Lecture 25 (Dec. 6, 2017)

25.1 Degenerate Perturbation Theory

Previously, when discussing perturbation theory, we restricted ourselves to the case where the unperturbed energy levels were not degenerate. We will now consider the case where the unperturbed Hamiltonian has degeneracies. Suppose the eigenstate $|n_0\rangle$ is degenerate with $|k_0\rangle$, i.e., $E_{n,0} = E_{k,0}$. We clearly cannot use the formula from last class for the first-order correction to the eigenstate,

$$|n\rangle = |n_0\rangle + \lambda \sum_{m \neq n} \frac{|m_0\rangle \langle m_0|V|n_0\rangle}{E_{n,0} - E_{m,0}}, \tag{25.1}$$

because the denominator vanishes at $m = k$.

The solution is to restrict our attention to the degenerate subspace and then diagonalize the perturbation on this subspace. Within the subspace of degenerate states of the unperturbed Hamiltonian of energy $E_{n,0}$ (referred to as the *degenerate manifold of* $E_{n,0}$), we diagonalize V. Within this subspace, $H_0 \propto \mathbb{1}$ by definition (since every state in this space has the same energy eigenvalue). Thus, $PH_0P \propto \mathbb{1}$, where P is the projector onto the degenerate subspace, and so PH_0P commutes with PVP. We can then diagonalize the projected V simultaneously with the projected H_0. In the orthonormal basis that diagonalizes PVP, the off-diagonal matrix elements of PVP are zero, so we can return to using the formulas of ordinary perturbation theory. The terms where $E_{n,0} - E_{k,0}$ vanish do not occur, as the numerator also vanishes.

25.1.1 Linear Stark Effect

As an example, consider an atom in an electric field. In the case of a hydrogen atom, we found that the energy of the electron in the atom changed quadratically in the electric field (for small electric field). This was the phenomenon known as the quadratic Stark effect. Now we will discuss a situation in which the energy changes linearly in the applied electric field.

Let us choose $\boldsymbol{E} = E\hat{\boldsymbol{z}}$. Now, we consider the $n = 2$ levels of a hydrogenic atom. There are four degenerate states (ignoring spin) of the form $|n, \ell, m\rangle$, which are

$$\underbrace{|2, 1, 1\rangle, \quad |2, 1, 0\rangle, \quad |2, 1, -1\rangle}_{2p}, \quad \underbrace{|2, 0, 0\rangle}_{2s}. \tag{25.2}$$

Our perturbation is $V = -eEz$. Consider V in the subspace of the four $n = 2$ levels. We need to compute

$$\langle 2, \ell', m'|z|2, \ell, m\rangle. \tag{25.3}$$

Because $[z, J_z] = 0$, we have

$$0 = \langle 2, \ell', m'|(zJ_z - J_z z)|2, \ell, m\rangle = (m - m')\langle 2, \ell', m'|z|2, \ell, m\rangle. \tag{25.4}$$

Thus,

$$\langle 2, \ell', m'|z|2, \ell, m\rangle = 0, \quad \text{if } m' \neq m. \tag{25.5}$$

Note also that under parity, $z \to -z$, so

$$\langle n, \ell, m'|z|n, \ell, m\rangle = 0, \tag{25.6}$$

i.e., we will only find a non-vanishing matrix element for $\ell' \neq \ell$.

Thus, the only non-vanishing matrix elements are

$$\langle 2,1,0|z|2,0,0 \rangle = \langle 2,0,0|z|2,1,0 \rangle^* \,. \tag{25.7}$$

We can compute these entries exactly, because we know the hydrogen atom wavefunctions. Explicitly, we find

$$V = \begin{pmatrix} 0 & 3ea_0E & 0 & 0 \\ 3ea_0E & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \tag{25.8}$$

where a_0 is the Bohr radius. This matrix has eigenvalues $0, 0, \pm 3ea_0E$. Specifically, the states $|2,1,1\rangle$ and $|2,1,-1\rangle$ have no energy shift, while the state $(|2,0,0\rangle + |2,1,0\rangle)/\sqrt{2}$ has shift $+3ea_0E$ and the state $(|2,0,0\rangle - |2,1,0\rangle)/\sqrt{2}$ has shift $-3ea_0E$. This energy shift is linear in the strength of the electric field, hence the effect is called the linear Stark effect.

