# Lecture 3


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After covering an important identity regarding differentiating exponentials of operators, this lecture will be entirely dedicated to deriving Rayleigh-Schrödinger perturbation theory, and, time-permitting, time-dependent perturbation theory.


## I. DIFFERENTIATING EXPONENTIALS

For homework, you will need the following identity for differentiating the exponential of an operator

$$\frac{d}{dt}e^{A(t)} = \int_0^1 ds e^{(1-s)A(t)} \frac{dA(t)}{dt} e^{sA(t)}. \tag{1}$$

To prove this, let's consider a more general identity,

$$e^{-sA(t)} \frac{d}{dt} e^{sA(t)} = \int_0^s ds' e^{-s'A(t)} \frac{dA(t)}{dt} e^{s'A(t)}. \tag{2}$$

If this is proved, the previous one results by setting $s = 1$. To prove the second identity, let's differentiate it on both sides with respect to $s$. The derivative with respect to $s$ of the left hand side is $-e^{-sA(t)}A(t)\frac{d}{dt}e^{sA(t)} + e^{-sA(t)}\frac{d}{dt}\left(A(t)e^{sA(t)}\right) = e^{-sA(t)}\frac{dA}{dt}e^{sA(t)}$, which is exactly the derivative with respect to $s$ of the right-hand side.

In the homework set, you will have at some point to evaluate the time-derivative of the


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displacement operator, i.e.

$$\begin{aligned}
\frac{d}{dt}D[\alpha(t)] &= \int_0^1 dse^{(1-s)(-\alpha^*(t)a+\alpha(t)a^\dagger)}(-\dot{\alpha}^*(t)a+\dot{\alpha}(t)a^\dagger)e^{s(-\alpha^*(t)a+\alpha(t)a^\dagger)} \\
&= D[\alpha(t)]\int_0^1 dsD^\dagger[s\alpha(t)](-\dot{\alpha}^*(t)a+\dot{\alpha}(t)a^\dagger)D[s\alpha(t)] \\
&= D[\alpha(t)]\int_0^1 ds\left[-\dot{\alpha}^*(t)(a+s\alpha)+\dot{\alpha}(a^\dagger+s\alpha^*)\right] \\
&= D[\alpha(t)]\left\{-\dot{\alpha}^*(t)a+\dot{\alpha}(t)a^\dagger-\frac{1}{2}\left[\dot{\alpha}^*(t)\alpha(t)-\dot{\alpha}(t)\alpha^*(t)\right]\right\},
\end{aligned} \tag{3}$$

such that the displacement operator applied to the time-derivative operator gives

$$D^\dagger[\alpha(t)]\frac{d}{dt}D[\alpha(t)] = -\dot{\alpha}^*(t)a+\dot{\alpha}(t)a^\dagger-\frac{1}{2}\left[\dot{\alpha}^*(t)\alpha(t)-\dot{\alpha}(t)\alpha^*(t)\right]. \tag{4}$$

## II. TIME-INDEPENDENT PERTURBATION THEORY

For this and the next section, we use J. J. Sakurai, *Modern quantum mechanics*, Addison-Wesley Publishing Company (1993). For a more detailed discussion and exercises, readers are encouraged to refer to that textbook.

### A. Non-degenerate perturbation theory

Consider the time-independent Hamiltonian

$$H = H_0 + \lambda V, \tag{5}$$

with $\lambda$ a real parameter. We define solutions to the time-independent Schrödinger equation for $H$ and $H_0$ as follows

$$\begin{aligned}
H_0\left|n^{(0)}\right\rangle &= E_n^{(0)}\left|n^{(0)}\right\rangle, \\
H\left|n\right\rangle &= E_n\left|n\right\rangle.
\end{aligned} \tag{6}$$

It is understood that the solution to the eigenproblem of $H_0$ is known, and we want to find expressions as series in $\lambda$ for the solutions to the eigenproblem of $H$. In the following, we will assume a non-degenerate unperturbed spectrum, i.e. $E_n^{(0)} \neq E_m^{(0)}$ for any $m \neq n$. We let $\Delta_n = E_n - E_n^{(0)}$. By rearranging the second Eq. (6), we get

$$(E_n^{(0)} - H_0)\left|n\right\rangle = (\lambda V - \Delta_n)\left|n\right\rangle. \tag{7}$$

