HW #3, Prob. 1, part (ii).

12.1 Time-dependent potentials: general formalism

Consider then the Hamiltonian $\hat{H} = \hat{H}_0 + V(t)$, where all time-dependence enters through the potential $V(t)$. In the **Schrödinger representation**, the dynamics of the system are specified by the time-dependent wavefunction, $|\psi(t)\rangle_{\rm S}$ through the Schrödinger equation $i\hbar\partial_t|\psi(t)\rangle_{\rm S} = \hat{H}|\psi(t)\rangle_{\rm S}$. However, in many cases, and in particular with the current application, it is convenient to work in the **Interaction representation**,[1] defined by

$$|\psi(t)\rangle_{\rm I} = e^{i\hat{H}_0 t/\hbar}|\psi(t)\rangle_{\rm S}$$

where $|\psi(0)\rangle_{\rm I} = |\psi(0)\rangle_{\rm S}$. With this definition, one may show that the wavefunction obeys the equation of motion (exercise)

$$i\hbar\partial_t|\psi(t)\rangle_{\rm I} = V_{\rm I}(t)|\psi(t)\rangle_{\rm I} \tag{12.1}$$

where $V_{\rm I}(t) = e^{i\hat{H}_0 t/\hbar}Ve^{-i\hat{H}_0 t/\hbar}$. Then, if we form the eigenfunction expansion, $|\psi(t)\rangle_{\rm I} = \sum_n c_n(t)|n\rangle$, and contract the equation of motion with a general state, $\langle n|$, we obtain

$$\boxed{i\hbar\dot{c}_m(t) = \sum_n V_{mn}(t)e^{i\omega_{mn}t}c_n(t)\,,} \tag{12.2}$$

[1] Note how this definition differs from that of the **Heisenberg representation**, $|\psi\rangle_{\rm H} = e^{i\hat{H}t/\hbar}|\psi(t)\rangle_{\rm S}$ in which all time-dependence is transferred into the operators.

▷ INFO. The **two-level system** plays a special place in the modern development of quantum theory. In particular, it provides a platform to encode the simplest quantum logic gate, the **qubit**. A classical computer has a memory made up of bits, where each bit holds either a one or a zero. A quantum computer maintains a sequence of qubits. A single qubit can hold a one, a zero, or, crucially, any quantum superposition of these. Moreover, a pair of qubits can be in any quantum superposition of four states, and three qubits in any superposition of eight. In general a quantum computer with n qubits can be in an arbitrary superposition of up to 2^n different states simultaneously (this compares to a normal computer that can only be in one of these 2^n states at any one time). A quantum computer operates by manipulating those qubits with a fixed sequence of quantum logic gates. The sequence of gates to be applied is called a quantum algorithm.

An example of an implementation of qubits for a quantum computer could start with the use of particles with two spin states: $|\downarrow\rangle$ and $|\uparrow\rangle$, or $|0\rangle$ and $|1\rangle$). In fact any system possessing an observable quantity A which is conserved under time evolution and such that A has at least two discrete and sufficiently spaced consecutive eigenvalues, is a suitable candidate for implementing a qubit. This is true because any such system can be mapped onto an effective spin-1/2 system.

Homework #3, Prob. 2.

▷ EXAMPLE: **Dynamics of a driven two-level system:** Let us consider a two-state system with

$$\hat{H}_0 = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}, \qquad V(t) = \begin{pmatrix} 0 & \delta e^{i\omega t} \\ \delta e^{-i\omega t} & 0 \end{pmatrix}.$$

Specifying the wavefunction by the two-component vector, $\mathbf{c}(t) = (c_1(t)\, c_2(t))$, Eq. (12.2) translates to the equation of motion (exercise)

$$i\hbar\partial_t \mathbf{c} = \delta \begin{pmatrix} 0 & e^{i(\omega-\omega_{21})t} \\ e^{-i(\omega-\omega_{21})t} & 0 \end{pmatrix} \mathbf{c}(t)\,,$$

where $\omega_{21} = (E_2 - E_1)/\hbar$. With the initial condition $c_1(0) = 1$, and $c_2(0) = 0$, this equation has the solution,

$$|c_2(t)|^2 = \frac{\delta^2}{\delta^2 + \hbar^2(\omega-\omega_{21})^2/4} \sin^2 \Omega t, \qquad |c_1(t)|^2 = 1 - |c_2(t)|^2\,,$$

where $\Omega = ((\delta/\hbar)^2 + (\omega-\omega_{21})^2/4)^{1/2}$ is known as the **Rabi frequency**. The solution, which varies periodically in time, describes the transfer of probability from state 1 to state 2 and back. The maximum probability of occupying state 2 is a Lorentzian with

$$|c_2(t)|^2_{\max} = \frac{\gamma^2}{\gamma^2 + \hbar^2(\omega-\omega_{21})^2/4}\,,$$

taking the value of unity at resonance, $\omega = \omega_{21}$. There is no divergent denominator.

