they must be traceless

$$\alpha_i\beta + \beta\alpha_i = 0 \;\; \Rightarrow \;\; \alpha_i = -\beta\alpha_i\beta \;\; \Rightarrow \;\; \text{tr}\; \alpha_i = -\;\text{tr}\; \beta^2\alpha_i = -\;\text{tr}\; \alpha_i \;\; \Rightarrow \;\; \text{tr}\; \alpha_i = 0. \tag{291}$$

Similarly, we show that $\text{tr}\; \beta = 0$. Since they are traceless, they must each have an equal number of $+1$ and -1 eigenvalues, so they must be of even dimension N. $N = 2$ is however disallowed since we cannot find four such 2×2 matrices (see hw). The next simplest possibility is $N = 4$, and it turns out to be possible to find four 4×4 matrices satisfying the above conditions. This also means that the wave function $\psi(x, t)$ must be a four-component column vector (called a 'Dirac' spinor) rather than a two-component vector (sometimes called a 'Pauli' spinor). The adjoint $\psi^\dagger$ is a four component row vector. While we expected to need two components to describe the two spin projections of a spin half particle, the additional two components are unexpected, but forced upon us by internal consistency.

7.2.1 Dirac's 4×4 representation of $\vec{\alpha}, \beta$ matrices

• Just as it is convenient to express the spin operators of a non-relativistic particle in a particular basis (say one where S_z is diagonal), it is convenient to pick a basis to represent $\vec{\alpha}, \beta$ as specific numerical matrices to facilitate working out explicit solutions of the Dirac equation etc. The representation chosen by Dirac is one where β is diagonal. It facilitates passage to the non-relativistic limit, discussion of spin etc. It is a basis where β is diagonal and its $+1$ eigenvalues precede its -1 eigenvalues:

$$\beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \tag{292}$$

is clearly hermitian, traceless and squares to the identity. The condition that α_i anti-commute with β may be used to show that α_i must be block off diagonal. Along with hermiticity, this implies they must be of the form

$$\alpha_i = \begin{pmatrix} 0 & g_i \\ g_i^\dagger & 0 \end{pmatrix} \tag{293}$$

where g_i are 2×2 matrices. The conditions $[\alpha_i, \alpha_j]_+ = 2\delta_{ij}$ imply that the $[g_i, g_i^\dagger]_+ = 0$ for $i \neq j$ and $g_i g_i^\dagger = I$. The Pauli matrices satisfy these conditions and so we may take $g_i = \sigma_i$. Thus we have the four Dirac matrices

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}. \tag{294}$$

There are other ways to represent the 4×4 Dirac matrices, though they lead to the same physics.

7.2.2 Local conservation law and probability interpretation

• We seek a locally conserved density (hopefully positive) and current for the Dirac equation. By analogy with what worked for the Schrodinger and KG equations, we look for a bilinear

conservation law by taking the difference of the Dirac equation and its adjoint after multiplying by $\psi^\dagger$ from the left and ψ from the right respectively. The Dirac equation and its adjoint are

$$i\hbar\frac{\partial\psi}{\partial t} = -i\hbar c\alpha\cdot\nabla\psi + mc^2\beta\psi, \quad \text{and} \quad -i\hbar\frac{\partial\psi^\dagger}{\partial t} = i\hbar c\nabla\psi^\dagger\cdot\alpha + mc^2\psi^\dagger\beta \tag{295}$$

So we get

$$i\hbar\psi^\dagger\dot{\psi} = -i\hbar c\psi^\dagger\alpha\cdot\nabla\psi + mc^2\psi^\dagger\beta\psi \quad \text{and} \quad -i\hbar\dot{\psi}^\dagger\psi = i\hbar c\nabla\psi^\dagger\cdot\alpha\psi + mc^2\psi^\dagger\beta\psi. \tag{296}$$

Subtracting, we get a local conservation law

$$\frac{\partial}{\partial t}\left(\psi^\dagger\psi\right) + \nabla\cdot\left(\psi^\dagger c\vec{\alpha}\,\psi\right) = 0 \quad \text{or} \quad \frac{\partial P}{\partial t} + \nabla\cdot\vec{j} = 0 \tag{297}$$

where $P(x,t) = \psi^\dagger\psi$ and $\vec{j}(x,t) = \psi^\dagger c\alpha\,\psi$. Dirac interpreted $P(x,t)$ as a probability density as it is non-negative and j as a probability current density by analogy with Born's interpretation of the Schrödinger wave function. Thus, the problem of negative probabilities in the KG equation could be avoided in the case of the Dirac equation.

7.2.3 Plane waves and energy spectrum

• Each component of the Dirac wave function $\Psi(\vec{r},t)$ satisfies the KG eqn, which admits plane wave solutions. So it is reasonable to expect the Dirac equation to admit plane waves. We are also interested in energy eigenstates of the Dirac hamiltonian. These are plane waves, as expected of a free particle.

• To find solutions of the Dirac equation, let us proceed by separation of variables. Ψ depends on $\vec{x},t$ as well as spinor degrees of freedom. We make the SOV ansatz

$$\Psi(r,t) = u\psi(r)T(t) \tag{298}$$

where u is a constant (independent of r,t) 4-component Dirac spinor. Insertion in the Dirac equation $i\hbar\dot{\Psi} = (c\alpha\cdot p + \beta mc^2)\Psi$ and division by $\psi(r)T(t)$ gives

$$i\hbar u\frac{\dot{T}}{T} = -i\hbar c\frac{\nabla\psi}{\psi}\cdot\vec{\alpha}u + mc^2\beta u = Eu. \tag{299}$$

Lhs is a function of t while rhs a function of r, so both must equal a constant (spinor), which must be proportional to u from the lhs. We denote the proportionality constant E. Thus $T(t)\propto\exp(-iEt/\hbar)$ and

$$-i\hbar c\frac{\nabla\psi}{\psi}\cdot\vec{\alpha}u = (E - mc^2\beta)u \tag{300}$$

Now the rhs is independent of r while the lhs depends on r. So the lhs must be a constant spinor. The dependence of the lhs on r is entirely via the vector $-i\hbar\nabla\psi/\psi$. So this vector must be a constant vector, which we denote $\vec{p}$. Thus $\psi(r)$ and u must satisfy

$$-i\hbar\nabla\psi = \vec{p}\psi \;\text{ or }\; \psi\propto e^{i\vec{p}\cdot r/\hbar} \quad \text{and} \quad \left(c\alpha\cdot p + \beta mc^2\right)u = Eu \tag{301}$$

Thus, separable solutions of the Dirac equation are plane waves

$$\psi(\vec{r},t)\propto u\,e^{i(\vec{p}\cdot\vec{r}-Et)/\hbar}. \tag{302}$$

where u is a constant spinor satisfying $\left(c\alpha\cdot p+\beta mc^2\right)u=Eu$. This is a system of four homogeneous linear equations in four unknowns, the components of $u=u(E,\vec{p})$, which are constant in space and time, but could depend on the separation constants E and $\vec{p}$ as well as m and c. For non-trivial solutions to exist, the determinant of the 4×4 matrix of coefficients must vanish. This determinant is a quartic polynomial in E namely $(E^2-\vec{p}^2c^2-m^2c^4)^2$ (show this!). Thus, for non-trivial energy and momentum eigenstates to exist, E and $\vec{p}$ must satisfy $(E^2-\vec{p}^2c^2-m^2c^4)^2=0$, so the eigenvalues are $E=E_+,E_+,E_-,E_-$ where $E_\pm=\pm\sqrt{\vec{p}^2c^2+m^2c^4}$.

• Alternatively, we could obtain this relation by recalling that every component of a Dirac wave function must solve the KG equation, and this will be the case for the plane wave only if E and $\vec{p}$ satisfy the above mass-shell condition. We will obtain this condition in yet another way below.

• E is named energy as plane waves are eigenfunctions of the Dirac hamiltonian with eigenvalue E

$$H\Psi=i\hbar\dot{\Psi}=E\Psi. \tag{303}$$

$\vec{p}$ is called momentum since the above plane waves are eigenfunctions of the momentum operator $-i\hbar\nabla\psi=\vec{p}\psi$ with eigenvalue $\vec{p}$. Thus the plane waves are simultaneous eigenfunctions of the energy $i\hbar\frac{\partial}{\partial t}$, momentum $-i\hbar\nabla$ and hamiltonian H operators. This is to be expected, since the free particle hamiltonian is space and time-translation invariant.