It is tempting to try to invert the operator $E_n^{(0)} - H_0$ on the left-hand side, but it is not invertible. It has a zero eigenvalue corresponding to the eigenvector $\left|n^{(0)}\right\rangle$. An inverse can be devised if one projects into the complement of $\left|n^{(0)}\right\rangle$. To see this, acting with $\left\langle n^{(0)}\right|$ on the left of the above gives

$$\left\langle n^{(0)}\right| \lambda V - \Delta_n \left|n\right\rangle = 0. \tag{8}$$

That is, $(\lambda V - \Delta_n)\left|n\right\rangle$ has no component along the basis vector $\left|n^{(0)}\right\rangle$. As this is the case, we may define an inverse to the operator on the left-hand side of Eq. (7) by projecting it into the subspace complementary to $\left|n^{(0}\right\rangle$. Explicitly, let $\phi_n = 1 - \left|n^{(0)}\right\rangle\left\langle n^{(0)}\right| = \sum_{k\neq n}\left|k^{(0)}\right\rangle\left\langle k^{(0)}\right|$. Then, from the above we have $(\lambda V - \Delta_n)\left|n\right\rangle = \phi_n(\lambda V - \Delta_n)\left|n\right\rangle$.

The inverse that we were looking for above is defined if the operator $E_n^{(0)} - H_0$ multiplies $\phi_n$ from the left. Denoting the inverse as a fraction, we have

$$\frac{1}{E_n^{(0)} - H_0}\phi_n = \sum_{k\neq n}\frac{1}{E_n^{(0)} - E_k^{(0)}}\left|k^{(0)}\right\rangle\left\langle k^{(0)}\right|, \tag{9}$$

i.e. both sides of this equation are well defined, and in particular give zero, and not a divergent contribution, when acting on $\left|n^0\right\rangle$ from the left.

We are now ready to solve Eq. (7), at least formally. Due to the fact that both sides of Eq. (7) are normal to $\left|n^{(0)}\right\rangle$, we may equivalently write Eq. (7) as

$$(E_n^{(0)} - H_0)\left|n\right\rangle = \phi_n(\lambda V - \Delta_n)\left|n\right\rangle. \tag{10}$$

Now we can take the inverse of the operator on the left as argued above, and we obtain

$$\left|n\right\rangle = \frac{1}{E_n^{(0)} - H_0}\phi_n(\lambda V - \Delta_n)\left|n\right\rangle + c_n(\lambda)\left|n^{(0)}\right\rangle. \tag{11}$$

The first term in the above is just the result of taking the inverse. In the second term, we have written a residual term proportional to $\left|n^{(0)}\right\rangle$. This term gives a null contribution if we were to act on the left of the equation above with the operator $E_n^{(0)} - H_0$. One can always add to the formal solution $\left|n\right\rangle$ a solution to the homogenenous equation $(E_n^{(0)} - H_0)\left|n^{(0)}\right\rangle = 0$.

The solution to the homogeneous solution must satisfy

$$\lim_{\lambda\to 0} c_n(\lambda) = 1, \tag{12}$$

because the first term of Eq. (11) tends to 0 in the same limit $\lambda \to 0$. Moreover, by construction, since the first term of Eq. (11) is orthogonal to $\left|n^{(0)}\right\rangle$,

$$c_n(\lambda) = \left\langle n^{(0)}\middle|n\right\rangle. \tag{13}$$

Note that our task is to find a normalized $|n\rangle$, i.e. one for which $\langle n|n\rangle$. To keep the expressions below simple, we adopt temporarily the convention to renormalize $|n\rangle$ so that $c_n(\lambda) = 1$ for all $\lambda$. We will impose $\langle n|n\rangle = 1$ at the very end.

Before proceeding, we make a remark on notation. Since $\left[\frac{1}{E_n^{(0)}-H_0}, \phi_n\right] = 0$, we will write $\frac{\phi_n}{E_n^0-H_0} \equiv \frac{1}{E_n^0-H_0}\phi_n = \phi_n\frac{1}{E_n^0-H_0}$.