▷ EXERCISE. Derive the solution from the equations of motion for $\mathbf{c}(t)$. Hint: eliminate c_1 from the equations to obtain a second order differential equation for c_2.

▷ INFO. The dynamics of the driven two-level system finds practical application in the **Ammonia maser**: The ammonia molecule NH_3 has a pyramidal structure with an orientation characterised by the position of the "lone-pair" of electrons sited

on the nitrogen atom. At low temperature, the molecule can occupy two possible states, $|\mathrm{A}\rangle$ and $|\mathrm{S}\rangle$, involving symmetric (S) or an antisymmetric (A) atomic configurations, separated by a small energy splitting, ΔE. (More precisely, along the axis of three-fold rotational symmetry, the effective potential energy of the nitrogen atom takes the form of a double-well. The tunneling of the nitrogen atom through the double well leads to the symmetric and asymmetric combination of states.) In a time-dependent uniform electric field the molecules experience a potential $V = -\boldsymbol{\mu}_{\mathrm{d}} \cdot \mathbf{E}$, where $\mathbf{E} = E\hat{\mathbf{e}}_z \cos\omega t$, and $\boldsymbol{\mu}_{\mathrm{d}}$ denotes the electric dipole moment. Since $\boldsymbol{\mu}_{\mathrm{d}}$ is odd under parity transformation, $P\boldsymbol{\mu}_{\mathrm{d}}P = -\boldsymbol{\mu}_{\mathrm{d}}$, and $P|A\rangle = -|A\rangle$ and $P|S\rangle = |S\rangle$, the matrix elements of the electric dipole moment are off-diagonal: $\langle S|\boldsymbol{\mu}_{\mathrm{d}}|S\rangle = \langle A|\boldsymbol{\mu}_{\mathrm{d}}|A\rangle = 0$ and $\langle S|\boldsymbol{\mu}_{\mathrm{d}}|A\rangle = \langle S|\boldsymbol{\mu}_{\mathrm{d}}|A\rangle \neq 0$.

If we start with all of the molecules in the symmetric ground state, we have shown above that the action of an oscillating field for a particular time can can drive a collection of molecules from their ground state into the antisymmetric first excited state. The ammonia maser works by sending a stream of ammonia molecules, traveling at known velocity, down a tube having an oscillating field for a definite length, so the molecules emerging at the other end are all (or almost all, depending on the precision of ingoing velocity, etc.) in the first excited state. Application of a small amount of electromagnetic radiation of the same frequency to the outgoing molecules will cause some to decay, generating intense radiation and therefore a much shorter period for all to decay, emitting coherent radiation.

Charles Hard Townes 1915- (left) is an American Nobel prize-winning physicist and educator. Townes is known for his work on the theory and application of the maser – microwave amplification by stimulated emission of radiation, on which he got the fundamental patent, and other work in quantum electronics connected with both maser and laser devices. He received the Nobel Prize in Physics in 1964.

#3. Overview, before solution.

At time $t=0$, extra proton $\Rightarrow H'(t) = -\frac{e^2}{r}\theta(t)$.

Sudden approx. says that immediately after the change, the wfn has not changed, still $\psi^{H}_{1s}(r)$.

However, the system now has new eigenfns $\psi^{He}_{n1s}(r)$.

& $\psi^{H}_{1s}(r)$ "gets expanded" in these states.

Probability of being in state $\psi^{He}_{2s}(r)$ is $|\langle \psi^{H}_{1s} | \psi^{He}_{2s} \rangle|^2$. Most got this right.

This will not be zero. (Of course, $\langle \psi^{H}_{1s} | \psi^{H}_{2s} \rangle = 0$.)

Then – 1st order P.T., taking $t \to 0^+$, does not give the same result. Evidently this is not a small perturbation! The potential is doubled.