• To find the energy spectrum of the Dirac hamiltonian we must find those values of E for which there are non-trivial eigenspinors $u(\vec{p})$ satisfying

$$\begin{pmatrix} mc^2I & c\sigma\cdot\vec{p} \\ c\sigma\cdot\vec{p} & -mc^2I \end{pmatrix}u=Eu. \tag{304}$$

We are interested in a massive $m\neq 0$ particle (the electron). The simplest case is $\vec{p}=0$, when the plane wave does not travel, i.e., the particle is at rest. In this case, the hamiltonian $H=\beta mc^2$ is diagonal and the eigenspinors can be taken as the standard basis spinors

$$u^{(1)}=\begin{pmatrix}1\\0\\0\\0\end{pmatrix}=\begin{pmatrix}\uparrow\\0\end{pmatrix},\quad u^{(2)}=\begin{pmatrix}0\\1\\0\\0\end{pmatrix}=\begin{pmatrix}\downarrow\\0\end{pmatrix},\quad u^{(4)}=\begin{pmatrix}0\\0\\1\\0\end{pmatrix}=\begin{pmatrix}0\\\uparrow\end{pmatrix},\quad u^{(4)}=\begin{pmatrix}0\\0\\0\\1\end{pmatrix}=\begin{pmatrix}0\\\downarrow\end{pmatrix}. \tag{305}$$

with energy eigenvalues $E=mc^2,mc^2,-mc^2,-mc^2$. The first two $u^{(1)},u^{(2)}$ are positive energy eigenspinors with energy equal to that of a particle at rest. The presence of two linearly independent positive energy solutions is to be welcomed, since we wished to model the electron, which is a spin half particle. So without a priori assuming anything about spin, Dirac's formalism, which is based on the relativistic energy momentum dispersion relation, automatically produces an equation for a spin half particle. However, it produces some seemingly unwanted things as well, $u^{(3)},u^{(4)}$ are negative energy eigenspinors. Despite the Dirac equation being first order in time, negative energy solutions remain. Suitably interpreted, they turn out to be necessary, to accommodate anti-electrons, which are inevitably produced even if a single electron is accelerated to energies much more than its rest energy. So we retain the negative energy solutions, in anticipation of their physical utility.

• More generally, when $\vec{p}$ is not necessarily zero, we suspect that the top two components of u might be significant for positive energy plane waves while the lower components may be

significant for negative energy solutions. So it makes sense to write $u = \begin{pmatrix}\phi\\ \chi\end{pmatrix}$, they satisfy the coupled equations

$$\phi = \frac{c\sigma\cdot p}{E-mc^2}\chi \quad \text{and} \quad \chi = \frac{c\sigma\cdot p}{E+mc^2}\phi. \tag{306}$$

Eliminating χ we get

$$c^2(\sigma\cdot\vec{p})^2\phi = (E^2 - m^2c^4)\phi \quad \text{or} \quad (E^2 - m^2c^4 - p^2c^2)I\phi = 0 \tag{307}$$

Similarly we get

$$(E^2 - m^2c^4 - p^2c^2)I\chi = 0. \tag{308}$$

Each is (the same) homogeneous linear equation for a two-component spinor. We have non-trivial solutions provided the determinant of the coefficient matrix $(E^2 - p^2c^2 - m^2c^4)^2$ vanishes. Thus there are two distinct energy eigenvalues and each has multiplicity two

$$E_\pm = \pm\sqrt{\vec{p}^2c^2 + m^2c^4} \tag{309}$$

As the momentum $\vec{p}$ is varied, the spectrum of energies of a Dirac particle extends over the range $(-\infty, -mc^2] \cup [mc^2, \infty)$. This is just as for the Klein Gordon equation, except that here each energy level is twice as degenerate, due to the additional spin degrees of freedom. All energy levels (except $E = \pm mc^2$) are of course infinitely degenerate, as the same energy is obtained irrespective of the direction of momentum.

• Let us obtain the corresponding eigenvectors. Clearly, every two component vector φ solves $(E_+^2 - m^2c^4 - p^2c^2)I\varphi = 0$ and we *could* choose the standard basis $\uparrow = (1,0)^t$ and $\downarrow = (0,1)^t$ for the eigenvectors φ, though any other pair of linearly independent ϕ would also do. The corresponding $\chi's$ are fixed as $\chi = \frac{c\sigma\cdot p}{E+mc^2}\varphi$. Thus we have found two (orthogonal - check this!) eigenspinors corresponding to the positive energy eigenvalue $E = E_+$ (check that $(c\alpha\cdot p + \beta mc^2)u_{1,2} = E_+u_{1,2}$.)

$$u^{(1)} = \begin{pmatrix}\uparrow\\ \frac{c\sigma\cdot p}{E_+ + mc^2}\uparrow\end{pmatrix} \quad \text{and} \quad u^{(2)} = \begin{pmatrix}\downarrow\\ \frac{c\sigma\cdot p}{E_+ + mc^2}\downarrow\end{pmatrix} \tag{310}$$

• Similarly, we find two orthogonal negative energy $E = E_-$ eigenspinors

$$u^{(3)} = \begin{pmatrix}\frac{c(\sigma\cdot p)}{E_- - mc^2}\uparrow\\ \uparrow\end{pmatrix} \quad \text{and} \quad u^{(4)} = \begin{pmatrix}\frac{c(\sigma\cdot p)}{E_- - mc^2}\downarrow\\ \downarrow\end{pmatrix} \tag{311}$$

Notice that these eigenspinors reduce to the previously determined expressions in the limit $\vec{p} = 0$ where the particle is at rest.

• Combining, separable solutions of the Dirac equation are plane waves. They are simultaneous eigenstates of energy and momentum, so they may be labelled by the corresponding eigenvalues $E, \vec{p}$ which must however satisfy the mass shell condition $E^2 = p^2c^2 + m^2c^4$. An orthogonal basis for these plane waves is

$$\Psi^{(j)}(r,t) = u^{(j)}e^{i(\vec{p}\cdot\vec{r} - Et)/\hbar} \quad \text{for } j = 1,2,3,4. \tag{312}$$

So we can regard the plane waves as labelled by $\vec{p}$ and the sign of E. The corresponding energies are $E = E_+ = \sqrt{p^2c^2 + m^2c^4}$ for $j = 1,2$ and $E = E_- = -E_+$ for $j = 3,4$. There

however remains a two-fold degeneracy even after E and $\vec{p}$ have been specified, which may be traced to two possible spin projections, to be discussed below. The spectrum of energies is unbounded both above and below and continuous except for a gap $(-mc^2, mc^2)$ separating positive from negative energy eigenstates. The presence of negative energy solutions and a spectrum unbounded from below mean that the Dirac equation suffers from some of the same problems as the KG equation. More on this later.

7.2.4 Non-relativistic limit of plane waves

• What happens to the above plane waves in the non-relativistic limit? We consider a situation in which the energy eigenvalue is mostly rest energy and the velocity is small compared to the speed of light, $v \ll c$ or $p/mc \ll 1$. For positive energy solutions (which are our primary interest) this would mean $E = E_+ \approx mc^2$. For negative energy solutions. $E = E_- \approx -mc^2$.

• Recall that the eigenvalue problem (304) for the Dirac spinor $u = (\varphi \;\; \chi)^t$ could be written as

$$\chi = \frac{c\sigma \cdot p}{E + mc^2}\varphi, \quad \varphi = \frac{c\sigma \cdot p}{E - mc^2}\chi \tag{313}$$

For a positive energy solution, We see that the components of χ are suppressed compared to those of φ by a factor of order $p/mc \ll 1$. So χ is called the small component and φ the large component in the non-relativistic limit. In fact, in this limit, the positive energy solutions obtained above tend to the non-relativistic spin wave functions with the lower component playing no role

$$u^{(1)} \to \begin{pmatrix} \uparrow \\ 0 \end{pmatrix} \quad \text{and} \quad u^{(2)} \to \begin{pmatrix} \downarrow \\ 0 \end{pmatrix}. \tag{314}$$

Thus the two degenerate positive energy solutions incorporate the two linearly independent spin projections in the non-relativistic limit. In effect the Dirac spinors for plane waves reduce to Pauli spinors.

• For negative energy solutions, χ dominates over φ in the non-relativistic limit. The degenerate negative energy eigenstates $u^{(3)} \to (0 \;\; \uparrow)^t$ and $u^{(4)} \to (0 \;\; \downarrow)^t$ are again distinguished by their spin projections.

7.2.5 Spin and helicity

• In the non-relativistic limit, degenerate positive energy plane wave solutions of the Dirac equation with fixed momentum $\vec{p}$ differ by their spin projections; ditto for negative energy solutions. This is a reflection of the fact that momentum $\hat{p}$ and spin $\vec{S}$ commute with the non-relativistic free particle hamiltonian and we may use momentum and spin projection to label the different degenerate energy eigenstates ((H, p, S^2, S_z) are commuting observables). This degeneracy persists in the relativistic case and we have seen that energy and momentum commute. We seek an observable that commutes with both energy and momentum and can be used to label the plane wave eigenstates. What about spin? Based on the non-relativistic analogy, it is reasonable to introduce the Dirac spin (vector) operator, the 4×4 matrix (it acts as the identity on translational degrees of freedom)

$$\vec{S} = \frac{1}{2}\hbar\vec{\Sigma} = \frac{1}{2}\hbar \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{pmatrix} \tag{315}$$

The components S_x, S_y and S_z obviously satisfy the angular momentum commutation relations and $S^2 = (3/4)\hbar^2 I$ as for a spin half particle, except that here we have a doubling of the degrees of freedom. The component of spin in any direction, such as S_z, S_x, S_y or $\hat{n}\cdot S$ for any unit vector $\hat{n}$ has the eigenvalues $\pm\hbar/2$ each with two-fold degeneracy.