Corroborating the two facts above, we arrive at

$$|n\rangle = \left|n^{(0)}\right\rangle + \frac{\phi_n}{E_n^0 - H_0}\left(\lambda V - \Delta_n\right)|n\rangle . \tag{14}$$

Moreover, since $\left\langle n^{(0)}\right|\lambda V - \Delta_n|n\rangle = 0$, and since $\left\langle n^{(0)}|n\right\rangle = 1$ by our temporary normalization convention, we arrive at

$$\Delta_n = \lambda\left\langle n^{(0)}\right| V|n\rangle . \tag{15}$$

With Eq. (14) and Eq. (15) above we are now ready to find perturbation theory expressions for the eigenvectors $|n\rangle$ and eigenvalues $\Delta_n$. The strategy is to assume that both of these have an expansion over powers of $\lambda$

$$\begin{aligned} |n\rangle &= \left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \lambda^2\left|n^{(2)}\right\rangle \ldots, \\ \Delta_n &= \lambda\Delta^{(1)} + \lambda^2\Delta^{(2)} + \ldots \end{aligned} \tag{16}$$

Inserting Eq. (16) into Eq. (14) and Eq. (15), and equating coefficients in each power of $\lambda$, we will obtain the required expressions.

That is, plugging Eq. (16) into Eq. (15), we have the following set of equations

$$\begin{aligned} \lambda^1: &\quad \Delta_n^{(1)} = \left\langle n^{(0)}\right| V\left|n^{(0)}\right\rangle, \\ \lambda^2: &\quad \Delta_n^{(2)} = \left\langle n^{(0)}\right| V\left|n^{(1)}\right\rangle, \\ &\quad\vdots \\ \lambda^N: &\quad \Delta_n^{(N)} = \left\langle n^{(0)}\right| V\left|n^{(N-1)}\right\rangle, \\ &\quad\vdots \end{aligned} \tag{17}$$

To get the energy shift at order $N$, one needs the eigenvector at order $N-1$.

Turning to the eigenvectors, plugging in Eq. (16) into Eq. (14), we have

$$\begin{aligned} &\left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \lambda\left|n^{(2)}\right\rangle + \ldots \\ &= \left|n^{(0)}\right\rangle + \frac{\phi_n}{E_n^{(0)} - H_0}(\lambda V - \lambda\Delta_n^{(1)} - \lambda^2\Delta_n^{(2)} - \ldots)(\left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \lambda\left|n^{(2)}\right\rangle + \ldots). \end{aligned} \tag{18}$$

Equating coefficients of powers of $\lambda$, we arrive at the equations

$$\begin{aligned}
\lambda^0 : \quad & \left|n^{(0)}\right\rangle = \left|n^{(0)}\right\rangle , \\
\lambda^1 : \quad & \left|n^{(1)}\right\rangle = \frac{\phi_n}{E_n^{(0)} - H_0}(V - \Delta_n^{(1)}) \left|n^{(0)}\right\rangle \\
& \qquad\quad = \frac{\phi_n}{E_n^{(0)} - H_0} V \left|n^{(0)}\right\rangle ,
\end{aligned} \tag{19}$$

since $\phi_n \left|n^{(0)}\right\rangle = 0$.

Recall that the first-order eigenvector correction $\left|n^{(1)}\right\rangle$ was sufficient to calculate the corrected eigenenergy $\Delta_n^{(2)}$. Plugging $\left|n^{(1)}\right\rangle$ into the expression of $\Delta_n^{(2)}$, we have

$$\Delta_n^{(2)} = \left\langle n^{(0)}\right| V \frac{\phi_n}{E_n^{(0)} - H_0} V \left|n^{(0)}\right\rangle . \tag{20}$$

Going back to the kets, and collecting $\lambda^2$ terms, we have

$$\lambda^2 : \quad \left|n^{(2)}\right\rangle = \frac{\phi_n}{E_n^{(0)} - H_0} V \left|n^{(1)}\right\rangle - \frac{\phi_n}{E_n^{(0)} - H_0} \Delta_n^{(1)} \left|n^{(1)}\right\rangle \tag{21}$$

$$= \frac{\phi_n}{E_n^{(0)} - H_0} V \frac{\phi_n}{E_n^{(0)} - H_0} V \left|n^{(0)}\right\rangle - \frac{\phi_n}{E_n^{(0)} - H_0} \left\langle n^{(0)}\right| V \left|n^{(0)}\right\rangle \frac{\phi_n}{E_n^{(0)} - H_0} V \left|n^{(0)}\right\rangle . \tag{22}$$

One can iterate this procedure, using the eigenket and -energy correction found at some order in $\lambda$ to write the correction at the next order, according to Eq. (15) and Eq. (14).