3. i) The new Hamiltonian will be $H = \frac{p^2}{2m} - \frac{2e^2}{r}$, as we have 2 protons present

The old Hamiltonian was $H = \frac{p^2}{2m} - \frac{e^2}{r}$ $\Rightarrow$ $\boxed{H'(t) = -\frac{e^2}{r}\theta(t)}$ ✓

ii) Starts in $\psi_{1,0,0}$ state of H : $|\psi_1\rangle = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$

Ends in $\psi_{2,0,0}$ state of He, which is Hydrogen-like (so $a_0 \to a_0/2$) : $|\psi_2\rangle = \left(\frac{1}{\pi a_0^3}\right)^{1/2}\left(1-\frac{r}{a_0}\right)e^{-r/a_0}$

Sudden Approximation: $P_{1\to 2} = |\langle\psi_2|\psi_1\rangle|^2 = \left(\frac{1}{\pi a_0^3}\int\left(1-\frac{r}{a_0}\right)e^{-2r/a_0}\,d\Omega\right)^2$

$$\frac{1}{\pi a_0^3}\int\left(1-\frac{r}{a_0}\right)e^{-2r/a_0}\,d\Omega = \frac{1}{\pi a_0^3}\int_0^{\infty}\int_0^{2\pi}\int_0^{\pi}\left(1-\frac{r}{a_0}\right)e^{-2r/a_0} r^2\sin\theta\,d\theta\,d\phi\,dr$$

$$= \frac{4}{a_0^3}\int_0^{\infty}\left(r^2-\frac{r^3}{a_0}\right)e^{-2r/a_0}\,dr \qquad a = -\frac{2}{a_0}$$

From integral table $= \frac{4}{a_0^3}\left[-\frac{a_0 r^2}{2} - \frac{2ra_0^2}{4} - \frac{2a_0^3}{8}\right]e^{-2r/a_0}\Big|_0^{\infty} - \frac{4}{a_0^4}\left[-\frac{a_0 r^3}{2} - \frac{3ra_0^2}{4} - \frac{6a_0^3 r}{8} - \frac{6a_0^4}{16}\right]e^{-2r/a_0}\Big|_0^{\infty}$

$$= +\frac{4}{a_0^3}\left[\frac{a_0^3}{4}\right] - \frac{4}{a_0^3}\left[-\frac{3}{8}a_0^4\right] = -\frac{1}{2}$$

$$\to P_{1\to 2} = \left(-\frac{1}{2}\right)^2 = \frac{1}{4}$$

iii) 1st order time-dependent perturbation theory:

$H'(t) = -\frac{e^2}{r}\theta(t)$

$$a_f(t) = a_{1\to 2}(t) = +\frac{i}{\hbar}\int_0^t \langle\psi_2|\frac{e^2}{r}|\psi_1\rangle\, e^{i\omega_{21}t'}\,dt' \qquad \omega_{21} = \frac{E_f^0 - E_i^0}{\hbar}$$

$$\langle\psi_2|\frac{e^2}{r}|\psi_1\rangle = \frac{4e^2}{a_0^3}\int_0^{\infty}\left(r-\frac{r^2}{a_0}\right)e^{-2r/a_0}\,dr \overset{\text{from integral table}}{=} \frac{4e^2}{a_0^3}\left\{\left[-\frac{a_0 r}{2} - \frac{a_0^2}{4}\right]e^{-2r/a_0} - \frac{1}{a_0}\left[-\frac{a_0 r^2}{2} - \frac{2a_0^2 r}{4} - \frac{2a_0^3}{8}\right]e^{-2r/a_0}\right\}\Big|_0^{\infty}$$

$$= \frac{4e^2}{a_0^3}\left\{+\frac{a_0^2}{4} - \frac{a_0^2}{4}\right\}.$$ Anyway $\int_0^t \ldots dt'$ is proportional to t, going $\to 0$.

$$= 0$$

$\Rightarrow a_{1\to 2}(t) = 0$

$\Rightarrow P_{1\to 2}(t) = |a_{1\to 2}(t)|^2 = 0$

iv) Our result in iii had no time dependence, so if we let $t \to 0$, $P_{1\to 2}(0) = 0$. ✓

This would suggest a transition is impossible, which runs contrary to the result in ii that $P_{1\to 2} = 1/4$.

"perturbation" is not small

This means that in this simplified form we cannot apply perturbation theory. We would need to adapt the Hamiltonian to include the "scattered" electron if perturbation theory was to work.