• The free particle Schrödinger hamiltonian $H = \frac{1}{2m}p^2 \otimes I$ was proportional to the identity in spin space. However, even for a free Dirac particle, the hamiltonian $H = c\alpha\cdot p + \beta mc^2$ is not proportional to the identity in spin space, this situation is forced on us by the relativistic energy momentum dispersion relation which implies α and β cannot be proportional to the identity. A consequence is that the components of spin are in general not conserved in time. Indeed, spin does not commute with the Dirac hamiltonian in general[27]. We find using $[\vec{\sigma}\cdot\vec{p}, \vec{\sigma}] = 2i\vec{\sigma}\times\vec{p}$ that

$$[H, \vec{S}] = \frac{\hbar}{2}[c\alpha\cdot p + \beta mc^2, \vec{\Sigma}] = \frac{\hbar}{2}\begin{pmatrix} 0 & c[\sigma\cdot p, \vec{\sigma}] \\ c[\sigma\cdot p, \vec{\sigma}] & \end{pmatrix} = i\hbar c\vec{\alpha}\times\vec{p}. \tag{316}$$

It is not just the cartesian components of spin that do not in general commute with H, but also the component of spin in any direction $\hat{n}$. We find that

$$[H, \hat{n}\cdot\vec{S}] = -i\hbar c\vec{\alpha}\cdot\hat{n}\times\vec{p}. \tag{317}$$

However, the component of spin in the direction of momentum, which is called helicity $h = \hat{p}\cdot S$ does commute with H and is conserved

$$h = \vec{S}\cdot\hat{p} = \frac{\hbar}{2}\begin{pmatrix} \vec{\sigma}\cdot\hat{p} & 0 \\ 0 & \vec{\sigma}\cdot\hat{p} \end{pmatrix} \;\Rightarrow\; [H, \hat{p}\cdot\vec{S}] = 0. \tag{318}$$

The eigenvalues of helicity are $\pm\hbar/2 = \lambda\hbar$ with $\lambda = \pm\frac{1}{2}$. Thus, we may choose a basis for the two-dimensional subspace of positive energy E_+ plane waves with given momentum $\vec{p}$ in which helicity is also diagonal. However, $u^{(1,2,3,4)}$ are not helicity eigenstates in general, but positive energy helicity eigenstates may be obtained from linear combinations of $u^{(1)}$ and $u^{(2)}$ and negative energy helicity eigenstates from linear combinations of $u^{(3)}$ and $u^{(4)}$. The positive energy helicity eigenstates are obtained by choosing φ to be eigenvectors of $\hat{p}\cdot S$. If we use spherical polar coordinates for $\vec{p} = (p, \theta, \phi)$ we recall (from spin in a $\vec{B}$ field!), that the eigenvectors of $\hat{p}\cdot S$ corresponding to eigenvalues $\pm\hbar/2$ are

$$\varphi_+ = \chi_+ = \begin{pmatrix} \cos\frac{1}{2}\theta \\ e^{i\phi}\sin\frac{1}{2}\theta \end{pmatrix} \quad \text{and} \quad \varphi_- = \chi_- = \begin{pmatrix} e^{-i\phi}\sin\frac{1}{2}\theta \\ -\cos\frac{1}{2}\theta \end{pmatrix} \tag{319}$$

Thus the helicity eigenspinors with positive energy $E = E_+$ are

$$\lambda = +\frac{1}{2}: \;\; u_+ = \begin{pmatrix} \varphi_+ \\ \frac{c\sigma\cdot p}{E_+ + mc^2}\varphi_+ \end{pmatrix} \quad \text{and} \quad \lambda = -\frac{1}{2}: \;\; u_- = \begin{pmatrix} \varphi_- \\ \frac{c\sigma\cdot p}{E_+ + mc^2}\varphi_- \end{pmatrix} \tag{320}$$

Similarly, the negative energy helicity eigenspinors are

$$\lambda = +\frac{1}{2}: \;\; v_+ = \begin{pmatrix} \frac{c\sigma\cdot p}{E_- - mc^2}\chi_+ \\ \chi_+ \end{pmatrix} \quad \text{and} \quad \lambda = -\frac{1}{2}: \;\; v_- = \begin{pmatrix} \frac{c\sigma\cdot p}{E_- - mc^2}\chi_- \\ \chi_- \end{pmatrix} \tag{321}$$

Unlike the component of spin in a general direction, its component in the direction of motion ($\vec{p}$) is in a sense adapted to its own dynamics. So helicity is a very natural observable in addition to being a conserved quantity.

[27] However, the components of spin are conserved in the rest frame where $\vec{p} = 0$.

7.2.6 Dirac equation coupled to an EM field and non-relativistic limit

• In the presence of an external electromagnetic field arising from the potentials $\phi, \vec{A}$, the Dirac equation is modified by the replacements

$$E \to E - e\phi \quad \text{and} \quad \vec{p} \to \vec{\pi} = \vec{p} - e\vec{A} \tag{322}$$

Thus, for a spin half particle of charge e in an electromagnetic field, we get the wave equation

$$(\hat{E} - e\phi)\psi = c\alpha \cdot (\vec{p} - e\vec{A})\psi + mc^2\beta\psi \quad \text{or} \quad i\hbar\frac{\partial\psi}{\partial t} = \left[c\alpha \cdot (p - eA) + e\phi + \beta mc^2\right]\psi \tag{323}$$

In order to examine the non-relativistic limit, we write $\psi = \begin{pmatrix}\varphi \\ \chi\end{pmatrix}$ in terms of the so-called large and small components and get the equation

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\varphi \\ \chi\end{pmatrix} = c\vec{\sigma}\cdot\vec{\pi}\begin{pmatrix}\chi \\ \varphi\end{pmatrix} + mc^2\begin{pmatrix}\varphi \\ -\chi\end{pmatrix} + e\phi\begin{pmatrix}\varphi \\ \chi\end{pmatrix}. \tag{324}$$

• To study the non-relativistic limit, we concentrate on a situation where the energy (or its expectation value) is positive and mostly rest energy $E = mc^2 + \Delta E$ where $\Delta E \ll mc^2$. Change variables to

$$\begin{pmatrix}\varphi \\ \chi\end{pmatrix} = e^{-imc^2t/\hbar}\begin{pmatrix}\tilde{\varphi} \\ \tilde{\chi}\end{pmatrix} \tag{325}$$

where we have in mind that $\tilde{\chi}, \tilde{\varphi}$ are relatively slowly varying in time. Moreover, we anticipate that $\tilde{\chi}$ is relatively small and hope to eliminate it and get a self-contained equation for $\tilde{\varphi}$. But first we get the coupled pair of equations

$$\begin{aligned} i\hbar\partial_t\begin{pmatrix}\tilde{\varphi} \\ \tilde{\chi}\end{pmatrix} &= -2mc^2\begin{pmatrix}0 \\ \tilde{\chi}\end{pmatrix} + c\vec{\sigma}\cdot\vec{\pi}\begin{pmatrix}\tilde{\chi} \\ \tilde{\varphi}\end{pmatrix} + e\phi\begin{pmatrix}\tilde{\varphi} \\ \tilde{\chi}\end{pmatrix} \quad \text{or} \\ i\hbar\frac{\partial\tilde{\varphi}}{\partial t} = c\sigma\cdot\pi\tilde{\chi} + e\phi\tilde{\varphi} \quad &\text{and} \quad i\hbar\frac{\partial\tilde{\chi}}{\partial t} = -2mc^2\tilde{\chi} + c\sigma\cdot\pi\tilde{\varphi} + e\phi\tilde{\chi} \end{aligned} \tag{326}$$

The equation for χ in the non-relativistic approximation becomes

$$2mc^2\tilde{\chi} \approx c\sigma\cdot\pi\tilde{\varphi}, \tag{327}$$

assuming $\tilde{\chi}$ is slowly varying in time and the rest energy mc^2 is much more than the electric potential energy. To understand the slowly varying assumption, imagine we have an energy eigenstate ψ with $E = mc^2 + \Delta E$, then $i\hbar\,\partial_t\tilde{\chi} = \Delta E\;\tilde{\chi}$ which is small compared to the $2mc^2\tilde{\chi}$ term above. Eliminating

$$\tilde{\chi} = \frac{\vec{\sigma}\cdot\vec{\pi}}{2mc}\tilde{\varphi} \quad \text{we get} \quad i\hbar\frac{\partial\tilde{\varphi}}{\partial t} = \left[\frac{(\vec{\sigma}\cdot(\vec{p} - e\vec{A}))^2}{2m} + e\phi\right]\tilde{\varphi} \tag{328}$$

which we recognize as the Pauli equation for the wave function $\tilde{\varphi}(\vec{r}, t)$ of a non-relativistic spin half charged particle interacting with an electromagnetic field. The latter equation predicts the correct spin magnetic moment of the electron. This gives us some confidence in the correctness of the Dirac equation, at least in the non-relativistic limit and in the manner it incorporates spin.

7.2.7 Lorentz covariance of the Dirac equation

• Consider two frames (observers) related by a Lorentz transformation $x' = \Lambda x$. To implement the principles of relativity, we wish to specify how the wave function in the transformed frame $\psi'(x')$ may be constructed from the wave function used by the original observer $\psi(x)$, so that both observers can describe the same physical state. For the laws of physics to be the same for both observers, we want to know whether the Dirac equation and the law of local conservation of probability can be written in such a way that they take the same form in both frames.