Moreover, if one has to evaluate these expressions in practice, one needs to plug in the explicit form of $\phi_n$, to the following result

$$\begin{aligned}
\Delta_n &= E_n - E_n^{(0)} \\
&= \lambda V_{nn} + \lambda^2 \sum_{k \neq n} \frac{|V_{nk}|^2}{\Delta_{nk}} + \ldots ,
\end{aligned} \tag{23}$$

where we have introduced $V_{nk} = \left\langle n^{(0)}\right| V \left|k^{(0)}\right\rangle$, the matrix elements of the perturbation evaluated with respect to the unperturbed kets, and $\Delta_{nk} = E_n^{(0)} - E_k^{(0)}$, the transition frequencies in the unperturbed spectrum, and

$$|n\rangle = \left|n^{(0)}\right\rangle + \lambda \sum_{k \neq n} \left|k^{(0)}\right\rangle \frac{V_{kn}}{\Delta_{nk}} + \lambda^2 \left( \sum_{k \neq n} \sum_{l \neq n} \frac{\left|k^{(0)}\right\rangle V_{kl} V_{ln}}{\Delta_{nk} \Delta_{nl}} - \sum_{k \neq n} \frac{\left|k^{(0)}\right\rangle V_{nn} V_{kn}}{\Delta_{nk}^2} \right) . \tag{24}$$

Note that if two levels $i$ and $j$ are connected by a perturbation, say $V_{ij} \neq 0$, then the lower level, say $i$, gets pushed down in energy by an amount $\frac{V_{ij}^2}{\Delta_{ji}}$, while the energy of the higher level, $j$, gets pushed up by the same amount. This is a special case of the no-level-crossing theorem, which states that a pair of energy levels connected by a perturbation do not cross as the strength of the perturbation is varied.

The second-order energy shift is always non-positive for the ground state.

Recall that we had changed our normalization convention such that $\langle n^{(0)}|n\rangle = c_n(\lambda) = 1$, so the ket $|n\rangle$ found above is not normalized. Let's renormalize it, so we write $|n\rangle_N = Z_n^{1/2}|n\rangle$, such that ${}_N\langle n|n\rangle_N = 1$. Evaluating the inner product, $\langle n^{(0)}|n\rangle_N = Z_n^{1/2}\langle n^0|n\rangle = Z_n^{1/2}$. Since both $|n^{(0)}\rangle$ and $|n\rangle_N$ are normalized, $Z_n$ is then the probability for a system prepared in the pertubed eigenstate $|n\rangle_N$ to be measured in the unperturbed eigenstate $|n^{(0)}\rangle$ (i.e. one is measuring $H_0 = \sum E_n^{(0)}|n^{(0)}\rangle\langle n^{(0)}|$ projectively).

The probability $Z_n$ has an expansion over powers of $\lambda$. Since ${}_N\langle n|n\rangle_N = 1 = Z_n\langle n|n\rangle$, one has $Z_n = 1/\langle n|n\rangle$, and hence

$$Z_n^{-1} = \langle n|n\rangle = \left(\langle n^{(0)}| + \lambda\langle n^{(1)}| + \dots\right)\left(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \dots\right) \tag{25}$$

$$= 1 + \lambda^2\langle n^{(1)}|n^{(1)}\rangle + \dots \tag{26}$$

$$= 1 + \lambda^2\sum_{k\neq n}\frac{|V_{kn}|^2}{\Delta_{nk}^2} + O(\lambda^3), \tag{27}$$

whence

$$Z_n = 1 - \lambda^2\sum_{k\neq n}\frac{|V_{kn}|^2}{\Delta_{nk}^2} + O(\lambda^3) \tag{28}$$

is the probability to measure the system in the state $|n^{(0)}\rangle$, with the second term being the probability to find the system in any other one of the states $|k^{(0)}\rangle$ with $k \neq n$.

### B. Degenerate perturbation theory

Note: This subsection was not covered in class, but is included here for completeness.

The procedure described above works for non-degenerate spectra. For example, the ratio $\frac{V_{nk}}{\Delta_{nk}}$ blows up when $E_n^{(0)} - E_k^{(0)} = 0$ for $n \neq k$. In such situations, it is convenient to form linear combinations of the degenerate eigenstates. Intuitively, this will be done such that the matrix elements $V_{nk}$ vanish, i.e. the fraction above will have a zero numerator.

The procedure is to find in each degenerate subspace of $H_0$ a basis that diagonalizes $H$, or equivalently $\lambda V$, in that subspace. Let's consider a $g-$fold degenerate eigensubspace of

$H^{(0)}$, of energy $E_D^{(0)}$, and let's denote one choice of $g$ degenerate orthonormal eigenkets of $H_0$ by $\{|m^{(0)}\rangle\}$. Note that these $g$ kets can always be found, and, once found, are defined only up to a unitary transformation, i.e. a change of basis. Any linear combination of the $|m^{(0)}\rangle$ is again a ket in the degenerate subspace.