In general, it may be the case that diagonalizing V in the space of degenerate states does not split the degeneracy. In such a case, we must go to higher order in perturbation theory, until we are able to successfully split the degeneracy, after which point we can proceed by non-degenerate perturbation theory. If PVP does not split the degeneracy, then at the next order we will be considering operators of the form

$$PVP + \sum_{\substack{m \\ E_m \neq E_0}} P \frac{V|m\rangle\langle m|V}{E_0 - E_m} P \,. \tag{25.9}$$

25.2 Time-Dependent Perturbation Theory

We now consider time-dependent perturbations to the Hamiltonian. We begin with the Schrödinger equation,

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle = H|\psi(t)\rangle \,, \tag{25.10}$$

with

$$H = H_0 + H_1(t) \,, \tag{25.11}$$

where H_0 has a known spectrum and H_1 is some weak, time-dependent perturbation.

We may want to compute the probability that the initial H_0 eigenstate $|i\rangle$ transitions to the final H_0 eigenstate $|f\rangle$ in time t. If $H_1 = 0$, then the solution to the Schrödinger equation is of the form

$$|\psi(t)\rangle = \sum_n c_n e^{-iE_{n,0}t/\hbar}|n_0\rangle \,, \tag{25.12}$$

where the c_n are time-independent. If $H_1(t) \neq 0$, then there is additional time dependence coming from the perturbation; we can still expand any state in the basis of unperturbed energy eigenstates, so we can write the solutions to the Schrödinger equation in the form

$$|\psi(t)\rangle = \sum_n c_n(t) e^{-iE_{n,0}t/\hbar}|n_0\rangle \,, \tag{25.13}$$

where the coefficients $c_n(t)$ are now functions of time. We could absorb the time dependence in the exponential into the coefficients $c_n(t)$, but it is notationally convenient not to do so.

Applying the Schrödinger equation to Eq. (25.13),

$$(i\hbar\partial_t - H_0 - H_1)|\psi(t)\rangle = 0 \,, \tag{25.14}$$

we are left with

$$\sum_n [i\hbar \partial_t c_n(t) - H_1(t) c_n(t)] e^{-iE_{n,0}t/\hbar} |n_0\rangle = 0 \,. \tag{25.15}$$

Taking the inner product with

$$\langle f_0 | e^{iE_{f_0}t/\hbar} \,, \tag{25.16}$$

we arrive at

$$i\hbar \frac{\mathrm{d}c_f}{\mathrm{d}t} = \sum_n \langle f_0 | H_1(t) | n_0 \rangle e^{i\omega_{fn}t} c_n(t) \,, \tag{25.17}$$

where

$$\omega_{fn} = \frac{E_{f,0} - E_{n,0}}{\hbar} \,. \tag{25.18}$$

We can recognize this as a concrete example of working in the interaction picture; we have removed the time-dependence due to the unperturbed Hamiltonian, so the only time-dependence we see remaining comes from H_1.

What we have done so far is exact. We now assume that $|\psi(t = t_0)\rangle = |i\rangle$ and solve perturbatively in H_1. In the initial state,

$$c_n(t = t_0) = \delta_{ni} \,. \tag{25.19}$$

At first order, we then have

$$\frac{\mathrm{d}c_f}{\mathrm{d}t} = -\frac{i}{\hbar} \langle f_0 | H_1(t) | i_0 \rangle e^{i\omega_{fi}t} \,, \tag{25.20}$$

which can be integrated to yield

$$c_{fi} = \delta_{fi} - \frac{i}{\hbar} \int_{t_0}^t \mathrm{d}t' \, \langle f_0 | H_1(t') | i_0 \rangle e^{i\omega_{fi}t'} \,. \tag{25.21}$$

This is the transition amplitude between the states $|i_0\rangle$ and $|f_0\rangle$ to first order in the perturbation H_1.