• As a first step towards examining the transformation of Dirac's equation under Lorentz transformations, we introduce new notation. Recall the local conservation law

$$\frac{1}{c}\partial_t \psi^\dagger \psi + \nabla \cdot \psi^\dagger \vec{\alpha} \psi = 0 \quad \text{or} \quad \partial_\mu j^\mu = 0 \quad \text{where} \quad j^\mu = (\psi^\dagger \psi, \psi^\dagger \vec{\alpha} \psi) = \psi^\dagger \beta(\beta, \beta\vec{\alpha})\psi \tag{329}$$

For this equation to be Lorentz invariant, we want to choose the law of transformation $\psi(x) \mapsto \psi'(x')$ in such a way that j^μ transforms as a contra-variant 4-vector. In particular we want $\psi^\dagger\psi$ to transform as the zeroth component of a 4-vector. For this to be the case, ψ could not possibly transform as a scalar, as then $\psi'^\dagger(x')\psi'(x') = \psi^\dagger(x)\psi(x)$ which is not the way the zeroth component of a four vector transforms.

• To find the appropriate transformation law for ψ, it is convenient to define the 'Pauli adjoint spinor' $\bar{\psi} = \psi^\dagger\gamma^0$ and four new Dirac γ-matrices $\gamma^\mu = (\gamma^0, \gamma^1, \gamma^2, \gamma^3)$

$$\gamma^0 = \beta \quad \text{and} \quad \gamma^i = \beta\alpha_i \tag{330}$$

so that the conserved probability density and current density may be written

$$j^\mu = \bar{\psi}\gamma^\mu\psi. \tag{331}$$

$\bar{\psi} = \psi^\dagger\gamma^0$ is interesting since unlike $\psi^\dagger\psi$, $\bar{\psi}\psi$ turns out to be Lorentz invariant. Despite appearances, γ^μ is not a four-vector. The γ-matrices are constant matrices, just like α_i and β. There is only one 4×4 representation of Dirac matrices up to unitary equivalence (change of basis in Dirac spinor space). For simplicity, we use the same basis in all frames and take the same set of γ-matrices in every frame of reference[28]. One checks that they anti-commute in pairs and $(\gamma^0)^2 = -(\gamma^i)^2 = 2I$. So their anti-commutation relations may be written succinctly in terms of the (inverse) Minkowski metric

$$\{\gamma^\mu, \gamma^\nu\} \equiv [\gamma^\mu, \gamma^\nu]_+ = 2\eta^{\mu\nu} I. \tag{332}$$

The invariance of γ-matrices under Lorentz transformations is consistent with the fact that the Minkowski metric is unchanged under Lorentz transformations. While γ^0 is hermitian, γ^i are anti-hermitian, they are all traceless.

• In Dirac's basis, the γ-matrices are

$$\gamma^0 = \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \quad \text{and} \quad \gamma^i = \beta\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ -\sigma_i & 0 \end{pmatrix}. \tag{333}$$

[28] One could choose *different* γ matrices in each frame $\gamma^\mu(\Lambda) = U(\Lambda)\gamma^\mu U(\Lambda)^{-1}$, but this is an unnecessary complication and still would not imply that the γ^μ transform as the components of a four-vector.

• The advantage of the γ^μ over α_i, β is that now Dirac's equation can be written in terms of $p_\mu = i\hbar\partial_\mu$, whose behavior under Lorentz transformations is known. The Dirac equation

$$i\hbar\frac{\partial\psi}{\partial t} + ci\hbar\alpha_i\partial_i\psi - \beta mc^2\psi = 0 \tag{334}$$

upon multiplying by the non-singular matrix β/c becomes

$$i\hbar\left(\gamma^0\partial_0\psi + \gamma^i\partial_i\psi\right) - mc\psi = 0 \quad \text{or} \quad (i\hbar\gamma^\mu\partial_\mu - mc)\,\psi = 0 \quad \text{or} \quad (\gamma^\mu p_\mu - mc)\,\psi = 0 \tag{335}$$

Sometimes the Feynman slash notation $\not{\partial} = \gamma^\mu\partial_\mu$ is used to write the Dirac equation as $(i\hbar\not{\partial} - mc)\psi = 0$. Since γ^μ does not transform as a 4-vector, $\gamma^\mu p_\mu$ is not Lorentz invariant. So far, we only introduced new notation. Contraction of indices does not *in itself* imply that the Dirac equation is Lorentz invariant.

• Note that the free particle Dirac equation is manifestly space- and time-translation invariant, as neither x nor t appears explicitly in the hamiltonian, indeed both $\hat{P}$ and $\hat{E}$ commute with $\hat{H}$.

• Now we want to demand that the Dirac equation take the same form in frames related by Lorentz transformations. The question is whether we can prescribe suitable rules for the transformation of the Dirac spinor $\psi(x)$ so that the Dirac equation is Lorentz invariant. Let us make a Lorentz transformation $x' = \Lambda x$ or $x'^\mu = \Lambda^\mu_\nu x^\nu$ so that $x = \Lambda^{-1}x'$ and

$$\frac{\partial x'^\mu}{\partial x^\nu} = \Lambda^\mu_\nu \quad \text{and} \quad \frac{\partial x^\nu}{\partial x'^\mu} = (\Lambda^{-1})^\nu_\mu. \tag{336}$$

Under this Lorentz transformation $\psi(x) \mapsto \psi'(x')$. Since the Dirac equation is linear we suppose that the new spinor wave function is related to the old one by some non-singular linear transformation so that its linearity may be preserved. Let $S(\Lambda)$ be a 4×4 matrix acting on the old Dirac spinor, then

$$\psi'(x') = S(\Lambda)\psi(x) \quad \text{and} \quad \psi(x) = S(\Lambda)^{-1}\psi'(x'). \tag{337}$$

• If the Dirac equation takes the same form, then we must have in the old and new frames:

$$(i\hbar\gamma^\mu\partial_\mu - mc)\psi(x) = 0 \quad \text{and} \quad (i\hbar\gamma^\mu\partial'_\mu - mc)\psi'(x') = 0. \tag{338}$$

Can we choose $S(\Lambda)$ appropriately so that the former implies the latter?

• Writing $\partial'_\mu = \frac{\partial}{\partial x'^\mu} = \frac{\partial x^\nu}{\partial x'^\mu}\frac{\partial}{\partial x^\nu} = (\Lambda^{-1})^\nu_\mu\partial_\nu$ the Dirac equation in the new frame becomes

$$(i\hbar\gamma^\mu(\Lambda^{-1})^\nu_\mu\partial_\nu - mc)S(\Lambda)\psi(x) = 0. \quad \text{or} \quad (i\hbar S(\Lambda)^{-1}\gamma^\mu S(\Lambda)(\Lambda^{-1})^\nu_\mu\partial_\nu - mc)\psi(x) = 0 \tag{339}$$

on multiplying by $S(\Lambda)^{-1}$. For this to be implied by the Dirac equation in the old variables, we need

$$S(\Lambda)^{-1}\gamma^\mu S(\Lambda)(\Lambda^{-1})^\nu_\mu = \gamma^\nu \qquad \text{or} \qquad S(\Lambda)^{-1}\gamma^\mu S(\Lambda) = \Lambda^\mu_\nu\gamma^\nu. \tag{340}$$

The question is whether we can find a Λ-dependent 4×4 matrix $S(\Lambda)$ with this property.

• Given an infinitesimal Lorentz transformation $\Lambda^\mu_\nu \approx \delta^\mu_\nu + \omega^\mu_\nu$ (ω are infinitesimal real parameters) it is possible to show that the matrix that implements the Lorentz transformation on Dirac spinors is[29]

$$S(\Lambda) \approx I - \frac{i}{4}\sigma^{\mu\nu}\omega_{\mu\nu} \quad \text{where} \quad \sigma^{\mu\nu} = \frac{i}{2}[\gamma^\mu, \gamma^\nu] \quad \text{and} \quad S(\Lambda)^{-1} \approx I + \frac{i}{4}\sigma^{\mu\nu}\omega_{\mu\nu}. \tag{341}$$

[29] And $S(\Lambda) = \exp -\frac{i}{4}\sigma_{\mu\nu}\omega^{\mu\nu}$ for the corresponding finite transformation.