Assume that $V$ entirely removes the $g-$fold degeneracy, i.e. that there are $g$ perturbed kets, all with different energies. Let's denote that set of $g$ kets $\{|l\rangle\}$. As one takes $\lambda \to 0$, the $g$ nondegenerate kets go each to some limit $|l\rangle \to |l^{(0)}\rangle$. Importantly, $|l^{(0)}\rangle$ and $|m^{(0)}\rangle$ need not coincide, but both sets of kets have eigenenergy $E_D^{(0)}$ with respect to $H_0$. A priori $|l^{(0)}\rangle$ are unknown, and the limiting procedure above gives us the 'right' basis for our g-fold degenerate subspace. The scheme presented below allows us to make the limiting procedure explicit.

We can formally state the difference between the two bases of the degenerate subspace $\{|l^{(0)}\rangle\}$ and $\{|m^{(0)}\rangle\}$, in the form of a unitary change of basis between two orthonormal bases

$$|l^{(0)}\rangle = \sum_{m\in D} \langle m^{(0)}|l^{(0)}\rangle \, |m^{(0)}\rangle \, . \tag{29}$$

This just involved inserting the projector onto the degenerate subspace, in the form $P_0 = \sum_{m\in D} |m^{(0)}\rangle \langle m^{(0)}|$, into right hand side of the equation $|l^{(0)}\rangle = |l^{(0)}\rangle$. Let $P_1 = I - P_0$ be the projector onto the complement to the $g$-fold degenerate subspace of interest.

The time-independent Schrödinger equation reads for an arbitrary eigenket of $H$, $|l\rangle$, with eigenvalue $E$,

$$\begin{aligned} 0 &= (E - H_0 - \lambda V)\,|l\rangle = (E - H_0 - \lambda V)\,(P_0 + P_1)\,|l\rangle \\ &= \left(E - E_D^{(0)} - \lambda V\right) P_0\,|l\rangle + (E - H_0 - \lambda V)\,P_1\,|l\rangle \, . \end{aligned} \tag{30}$$

We obtain two equations from this by projecting from the left with either $P_0$ or $P_1$

$$\begin{aligned} \left(E - E_D^{(0)} - \lambda P_0 V\right) P_0\,|l\rangle - \lambda P_0 V P_1\,|l\rangle &= 0, \\ -\lambda P_1 V P_0\,|l\rangle + (E - H_0 - \lambda P_1 V)\,P_1\,|l\rangle &= 0. \end{aligned} \tag{31}$$

The second Eq. (31) can be solved in the $P_1$ subspace since $P_1\,(E - H_0 - \lambda P_1 V)\,P_1$ is not singular (i.e. it does not have a zero eigenvalue and is therefore invertible) in this subspace. To see this, note that we assume $E$ is close to $E_D^{(0)}$ at finite small $\lambda$. Relative to this separation, the eigenvalues of $P_1 H_0 P_1$ are all far from $E_D^{(0)}$. Therefore, applying $P_1$ from the left in the second Eq. (31), and inverting $P_1 \left(E - H_0 - \lambda P_1 V\right) P_1$, we arrive at the formal solution

$$P_1 \left|l\right\rangle = P_1 \frac{\lambda}{E - H_0 - \lambda P_1 V P_1} P_1 V P_0 \left|l\right\rangle . \tag{32}$$

We can expand as before in the non-degenerate case the sought-for ket in a series, $\left|l\right\rangle = \left|l^{(0)}\right\rangle + \lambda \left|l^{(1)}\right\rangle + \lambda^2 \left|l^{(2)}\right\rangle + \ldots$. Then

$$P_1 \left|l^{(1)}\right\rangle = \sum_{k \notin D} \frac{\left|k^{(0)}\right\rangle V_{kl}}{E_D^{(0)} - E_k^{(0)}}. \tag{33}$$

Note that this result for the part of the solution that belongs to the complement of degenerate subspace is exactly what one would expect from non-degenerate perturbation theory.