25.2.1   SHO in a Time-Dependent Electric Field

Consider a simple harmonic oscillator in a time-dependent electric field

$$\epsilon(t) = \epsilon_0 e^{-t^2/\tau^2} \,. \tag{25.22}$$

The Hamiltonian is

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 - ex\epsilon(t) \,. \tag{25.23}$$

If our initial state is the ground state, $|i\rangle = |0\rangle$, then we want to compute the transition amplitude to the state $|n\rangle$ after a time t. To first order, we find this probability to be

$$P_{0\to n}(t) = \frac{1}{\hbar^2} \left| \int_{-\infty}^t \mathrm{d}t' \, \langle n | H_1(t') | 0 \rangle e^{i\omega n t'} \right|^2 \,, \quad n \neq 0 \,. \tag{25.24}$$

Here, we have used $E_{n,0} - E_{0,0} = \omega n$ for the SHO. In the limit $t \to \infty$, this becomes

$$P_{0\to n}(t \to \infty) = \frac{1}{\hbar^2} \left| \int_{-\infty}^\infty \mathrm{d}t' \, \langle n | H_1(t') | 0 \rangle e^{i\omega n t'} \right|^2 \,, \quad n \neq 0 \,. \tag{25.25}$$

We can write the perturbation in the form

$$H_1(t) = -e\epsilon(t)\sqrt{\frac{\hbar}{2m\omega}}\left(a + a^\dagger\right), \tag{25.26}$$

and so we find

$$P_{0\to n}(t\to\infty) = \frac{e^2}{2m\omega\hbar}\left|\int_{-\infty}^{\infty}\mathrm{d}t'\,\epsilon(t')e^{i\omega nt'}\langle n|\left(a+a^\dagger\right)|0\rangle\right|^2, \quad n\neq 0. \tag{25.27}$$

Because $a|0\rangle = 0$ and $a^\dagger|0\rangle = |1\rangle$, we see that to this order, $P_{0\to n} = 0$ for $n > 1$. For $n = 1$, we find

$$\begin{aligned}
P_{0\to 1}(t\to\infty) &= \frac{e^2}{2m\hbar\omega}\left|\int_{-\infty}^{\infty}\mathrm{d}t'\,e^{i\omega t'}\epsilon_0 e^{-t^2/\tau^2}\right|^2 \\
&= \frac{\pi e^2\epsilon_0^2}{2m\hbar\omega}\tau^2 e^{-\omega^2\tau^2/4}.
\end{aligned} \tag{25.28}$$

If we work to higher orders, we will find nonzero transitions to higher excitation states $|n\rangle$. Note that $P_{0\to 1}$ is small both for $\omega\tau \gg 1$ (slow pulse) and $\omega\tau \ll 1$ (fast pulse), and peaks when $\omega\tau \sim 1$.

25.2.2   Second-Order Transition Amplitude

Iterating the solution for $c_n(t)$ to next order, we find

$$c_n^{(2)}(t) = \left(-\frac{i}{\hbar}\right)^2\sum_m\int_{t_0}^t\mathrm{d}t'\int_{t_0}^{t'}\mathrm{d}t''\,e^{i\omega_{nm}t'}H_{1,nm}(t')e^{i\omega_{mi}t''}H_{1,mi}(t''), \tag{25.29}$$

where

$$H_{1,jk}(t) = \langle j|H_1(t)|k\rangle. \tag{25.30}$$

Incorporating the higher-order terms, the transition probability is

$$P_{i\to n} = \left|c_n^{(1)}(t) + c_n^{(2)}(t) + \cdots\right|^2. \tag{25.31}$$

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