Let us sketch why this $S(\Lambda)$ satisfies $S^{-1}\gamma^\mu S = \Lambda^\mu_\nu \gamma^\nu$. First, for an infinitesimal LT, $\omega^{\mu\nu}$ are small and we can certainly write $S(\Lambda) \approx I - \frac{i}{4}\sigma^{\mu\nu}\omega_{\mu\nu}$ for some constant 4×4 matrices $\sigma^{\mu\nu}$ with $\mu,\nu = 0,1,2,3$. Moreover, the condition that Λ preserve the metric $\Lambda^\mu_\rho \Lambda^\nu_\sigma \eta_{\mu\nu} = \eta_{\rho\sigma}$ implies that $\omega_{\mu\nu}$ is anti-symmetric

$$(\delta^\mu_\rho + \omega^\mu_\rho)(\delta^\nu_\sigma + \omega^\nu_\sigma)\eta_{\mu\nu} = \eta_{\rho\sigma} \quad \Rightarrow \quad \omega_{\rho\sigma} + \omega_{\sigma\rho} = 0. \tag{342}$$

Thus, the part of $\sigma^{\mu\nu}$ that is symmetric in μ and ν, does not contribute to $S(\Lambda)$ and we may take $\sigma^{\mu\nu}$ to be anti-symmetric in μ,ν. The commutator $[\gamma^\mu,\gamma^\nu]$ is anti-symmetric in μ,ν and it is checked by a direct calculation that $S^{-1}\gamma^\mu S = \Lambda^\mu_\nu\gamma^\nu$ up to terms quadratic in ω. For this, use is made of the identity

$$[\gamma^\alpha,[\gamma^\mu,\gamma^\nu]] = 4(\eta^{\alpha\mu}\gamma^\nu - \eta^{\alpha\nu}\gamma^\mu) \tag{343}$$

• Thus, it can be shown that the Dirac equation takes the same form in all frames related by Lorentz transformations that can be built from infinitesimal ones, provided ψ *transforms as a spinor* under Lorentz transformations:

$$\psi'(x') = S(\Lambda)\psi(x) = e^{-\frac{i}{4}\sigma_{\mu\nu}\omega^{\mu\nu}}\psi(x) \approx \left(I - \frac{i}{4}\sigma^{\mu\nu}\omega_{\mu\nu} + \cdots\right)\psi(x). \tag{344}$$

7.2.8 Lorentz invariance of the continuity equation

• Let us now see whether the local conservation law for probability $\partial_\mu j^\mu = 0$ is Lorentz invariant if ψ transforms as a Lorentz spinor

$$\psi'(x') = S(\Lambda)\psi(x) \quad \text{and} \quad \psi'^\dagger(x') = \psi^\dagger(x)\, S(\Lambda)^\dagger. \tag{345}$$

For this we need to check whether $j^\mu(x) = \psi^\dagger(x)\gamma^0\gamma^\mu\psi(x)$ transforms as a four vector.

• The transformed probability and current density are

$$j'^\mu = \psi'^\dagger(x')\gamma^0\gamma^\mu\psi'(x') = \psi^\dagger(x)S^\dagger\gamma^0\gamma^\mu S\psi(x) = \psi^\dagger S^\dagger\gamma^0 S S^{-1}\gamma^\mu S\psi(x) = \psi^\dagger S^\dagger\gamma^0 S\Lambda^\mu_\nu\gamma^\nu\psi(x). \tag{346}$$

where use has been made of $S^{-1}\gamma^\mu S = \Lambda^\mu_\nu\gamma^\nu$. The question is whether $j'^\mu(x') = \Lambda^\mu_\nu j^\nu(x)$?

• For this to be the case, we need to show that[30]

$$S^\dagger\gamma^0 S = \gamma^0 \quad \text{or} \quad \gamma^0 S^\dagger\gamma^0 = S^{-1}. \tag{347}$$

We will show that $S^\dagger\gamma^0 S = \gamma^0$ for infinitesimal L.T. We first observe that as $\omega_{\mu\nu}$ are real,

$$S = I - \frac{i}{4}\sigma^{\mu\nu}\omega_{\mu\nu} \quad \Rightarrow \quad S^\dagger \approx I + \frac{i}{4}(\sigma^{\mu\nu})^\dagger\omega_{\mu\nu} \quad \text{where} \quad \sigma^{\mu\nu} = \frac{i}{2}[\gamma^\mu,\gamma^\nu] \tag{348}$$

It can be checked that σ^{ij} are hermitian while σ^{0i} are anti-hermitian. Thus we can write

$$S^\dagger \approx I + \frac{i}{4}(\sigma^{ij}\omega_{ij} - \sigma^{0i}\omega_{0i} - \sigma^{i0}\omega_{i0}) \quad \text{and} \quad S^{-1} = I + \frac{i}{4}\left(\sigma^{ij}\omega_{ij}\sigma^{0i}\omega_{0i} + \sigma^{i0}\omega_{i0}\right). \tag{349}$$

More over, γ^0 commutes with σ^{ij} while it anti-commutes with σ^{0i} and so also with σ^{i0} (show this!).

[30] Note that in general $S(\Lambda)$ is not unitary. It is unitary for rotations, but not for boosts.

• With these facts, we may now calculate to leading order in ω

$$\begin{aligned}\gamma^0 S^\dagger \gamma^0 &\approx \gamma^0 I + \frac{i}{4}\gamma^0\left[\sigma^{ij}\omega_{ij} - \sigma^{0i}\omega_{0i} - \sigma^{i0}\omega_{i0}\right]\gamma^0 \\ &= \left[\gamma^0 + \frac{i}{4}\left(\sigma^{ij}\omega_{ij}\gamma^0 + \sigma^{0i}\omega_{0i}\gamma^0 + \sigma^{i0}\omega_{i0}\gamma^0\right)\right]\gamma^0 = S^{-1}(\gamma^0)^2 = S^{-1} \qquad (350)\end{aligned}$$

Thus we have shown $\gamma^0 S^\dagger \gamma^0 \approx S^{-1}$ or $S^\dagger \gamma^0 S \approx \gamma^0$ for infinitesimal LT. A similar proof of $S^\dagger \gamma^0 S = \gamma^0$ also works for finite Lorentz transformations where $S(\Lambda) = \exp -\frac{i}{4}\sigma^{\mu\nu}\omega_{\mu\nu}$. It follows that the current transforms as a contravariant four vector. Hence the law of conservation of probability $\partial_\mu j^\mu = 0$ is Lorentz invariant!

7.2.9 Dirac equation in a Coulomb potential: relativistic corrections

• The mean speed of an electron in the hydrogen atom is of order $\alpha c = \frac{e^2}{4\pi\epsilon_0 \hbar}$. So $\beta = v/c \sim \alpha \approx 1/137$. Thus, the effects of c being finite are small, so we might treat them in perturbation theory. But they could not be ignored, since discrepancies between the non-relativistic spectrum $E_n = -\mathbb{R}/n^2 = -\frac{mc^2\alpha^2}{2n^2}$ and experimental measurements were found.

• To find relativistic corrections to the hydrogen spectrum, we study energy eigenstates of the Dirac hamiltonian in the spherically symmetric potential $V(r)$ in the rest frame of the nucleus. For a hydrogen atom $V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$, but we will work with a general $V(\vec{r})$ to begin with. It is possible to solve the Dirac equation in a Coulomb potential by separation of variables. However, we will not pursue this approach here. Rather we find the leading corrections to the non-relativistic hamiltonian implied by the Dirac equation. These corrections have interesting physical interpretations and lead to the so-called fine-structure of the hydrogen spectrum. The fine structure effects produce corrections of order $\alpha^4 mc^2$ to the Bohr spectrum which is of order $\alpha^2 mc^2$.

• We look for eigenstates with energies a little more than the electron rest energy $\mathcal{E} = mc^2 + E$ where $E \ll mc^2$. Writing the Dirac equation $i\hbar\partial_t\Psi = (c\alpha\cdot p + \beta mc^2 + V)\Psi$ in terms of two-component spinors,

$$\Psi(\vec{r},t) = e^{-i\mathcal{E}t/\hbar}\begin{pmatrix}\varphi(\vec{r})\\ \chi(\vec{r})\end{pmatrix} \quad\Rightarrow\quad E\begin{pmatrix}\varphi\\ \chi\end{pmatrix} = \begin{pmatrix}VI & c\sigma\cdot p\\ c\sigma\cdot p & (V-2mc^2)I\end{pmatrix}\begin{pmatrix}\varphi\\ \chi\end{pmatrix} \qquad (351)$$

we get the system

$$V\varphi + c\sigma\cdot p\,\chi = E\,\varphi \quad\text{and}\quad c\sigma\cdot p\,\varphi - (2mc^2 - V)\chi = E\,\chi. \qquad (352)$$

In the non-relativistic limit, the electric potential energy from $V(r)$ as well as E are small compared to mc^2, so we expect χ to be suppressed relative to φ by a factor of order v/c. But rather than make any approximation, we eliminate χ by expressing it in terms of φ

$$\chi = (2mc^2 + E - V(r))^{-1} c(\sigma\cdot p)\varphi \qquad (353)$$

Here $(2mc^2 + E - V(r))$ is a diagonal operator in position space, and we have its inverse appearing above.