To now approach the harder problem of finding the part of the solution that belongs to the degenerate subspace, we plug in the formal solution for the part of the solution living in the complement, $P_1 \left|l\right\rangle$ of Eq. (32), into the first Eq. (31), corresponding to the formal equation for the part of the solution in the degenerate subspace, $P_0 \left|l\right\rangle$. We obtain

$$\left(E - E_D^{(0)} - \lambda P_0 V P_0 - \lambda^2 P_0 V P_1 \frac{1}{E - H_0 - \lambda V} P_1 V P_0\right) P_0 \left|l\right\rangle = 0. \tag{34}$$

To order $\lambda$, this is

$$\left(E - E_D^{(0)} - \lambda P_0 V P_0\right) P_0 \left|l^{(0)}\right\rangle = 0. \tag{35}$$

As mentioned above, this is an equation in the $g-$dimensional subspace. Writing the energy also as a series in $\lambda$, i.e. $E - E_D^{(0)} = \lambda \Delta^{(1)} + \lambda^2 \Delta^{(2)} + \ldots$, the order-$\lambda$ contribution is the root of the following characteristic polynomial

$$\det\left[P_0 V P_0 - \Delta^{(1)}\right] = 0. \tag{36}$$

More concretely, to solve this equation, one needs to write the matrix representation of $P_0 V P_0$ in the basis $\{\left|m^{(0)}\right\rangle\}$. This is a matrix with elements $V_{mm'} \equiv \left\langle m^{(0)}\right| V \left|m'^{(0)}\right\rangle$. The eigenvectors of this matrix are $\left|l^{(0)}\right\rangle$, the basis of the degenerate subspace in which the perturbation is diagonal. In matrix form, this can be written as follows

$$\begin{pmatrix} V_{11} & V_{12} & \ldots \\ V_{21} & V_{22} & \\ \vdots & & \ddots \end{pmatrix} \begin{pmatrix} \left\langle 1^{(0)} \middle| l^{(0)} \right\rangle \\ \left\langle 2^{(0)} \middle| l^{(0)} \right\rangle \\ \vdots \\ \left\langle m^{(0)} \middle| l^{(0)} \right\rangle \\ \vdots \end{pmatrix} = \Delta_l^{(1)} \begin{pmatrix} \left\langle 1^{(0)} \middle| l^{(0)} \right\rangle \\ \left\langle 2^{(0)} \middle| l^{(0)} \right\rangle \\ \vdots \\ \left\langle m^{(0)} \middle| l^{(0)} \right\rangle \\ \vdots \end{pmatrix}. \tag{37}$$

Solving this eigenvalue problem gives $g$ eigenvalues for $\Delta_l^{(1)}$, and $g$ eigenvectors $\left|l^{(0)}\right\rangle$. That is, we are getting both the first order correction to the eigenvalues, and the zeroth-order eigenvectors. With the risk of overemphasizing this point, the zeroth-order order eigenvectors form the 'right' basis for the degenerate subspace.

To obtain the next-order corrections, we return to Eq. (38), and keep all terms up to order $\lambda^2$. This amounts to dropping all contributions at order $\lambda$ from the denominator in Eq. (38), that is

$$\left(E - E_D^{(0)} - \lambda P_0 V P_0 - \lambda^2 P_0 V P_1 \frac{1}{E_D^{(0)} - H_0} P_1 V P_0\right) P_0 \left|l\right\rangle = 0. \tag{38}$$

We have solved this to order $\lambda$ above, and assumed that we obtain a non-degenerate spectrum for $P_0 V P_0$ at first order in $\lambda$, i.e. that $\Delta_l^{(1)} \neq \Delta_{l'}^{(1)}$ for all $l \neq l'$ belonging to the $P_0$ subspace. Then we can treat the order-$\lambda^2$ term in the parenthesis as a perturbation, and use the rules of non-degenerate perturbation theory. For the eigenvectors, we find

$$\lambda P_0 \left|l^{(1)}\right\rangle = \sum_{l' \in D, l' \neq l} \lambda \frac{P_0 \left|l'^{(0)}\right\rangle}{\Delta_{l'}^{(0)} - \Delta_l^{(0)}} \left\langle l'^{(0)}\right| V P_1 \frac{1}{E_D^{(0)} - H_0} P_1 V \left|l^{(0)}\right\rangle. \tag{39}$$