• Thus the self-consistent equation for φ prior to making any approximation is

$$c(\sigma\cdot p)(2mc^2 + E - V)^{-1} c\sigma\cdot p\varphi + V\varphi = E\,\varphi$$

$$\text{or} \quad \frac{1}{2m}(\sigma\cdot p)\left[1+\frac{E-V}{2mc^2}\right]^{-1}(\sigma\cdot p)\varphi + V\varphi = E\,\varphi. \tag{354}$$

We treat the electric potential energy and E as small compared $2mc^2$ and expand the inverse in a series keeping only the first two terms to get (the 'hamiltonian' operator H_E below is hermitian)

$$H_E\,\varphi = \left[\left(\frac{p^2}{2m}+V\right) - \frac{1}{2m}(\sigma\cdot p)\frac{(E-V)}{2mc^2}(\sigma\cdot p)\right]\varphi \approx E\,\varphi. \tag{355}$$

In the n.r. limit $c\to\infty$, the second term in H_E drops out and we recover Pauli's equation for two component spinors. The leading departure from the n.r. limit is obtained by analyzing this new term. The part of this term involving E is written

$$-\frac{1}{4m^2c^2}E(\sigma\cdot p)^2 = -\frac{1}{8m^2c^2}(p^2E+Ep^2). \tag{356}$$

• The part involving the potential is is rewritten using $\vec{p}V(\vec{r}) = V(\vec{r})\vec{p} - i\hbar\vec{\nabla}V = V\vec{p} + (\vec{p}V)$. We have

$$(\sigma\cdot p)V(\sigma\cdot p) = (\vec{\sigma}\cdot(\vec{p}V))(\sigma\cdot p) + Vp^2 \tag{357}$$

Though the lhs is manifestly hermitian, the two terms on the rhs are *not individually* hermitian (though their sum is!). Since these two terms contribute to different physical processes, we would like to write each in a manifestly hermitian form. We may do so by adding the adjoint and dividing by two:

$$(\sigma\cdot p)V(\sigma\cdot p) = \frac{1}{2}\left(Vp^2+p^2V\right) + \frac{1}{2}\left[(\sigma\cdot(pV))(\sigma\cdot p) - (\sigma\cdot p)(\sigma\cdot(\vec{p}V))\right] \tag{358}$$

Show that the adjoint of $(\sigma\cdot(pV))(\sigma\cdot p)$ is as indicated. Now use $(\sigma\cdot a)(\sigma\cdot b) = a\cdot b + i\sigma\cdot a\times b$ to write this as

$$(\sigma\cdot p)V(\sigma\cdot p) = \frac{1}{2}\left(Vp^2+p^2V\right) + \frac{1}{2}\left[(pV)\cdot p - p\cdot(pV) + i\sigma\cdot(pV)\times p - i\sigma\cdot p\times(pV)\right]. \tag{359}$$

Furthermore, we simplify

$$\vec{\sigma}\cdot(\vec{p}V)\times\vec{p} - \vec{\sigma}\cdot\vec{p}\times(\vec{p}V) = 2\vec{\sigma}\cdot(\vec{p}V)\times\vec{p} \quad\text{and}\quad (pV)\cdot p - p\cdot(pV) = -(p^2V) = \nabla^2V. \tag{360}$$

Thus

$$(\sigma\cdot p)V(\sigma\cdot p) = \frac{1}{2}\left(Vp^2+p^2V\right) + \frac{1}{2}\left[\nabla^2V + 2i\vec{\sigma}\cdot(\vec{p}V)\times\vec{p}\right]. \tag{361}$$

So the hamiltonian becomes

$$H_E = \frac{p^2}{2m} + V - \frac{1}{8m^2c^2}\left(p^2E + Ep^2 - Vp^2 - p^2V\right) + \frac{\hbar^2}{8m^2c^2}\nabla^2V + \frac{\hbar}{4m^2c^2}\vec{\sigma}\cdot(\vec{\nabla}V)\times\vec{p}. \tag{362}$$

Since the 3$^{\text{rd}}$ term is suppressed by $1/c^2$ we may approximate $(E-V)\,\varphi$ by its non-relativistic value $\frac{p^2}{2m}\varphi$. So, at leading order beyond the n.r. limit, we have (writing H for H_E as E no longer appears in it)

$$H\varphi = \left[\frac{p^2}{2m} + V(\vec{r}) - \frac{p^4}{8m^3c^2} + \frac{\hbar^2}{8m^2c^2}\nabla^2V + \frac{\hbar}{4m^2c^2}\vec{\sigma}\cdot(\vec{\nabla}V)\times\vec{p}\right]\varphi = E\varphi. \tag{363}$$

We recognize $\frac{p^4}{8m^3c^2}$ as arising from expanding the square-root $(m^2c^4+p^2c^2)^{\frac{1}{2}} = mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \cdots$. But interestingly, the Dirac equation implies two additional relativistic corrections (at order $1/c^2$), that are absent in this expansion. In particular, the last term is a spin-dependent energy, which is absent in the n.r. hydrogen hamiltonian. Thus, it is possible to distinguish between the relativistic corrections predicted by the Dirac equation from those predicted by the KG equation or its 'square-root' $i\hbar\partial_t\psi = \sqrt{m^2c^4 - \hbar^2c^2\nabla^2}\psi$. Of course, the KG equation and its 'square root' do not incorporate spin half and therefore are somewhat inadequate to describe an electron.

• The relativistic corrections predicted by the Dirac equation simplify for a central potential, where $\nabla V = \hat{r}\partial_r V$ and $\nabla V \cdot \nabla\varphi = \partial_r V \partial_r \varphi$ and $\nabla V \times \vec{p}\varphi = r^{-1}\partial_r V(\vec{r}\times\vec{p})\varphi$. Thus eigenstates must satisfy

$$H\varphi = \left[\frac{p^2}{2m} + V(\vec{r}) - \frac{p^4}{8m^3c^2} + \frac{\hbar^2}{8m^2c^2}(\nabla^2 V) + \frac{1}{2m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\vec{L}\cdot\vec{S}\right]\varphi \approx E\,\varphi. \tag{364}$$

The last three terms in H, are all suppressed by c^{-2} compared to the non-relativistic hamiltonian. They lead to the so-called fine-structure of the hydrogen spectrum. The first of these $H_{\rm rel}$ may be attributed to the relativistic energy momentum dispersion relation. The last term $H_{\rm SO}$ represents energy due to so-called spin-orbit coupling and the penultimate term is another relativistic correction called the Darwin term H_D.

7.2.10 Fine structure of hydrogen spectrum

• If we treat these relativistic corrections as perturbations to $H_0 = \frac{p^2}{2m} + V(r)$, then in first order perturbation theory, they lead to shifts in the energies of unperturbed eigenstates. The Bohr spectrum is of course highly degenerate, for fixed principal quantum number n, there are $2n^2$ linearly independent states degenerate in energy $-\mathbb{R}/n^2$. The first order correction to energies in degenerate perturbation theory is given by the eigenvalues of the matrix of the perturbing hamiltonian within the degenerate subspace. To find the matrix elements of the perturbing hamiltonians $H_D, H_{\rm SO}, H_{\rm rel}$ within in the degenerate subspace of fixed n, we must pick a basis for that subspace. A basis for the degenerate subspace can be chosen as common eigenstates of the pairwise commuting operators H_0, L^2, L_z, S^2, S_z leading to the labels $n, l, m_l, s = \frac{1}{2}, m_s$ corresponding to the 'uncoupled' basis. But there is nothing sacred about this basis. We could also choose within a degenerate energy eigenspace a basis in which H_0, J^2, J_z, L^2, S^2 are diagonal, leading to the labels njm_jls.

• For hydrogen, $V(r) = -ke^2/r$ where $k = 1/4\pi\epsilon_0$. Since $\nabla^2\frac{1}{r} = -4\pi\delta^3(\vec{r})$ we find

$$H_{\rm Darwin} = \frac{\hbar^2}{8m^2c^2}(\nabla^2 V) = \frac{\pi k e^2\hbar^2}{2m^2c^2}\delta^3(\vec{r}). \tag{365}$$

Thus the H_D represents a point-like repulsion at the origin. H_D is a spherically symmetric perturbing potential, and it commutes with L^2, L_z, S^2, S_z. So H_D is in fact diagonal in the uncoupled basis for a degenerate subspace of fixed n: $\langle nl'm_l'm_s'|H_D|nlm_lm_s\rangle \propto \delta_{ll'}\delta_{m_lm_l'}\delta_{m_sm_s'}$. Its diagonal matrix elements are its eigenvalues and they are the 1st order shifts to the unperturbed energies. Since $H_D \propto \delta^3(\vec{r})$ the expectation value of H_D vanishes in an unperturbed state whose wave function vanishes at the origin. Since $\psi_{nlm} \propto r^l e^{-r/na_0}$, the Darwin term can

only affect the energies of S-wave states. So for $l = 0$,

$$\Delta E_D = \frac{\pi k e^2 \hbar^2}{2m^2c^2}\langle\psi_{n00}|\delta^3(\vec{r})|\psi_{n00}\rangle = \frac{\pi e^2\hbar^2}{2m^2c^2(4\pi\epsilon_0)}|\psi_{n00}(\vec{0})|^2 \tag{366}$$

Moreover, from tabulated hydrogen wave functions, $|\psi_{n00}(\vec{0})|^2 = |R_{n0}(0)|^2/4\pi = 1/(\pi a_0^3 n^3)$. Thus

$$\Delta E_D = \frac{m(ke^2)^4}{2\hbar^4c^2n^3} = \frac{1}{2}mc^2\alpha^4\frac{1}{n^3}\delta_{l0}. \tag{367}$$

• The perturbation due to relativistic dispersion relation $H_{\rm rel} = -\frac{p^4}{8m^3c^2}$ also commutes with L^2, L_z, S^2, S_z so it is diagonal within each degenerate subspace of H_0. At first order in P.T. it leads to a correction in energies of $\Delta E_{\rm rel} = \langle\psi|H_{\rm rel}|\psi\rangle$ where ψ_{nlm} are the normalized eigenfunctions of the n.r. hydrogen atom. Using hermiticity of p^2 and the fact that $\left(\frac{p^2}{2m} + V\right)\psi = E_n\psi$ where $E_n = -\mathbb{R}/n^2$ for the unperturbed hydrogen eigenstates, we have the first order correction

$$\begin{aligned}\Delta E_{\rm rel} &= -\frac{1}{8m^3c^2}\langle p^2\psi|p^2\psi\rangle = -\frac{1}{2mc^2}\langle\psi|(E-V)^2|\psi\rangle = -\frac{1}{2mc^2}\left[E_n^2 + \langle V^2\rangle - 2E_n\langle V\rangle\right] \\ &= -\frac{1}{2mc^2}\left[E_n^2 + k^2e^4\langle r^{-2}\rangle + 2E_nke^2\langle r^{-1}\rangle\right] \quad \text{where} \quad k = \frac{1}{4\pi\epsilon_0}.\end{aligned} \tag{368}$$

The expectation value of $1/r$ and $1/r^2$ in hydrogen eigenstates can be calculated (the former can also be obtained in a quick and dirty manner from the Bohr model[31]) and the results are (see Liboff or Griffiths)

$$\langle r^{-1}\rangle = \frac{1}{n^2a_0} \quad \text{and} \quad \langle r^{-2}\rangle = \frac{1}{n^3\left(l+\frac{1}{2}\right)a_0^2} \tag{369}$$

The resulting relativistic-p^4 correction to energies at 1st order in PT is (use $a_0 = \frac{\hbar^2}{mke^2}$, $E_n = -\frac{mc^2\alpha^2}{2n^2}$)

$$\Delta E_{\rm rel} = -\frac{1}{2mc^2}\left[E_n^2 + \frac{2E_nmk^2e^4}{n^2\hbar^2} + \frac{(mk^2e^4)^2}{(l+\frac{1}{2})n^3\hbar^4}\right] = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{l+\frac{1}{2}} - 3\right] = -\frac{mc^2\alpha^4}{8n^4}\left[\frac{4n}{l+\frac{1}{2}} - 3\right] \tag{370}$$

Thus, the relativistic correction to energy levels is down by a factor of $\alpha^2 \sim (1/137)^2 \approx 5\times10^{-5}$ compared to the unperturbed energies. So the relativistic corrections are of order 10^{-4} – 10^{-5} eV.

• For the Coulomb potential, the perturbation due to spin-orbit coupling is[32]

$$H_{\rm SO} = \frac{ke^2}{2m^2c^2}\frac{1}{r^3}\vec{L}\cdot\vec{S}. \tag{371}$$

[31] $E = T+V = \frac{1}{2}mv^2 - ke^2/r$, $mv^2/r = ke^2/r^2$ and $mvr = n\hbar$ give $V_n = -2T_n$. So $-ke^2\langle r^{-1}\rangle = -ke^2/n^2a_0$.

[32] The spin-orbit energy can be motivated by a classical model, by considering the magnetic dipole energy $H = -\mu\cdot B$ of the electron spin in the magnetic field $\vec{B}$ produced by the proton. In the electron rest frame, the proton goes round it uniformly in a horizontal circle, producing in effect a circular current loop of radius r and current $I = e/T$ where e is the proton charge and T is the period. The magnetic field so produced at the electron is $B = \mu_0 I/2r = \mu_0 e/2rT$ pointing vertically upwards. This B is proportional to the angular momentum of the electron, in the rest frame of the proton, which also points vertically, $\vec{L} = mvr = 2\pi mr^2/T$. So $\vec{B} = \frac{\mu_0 e\vec{L}}{4\pi mr^3} = \frac{ke\vec{L}}{mc^2r^3}$. On the other hand, the electron spin magnetic moment is $\vec{\mu} = (-eg/2m)\vec{S}$ where $g \approx 2$. Combining these one gets a spin-orbit energy $H = -\mu\cdot B = \frac{ke^2}{m^2c^2r^3}\vec{L}\cdot\vec{S}$. The result from this simple-minded calculation is twice as big as that obtained from the Dirac equation. The discrepancy was explained by Thomas and is due to fact that the electron's rest frame is not an inertial frame compared to the proton rest frame.

$H_0 = \frac{p^2}{2m} + V(r)$ and L^2, L_z, S^2, S_z are simultaneously diagonalizable. But $L \cdot S$ does not commute with L_z nor S_z though it does commute with any function of the radial coordinate. So m_l, m_s are no-longer good quantum numbers in the presence of spin orbit coupling. However, $\vec{J} = \vec{L} + \vec{S}$ does commute with L^2, S^2 and $\vec{L} \cdot \vec{S}$. So $H_{\rm SO}$ is diagonal in the simultaneous eigenbasis of J^2, J_z, L^2 and S^2. So we use the coupled basis $|n, j, l, s, m_j\rangle$ instead of the uncoupled one $|n, l, m_l, s, m_s\rangle$. In the coupled basis, both H_0 and $H_{\rm SO}$ are diagonal. So the shifts in energy due to spin-orbit coupling is given by the expectation value of $H_{\rm SO}$ in state $|njm_jls\rangle$

$$L \cdot S|njlm_j\rangle = \frac{\hbar^2}{2}\left(j(j+1) - l(l+1) - \frac{3}{4}\right)|njlm_j\rangle. \tag{372}$$

$L \cdot S$ has eigenvalue zero for S-wave states so there is no spin-orbit correction to the energy for $l = 0$. Moreover, the expectation value of $1/r^3$ in the same unperturbed eigenstates is

$$\left\langle njlm_j \left| \frac{1}{r^3} \right| njlm_j \right\rangle = \frac{1}{l(l+\frac{1}{2})(l+1)n^3a_0^3}, \quad \text{for} \quad l \neq 0. \tag{373}$$

Thus the spin-orbit correction to energies at first order in perturbation theory is ($a_0 = \frac{\hbar^2}{mke^2}$)

$$\begin{aligned} \Delta E_{\rm SO} &= \frac{ke^2}{2m^2c^2}\frac{\hbar^2[j(j+1) - l(l+1) - 3/4]}{2l(l+\frac{1}{2})(l+1)n^3a_0^3} = \frac{E_n^2}{mc^2}\frac{n[j(j+1) - l(l+1) - 3/4]}{l(l+\frac{1}{2})(l+1)} \\ &= \frac{1}{4}\alpha^4 mc^2 \frac{[j(j+1) - l(l+1) - 3/4]}{n^3 l(l+\frac{1}{2})(l+1)} \quad \text{for} \quad l \neq 0. \end{aligned} \tag{374}$$

The spin-orbit correction vanishes for $l = 0$.

• Let us collect our results so far

$$\begin{aligned} \Delta E_{\rm rel} &= -\frac{mc^2\alpha^4}{8n^4}\left[\frac{4n}{l+\frac{1}{2}} - 3\right], \\ \Delta E_D &= \frac{1}{2}mc^2\alpha^4\frac{1}{n^3}\delta_{l0}, \\ \Delta E_{\rm SO} &= (1-\delta_{l0})\frac{1}{4}\alpha^4 mc^2\frac{[j(j+1) - l(l+1) - 3/4]}{n^3 l(l+\frac{1}{2})(l+1)}. \end{aligned} \tag{375}$$

The fine-structure correction is the sum of these three. For $l = 0$ only ΔE_D and $\Delta E_{\rm rel}$ contribute, so

$$\Delta E^{l=0} = \Delta E_D + \Delta E_{\rm rel} = -\frac{1}{2}mc^2\frac{\alpha^4}{n^2}\left[\frac{1}{n^2}\left(2n - \frac{3}{4}\right) - \frac{1}{n}\right] = -\frac{1}{2}mc^2\frac{\alpha^2}{n^2}\frac{\alpha^2}{n^2}\left[n - \frac{3}{4}\right]. \tag{376}$$

For $l > 0$ only $\Delta E_{\rm SO}$ and $\Delta E_{\rm rel}$ contribute, so

$$\Delta E^{l>0} = \Delta E_{\rm rel} + \Delta E_{\rm SO} = \frac{mc^2\alpha^4}{2n^4}\left[\frac{3}{4} - n\left\{\frac{1}{l+\frac{1}{2}} - \frac{j(j+1) - l(l+1) - 3/4}{2l(l+\frac{1}{2})(l+1)}\right\}\right] = \frac{1}{2}\frac{mc^2\alpha^4}{n^4}\left[\frac{3}{4} - \frac{n}{j+\frac{1}{2}}\right].$$

The last equality follows by noting that $\vec{J} = \vec{L} + \vec{S}$ and $s = \frac{1}{2}$. By the rules for addition of angular momentum, $j = l \pm \frac{1}{2}$ for $l > 0$. Consequently, it is possible to eliminate l in favor of j and one finds the remarkably simple expression given. What is more, this formula reduces to the previous expression for $\Delta E^{l=0}$ when $l = 0$.