Using the explicit form for the projector onto the complement $P_1$, the above is rewritten as

$$\lambda P_0 \left|l^{(1)}\right\rangle = \sum_{l' \in D, l' \neq l} \lambda \frac{P_0 \left|l'^{(0)}\right\rangle}{\Delta_{l'}^{(0)} - \Delta_l^{(0)}} \sum_{k \notin D} \left\langle l'^{(0)}\right| V \left|k^{(0)}\right\rangle \frac{1}{E_D^{(0)} - E_k^{(0)}} \left\langle k^{(0)}\right| V \left|l^{(0)}\right\rangle \tag{40}$$

$$= \sum_{l' \in D, l' \neq l} \lambda \frac{P_0 \left|l'^{(0)}\right\rangle}{\Delta_{l'}^{(0)} - \Delta_l^{(0)}} \sum_{k \notin D} \frac{V_{l'k} V_{kl}}{E_D^{(0)} - E_k^{(0)}}. \tag{41}$$

This, together with Eq. (33), gives the correction to the eigenvector to order $\lambda$.

As in the non-degenerate case, we have taken $\left\langle l^{(0)} \middle| l\right\rangle = 1$. Then Eq. (15) and Eq. (14) give

$$\lambda \left\langle l^{(0)}\right| V \left|l\right\rangle = \Delta_l = \lambda \Delta_l^{(1)} + \lambda^2 \Delta_l^{(2)} + \ldots, \tag{42}$$

such that $\Delta_l^{(1)} = V_{ll}$, and

$$\Delta_l^{(2)} = \left\langle l^{(0)}\right| V \left|l^{(1)}\right\rangle = \left\langle l^{(0)}\right| V P_1 \left|l^{(1)}\right\rangle + \left\langle l^{(0)}\right| V P_0 \left|l^{(1)}\right\rangle, \tag{43}$$

where the second term is vanishing by Eq. (41) and the fact that $\left|l^{(0)}\right\rangle$ is an eigenket of $V$ in the $P_0$ subspace. Therefore by Eq. (33) we have

$$\Delta_l^{(2)} = \sum_{k \notin D} \frac{|V_{kl}|^2}{E_D^{(0)} - E_k^{(0)}}. \tag{44}$$

One can iterate this procedure further using non-degenerate perturbation theory to obtain higher-order corrections.

We summarize here the main steps of degenerate perturbation theory: one has to identify degenerate unperturbed kets, and construct the perturbation matrix $P_0VP_0$. Next, one diagonalizes that matrix. The roots of the corresponding secular equation are the first order corrections to the energies. The basis in which $P_0VP_0$ is diagonal constitutes the correct zeroth order kets to which perturbed kets tend in the limit $\lambda \to 0$. For higher orders, one uses the formulas of non-degenerate perturbation theory, except in summations, where we exclude all contributions from the unperturbed kets belonging to the degenerate subspace $D$.

## III. TIME-DEPENDENT PERTURBATION THEORY

Consider a static Hamiltonian with a time-dependent perturbation,

$$H(t) = H_0 + \lambda V(t). \tag{45}$$

We want to find $|\psi(t)\rangle$ that solves the time-dependent Schrödinger equation, expanded over the known eigenbasis $|n\rangle$ of $H_0$ (note the change of notation from the previous section).

Let's revisit in this notation the interaction picture, introduced previously in Lecture 2. We can define

$$|\psi(t)\rangle_I = e^{iH_0t/\hbar} |\psi(t)\rangle_S , \tag{46}$$

$$O_I = e^{iH_0t/\hbar} O_S e^{-iH_0t/\hbar}, \tag{47}$$

where we recall that the subscript $S$ appears to distinguish Schrödinger picture operators from interaction-picture operators. Here, using the second equation for the perturbation operator appearing in Eq. (45), we get

$$V_I(t) = e^{iH_0t/\hbar} V(t) e^{-iH_0t/\hbar}. \tag{48}$$

Then the following Schrödinger-like equation holds for the interaction-picture wavefunction

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle_I = V_I(t) |\psi(t)\rangle_I , \tag{49}$$

and the following Heisenberg-like equation holds for operators in the interaction picture

$$\frac{dO_I(t)}{dt} = \frac{1}{i\hbar}[O_I(t), H_0]. \tag{50}$$

The problem to find $|\psi(t)\rangle$ reduces to finding its expansion over the eigenbasis of $H_0$

$$|\psi(t)\rangle = \sum_n c_n(t) |n\rangle . \tag{51}$$

To do perturbation theory, we shall assume that $c_n(t)$ can be expanded as a series

$$c_n(t) = c_n^{(0)} + c_n^{(1)} + \ldots, \tag{52}$$

where the superscript indicates the order in $\lambda$.