• Combining we get a common formula for the hydrogen spectrum including fine structure

$$E_{n,j} = mc^2 - \frac{mc^2\alpha^2}{2n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right) + \cdots\right]. \tag{377}$$

• The energy eigenstates of hydrogen, after including effects of spin-orbit coupling, relativistic p^4-correction and Darwin term, may be labelled by the good quantum numbers n, j, m_j, l, s, while m_l, m_s are no-longer good quantum numbers. However, the energies depend only on n and j. So for fixed n and j, states with different values of m_j and l are degenerate in energy. For fixed n, $l = 0, 1, \cdots, n-1$, $j = l - \frac{1}{2}, l + \frac{1}{2}$ (except when $l = 0$ when $j = \frac{1}{2}$), $m_j = -j, -j+1, \cdots, j-1, j$. The non-relativistic degeneracy among states with a common value of n is partly lifted by relativistic effects. This is called fine structure splitting and its magnitude is controlled by α, which was called the fine-structure constant by Sommerfeld. For fixed 'n', the n levels $j = \frac{1}{2}, 3/2, \cdots, n - \frac{1}{2}$ form a so-called fine structure multiplet. Since the fine-structure correction is negative definite (as the smallest possible value of $n/(j+\frac{1}{2})$ is 1), the net effect of relativistic corrections is to increase the binding energy compared to what one expects based on a non-relativistic treatment.

• It is conventional, following the non-relativistic spectroscopic notation, to denote the energy levels by specifying n, l and j in the form nL_j where L is the letter $S, P, D, F, G \ldots$ standing for[33] $l = 0, 1, 2, 3, 4 \ldots$ e.t.c. So the g.s. is $1S_{\frac{1}{2}}$. m_j is not explicitly indicated.

• In general, within a fine structure multiplet, (fixed n), states with higher j have higher energy (less binding energy). The spectroscopic notation for low-lying hydrogen energy levels are given below in increasing order of energy, with degeneracy indicated by equality.

$$1S_{\frac{1}{2}} \;<\; 2S_{\frac{1}{2}} = 2P_{\frac{1}{2}} \;<\; 2P_{3/2} \;<\; 3S_{\frac{1}{2}} = 3P_{\frac{1}{2}} \;<\; 3P_{3/2} = 3D_{3/2} \;<\; 3D_{5/2}, \ldots \tag{378}$$

These energy levels are additionally degenerate since for each n, l, j, there are $2j+1$ linearly independent degenerate states corresponding to distinct values of m_j. For example, the g.s. $1S_{\frac{1}{2}}$ is doubly degenerate corresponding to $m_j = \pm\frac{1}{2}$. This degeneracy can be broken by an external $\vec{B}$ field (Zeeman effect).

• The fine structure splitting within the $n = 2$ multiplet is $\Delta E = E(2P_{3/2}) - E(2S_{1/2}) = \frac{mc^2\alpha^4}{32} = 4.5 \times 10^{-5}$ eV. A transition between $2P_{3/2}$ and $2S_{1/2}$ therefore corresponds to a spectral line of wave length $\lambda = hc/\Delta E = 2.8$ cm or a frequency 10.9 GHz corresponding to radio or radar waves.

• It is possible to get the hydrogen bound state spectrum by solving the Dirac equation without expanding around the non-relativistic limit. The result is the same as that obtained by Sommerfeld (1916) using the Bohr-Sommerfeld quantization conditions in the old quantum theory

$$E = mc^2\left[1 + \frac{\alpha^2}{\left(n_r + \sqrt{n_\phi^2 - \alpha^2}\right)^2}\right]^{-1/2} \tag{379}$$

where the 'azimuthal' quantum number $n_\phi = (j + \frac{1}{2})$ and the 'radial' quantum number $n_r = n - n_\phi = n - (j + \frac{1}{2})$. When expanded in powers of α for small α, the first three terms

[33] S= sharp, P = principal, D = diffuse, F = fundamental denote the originating level in a spectral emission.

reproduce the rest energy, Bohr spectrum and fine structure corrections obtained above. The fine structure corrections are in good agreement with experimental measurements and there was no known discrepancy till experiments by Lamb and Retherford (1948) showed that the $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ levels were not degenerate, this is called the Lamb shift, it is not accounted for by the Dirac equation. It required a quantum theory of the electromagnetic field to explain the Lamb shift.

7.2.11 Negative energy states, holes and anti-particles

• The negative energy solutions of the Dirac equation have not admitted any physical interpretation. They are problematic since the energy spectrum is not bounded below. An electron at rest is then unstable to radiative decay to indefinitely lower energies, in the process radiating an infinite amount energy.

• To avoid this unobserved instability, Dirac (1929) proposed that the zero energy state (the vacuum) is not the one where all states are empty, but one where the negative energy states are all filled with electrons, one per available state (Pauli exclusion), and the positive energy states are empty. This is as in a multi-electron atom, where the inner shells are all filled with electrons. This vacuum state is called the Dirac vacuum, the filled negative energy states are called the filled Dirac sea. A single electron at rest (say from ionizing a hydrogen atom) would then occupy the positive energy state $E = mc^2, \vec{p} = 0$, and would be stable against radiative decay, since the negative energy states are all filled. Thus the instability problem is addressed. Physically realizable situations are regarded as finite departures from the Dirac vacuum. We specify energy and charge by mentioning their values relative to the Dirac vacuum, which by definition is a zero energy, zero charge state.

For instance, a radiative excitation (induced by a photon of energy $> 2mc^2$) could promote an electron from the Dirac sea to a positive energy state. In this process, we would have both the excited electron and a hole in the sea, this process is called pair creation. The hole could move around the Dirac sea by exchanging places with one of the electrons there. Since the motion of the hole corresponds to the oppositely directed motion of the electron it displaces, holes behave like particles of positive charge. Thus, holes have energy and momentum and behave like particles of positive charge and positive energy and the same mass as electrons. A hole is called an anti-electron or positron. On the other hand, if we had a hole in the Dirac sea, then an electron in a positive energy state could suffer radiative decay, and fall into the hole. As a result, the hole and electron both vanish leaving the Dirac vacuum along with 2 or more photons that are emitted. This process is called electron positron annihilation. Positrons were experimentally observed in cloud chamber experiments by Anderson (1932) and Blackett (1932). Since positrons have opposite electric charge, they bend in the opposite direction to electrons in a constant magnetic field that is applied across the cloud chamber. An annihilation event is identified by two such tracks in a cloud chamber, which meet at a point and abruptly end. At least two photons are produced, which is understandable as a single photon would not conserve momentum (most easily seen in the c.m. frame of the colliding electron and positron). In pair creation, two oppositely bending tracks start all of a sudden from a point. The photons do not leave a track in the cloud chamber since they are uncharged. e^+ e^- pair production from cosmic ray photons was observed when the gamma ray interacted with a nucleus. The nucleus is necessary, again for conservation of momentum.

• In this new interpretation, the number of electrons is not conserved, due to the processes

of pair creating and annihilation, though electric charge is conserved. The Dirac equation by itself is not adequate to describe a system with an indefinite number of particles. For one thing, our interpretation of $\int \psi^\dagger \psi \, d^3x$ as the conserved total probability of finding an electron in the system, would not be consistent, since the number of electrons is not conserved. A new formalism, allowing for creation and annihilation of particles is needed. This is the framework of quantum field theory, which was developed beginning in the 1930s. In the new formalism, there is no need for a filled Dirac sea or for holes in the sea, one directly deals with creation operators for electrons and positrons. However, the physical picture of a filled Dirac sea is still valuable as an aid to thought.

• There are some situations where the contributions of the negative energy solutions of Dirac's equation can be ignored. For instance, we have seen that in the nearly non-relativistic limit, (where energies involved are small compared to electron rest energy 511 KeV) $pc \ll mc^2$, the Dirac equation reduces to the Pauli equation for the upper two components of the Dirac spinor, plus small relativistic corrections.

• Alternatively, suppose we want to build an electron wave packet localized in space with a width of order $|\vec{r}| \lesssim d$, by superposing plane wave solutions of the Dirac equation. The localization in position implies a certain spread of momenta of plane waves that enter the superposition, of order $|p| \lesssim h/d$. It turns out that for localization in position, one necessarily has to include some negative energy plane waves in the superposition, this is seen by Fourier decomposing a wave packet. However, it can be shown that the amplitudes of the negative energy plane waves become appreciable only when their momenta are of order $p \sim mc$. So, as long as $mc \gg \frac{h}{d}$, the negative frequency components contribute negligibly. This is the condition $d \gg \lambda_{Compton} = h/mc$. Thus, as long as we are studying a system where an electron is localized over a region whose linear dimension is large compared to the electron Compton wave length, we may ignore the effects of the negative energy solutions. This condition is satisfied in most of atomic physics, where the electron is localized roughly within a Bohr radius $.5 \times 10^{-10}$ of the nucleus, which is about 20 times its Compton wavelength $2.4 \times 10^{-12} m$. Thus, the predictions of the Dirac equation are accurate in most of atomic physics.