The time evolution operator $U_I(t, t_0)$ in the interaction picture is defined as

$$|\psi(t)\rangle_I = U_I(t, t_0) |\psi(t_0)\rangle_I , \tag{53}$$

which together with the Schrödinger equation gives the following equation of motion for the time evolution operator

$$i\hbar \frac{d}{dt} U_I(t, t_0) = V_I(t) U_I(t, t_0), \tag{54}$$

with initial condition $U_I(t_0, t_0) = I$. This ordinary differential equation can be brought to integral form

$$U_I(t, t_0) = I - \frac{i}{\hbar} \int_{t_0}^{t} V_I(t') U_I(t', t_0) dt'. \tag{55}$$

The main result of this section, the Dyson series, is derived by iteratively plugging in the left-hand side of this equation into its right-hand side

$$\begin{aligned}
U_I(t, t_0) &= I - \frac{i}{\hbar} \int_{t_0}^{t} dt' V_I(t') \left[ 1 - \frac{i}{\hbar} \int_{t_0}^{t'} dt'' V_I(t'') U_I(t'', t_0) \right] \\
&= I - \frac{i}{\hbar} \int_{t_0}^{t} dt' V_I(t') \\
&\quad + \left( \frac{-i}{\hbar} \right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' V_I(t') V_I(t'') \\
&\quad + \ldots \\
&\quad + \left( \frac{-i}{\hbar} \right)^n \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \ldots \int_{t_0}^{t^{(n-1)}} dt^{(n)} V_I(t') V_I(t'') \ldots V_I(t^{(n)}) \\
&\quad + \ldots
\end{aligned} \tag{56}$$

The Dyson series allows us to evaluate *transition probabilities*.

**Transition probabilities**

Note that

$$|\psi(t)\rangle_I = U_I(t,t_0)\,|i\rangle = \sum_n |n\rangle\,\langle n|\,U_I(t,t_0)\,|i\rangle \equiv \sum_n |n\rangle\,c_n(t) \tag{57}$$

So the coefficient $c_n(t)$ in the expansion of the wavefunction in the interaction picture corresponds to a matrix element of the time evolution operator in the interaction picture. Moreover, this is easily related to matrix elements of the time evolution operator in the Schrödinger picture, that is

$$\langle n|\,U_I(t,t_0)\,|i\rangle = e^{i(E_n t - E_i t_0)/\hbar}\,\langle n|\,|U(t,t_0)\,|i\rangle\,, \tag{58}$$

since by definition $U_I(t,t_0) = e^{iH_0t/\hbar}U(t,t_0)e^{-iH_0t_0/\hbar}$. Here, $\langle n|\,U(t,t_0)\,|i\rangle$ is interpreted as the transition amplitude for a transition into state $|n\rangle$ at time $t$ if the system was prepared in state $|i\rangle$ at time $t_0$. Then $|\,\langle n|\,U(t,t_0)\,|i\rangle\,|^2$ is interpreted as the *transition probability.* Note that the transition probability is the same whether evaluated in the Schrödinger picture or in the interaction picture, as the two amplitudes differ only by a phase factor *when* $|n\rangle$ *and* $|i\rangle$ *are energy eigenstates of* $H_0$.

Then the probability to measure the system in state $|n\rangle$ at time $t$, having prepared the system in state $|i\rangle$ at time $t_0$, is

$$|c_n(t)|^2 = |\,\langle n|\,U_I(t,t_0)\,|i\rangle\,|^2 = |c_n^{(0)}(t) + c_n^{(1)}(t) + \ldots|^2, \tag{59}$$

where the first two terms are given by

$$\begin{aligned}
c_n^{(0)}(t) &= \delta_{ni},\\
c_n^{(1)}(t) &= -\frac{i}{\hbar}\int_{t_0}^{t} dt'\,\langle n|\,V_I(t')\,|i\rangle\\
&\equiv -\frac{i}{\hbar}\int_{t_0}^{t} dt' e^{i\omega_{ni}t'}V_{ni}(t')\\
c_n^{(2)}(t) &= \left(\frac{-i}{\hbar}\right)^2 \sum_m \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' e^{i\omega_{nm}t'}V_{nm}(t')e^{i\omega_{mi}t''}V_{mi}(t''),
\end{aligned} \tag{60}$$

with $\omega_{ni} = \Delta_{ni}/\hbar$ and $\Delta_{ni} = E_n - E_i$, analogous to the notation in the previous section. Then the transition probability is $P(i \to n) = |c_n^{(1)}(t) + c_n^{(2)}(t) + \ldots|^2$.