Using non-degenerate perturbation theory in the degenerate case

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I. SHORT RECAPITULATION OF DEGENERATE PERTURBATION THEORY

In the lectures we considered a system described by a Hamiltonian $H = H_0 + \lambda V$, for which we cannot find the exact solutions of the Schrödinger equation

$$H|\psi\rangle = E|\psi\rangle, \tag{1}$$

but where we know the exact solutions for the unperturbed system,

$$H_0|n,r\rangle = E_n^0|n,r\rangle, \tag{2}$$

where n labels the unperturbed energy states, and $r = 1, 2, \ldots, g_n$ labels the g_n degenerate states of energy level n. By writing the unknown states and energies as power series in λ,

$$|\psi_{n\alpha}\rangle = |\psi_{n\alpha}^{(0)}\rangle + \lambda|\psi_{n\alpha}^{(1)}\rangle + \ldots, \tag{3}$$

$$E_{n\alpha} = E_n^0 + \lambda E_{n\alpha}^{(1)} + \ldots \tag{4}$$

and

$$|\psi_{n\alpha}^{(0)}\rangle = \sum_{r=1}^{g_n} U_{r\alpha}|n,r\rangle, \tag{5}$$

with $\alpha = 1, 2, \ldots, g_n$, we arrived at the matrix equation

$$\begin{pmatrix} V_{11} - E_{n\alpha}^{(1)} & V_{12} & \ldots & V_{1g_n} \\ V_{21} & V_{22} - E_{n\alpha}^{(1)} & \ldots & \vdots \\ \vdots & \ddots & \ddots & \vdots \\ V_{g_n 1} & \ldots & \ldots & V_{g_n g_n} - E_{n\alpha}^{(1)} \end{pmatrix} \begin{pmatrix} U_{1\alpha} \\ U_{2\alpha} \\ \vdots \\ U_{g\alpha} \end{pmatrix} = 0, \tag{6}$$

where

$$V_{sr} \equiv \langle n,s|V|n,r\rangle, \tag{7}$$

with $r, s = 1, 2, \ldots, g_n$. Non-trivial solutions are found by requiring that the determinant of the matrix is equal to zero, resulting in an equation of degree g_n with solutions corresponding to the first-order energy corrections $E_{n\alpha}^{(1)}$.

In some cases all off-diagonal matrix elements in eq. (6) are equal to zero,

$$V_{sr} = 0 \text{ if } s \neq r, \tag{8}$$

meaning that the first-order corrections are given directly by

$$E_{nr} = V_{rr} = \langle n,r|V|n,r\rangle, \tag{9}$$

which is the same result obtained in the non-degenerate case. We then call the states $|n,r\rangle$ "good" states, and we get a diagonal matrix in eq. (6) because we started our analysis using the "limit" states $|\psi_{n\alpha}^{(0)}\rangle$ the system evolves to in the limit $\lambda \to 0$, see eq. (3). We will now take a more systematic look at how we can find these "good" states without solving the matrix equation, thus allowing us to use the simpler non-degenerate perturbation theory even for degenerate levels.

II. SIMULTANEOUS EIGENSTATES

If two Hermitian operators A and B commute,

$$[A, B] = 0, \tag{10}$$

they have simultaneous eigenstates. This can be shown by considering an eigenstate of the operator B,

$$B|\psi\rangle = b|\psi\rangle, \tag{11}$$

and operating with AB and BA on $|\psi\rangle$. If A and B commute, we must have

$$BA|\psi\rangle = AB|\psi\rangle = Ab|\psi\rangle = bA|\psi\rangle, \tag{12}$$

meaning that $A|\psi\rangle$ must be an eigenstate of B with the same eigenvalue b as $|\psi\rangle$. (i) If the eigenvalue b is *non-degenerate*, we get directly that $|\psi\rangle$ must also be an eigenstate of A,

$$A|\psi\rangle = a|\psi\rangle. \tag{13}$$

(ii) If b is degenerate, meaning that there are g eigenstates of B with the same eigenvalue b, it is still possible to create linear combinations of the eigenstates of B which are also eigenstates of A, such that

$$B|\psi_r\rangle = b|\psi_r\rangle, \quad A|\psi_r\rangle = a_r|\psi_r\rangle, \tag{14}$$

with $r = 1, 2, \ldots, g$, and a_r is the eigenvalues of A for the state $|\psi_r\rangle$.

If two eigenstates $|\psi_r\rangle$ and $|\psi_s\rangle$ of A and B have different eigenvalues of A, $a_r \neq a_s$ if $s \neq r$, the two states are orthogonal. This can be shown by considering,

$$\begin{aligned} \langle\psi_s|A|\psi_r\rangle &= \langle\psi_s|a_r|\psi_r\rangle = a_r\langle\psi_s|\psi_r\rangle \\ &= \langle\psi_r|A|\psi_s\rangle^* = \langle\psi_r|a_s|\psi_s\rangle^* = a_s^*\langle\psi_s|\psi_r\rangle. \end{aligned} \tag{15}$$

where we have used the definition of the Dirac bracket or scalar product. Since A is Hermitian, the eigenvalues a_r and a_s have to be real, and if $a_r \neq a_s$ for $s \neq r$, the only way to satisfy the above equality is if $\langle\psi_s|\psi_r\rangle = 0$, meaning that the eigenstates of A with different eigenvalues are orthogonal.

III. FINDING THE "GOOD" STATES

If we find an operator F which commutes with H_0, we can construct linear combinations of the degenerate eigenstates $|n,r\rangle$ of H_0 which also are eigenstates of F,

$$F|n,i\rangle = f_i|n,i\rangle, \quad (i = 1,2,\dots g_n) \tag{16}$$

where f_i are the eigenvalues of F, and

$$|n,i\rangle = \sum_{r=1}^{g_n} c_{ir}|n,r\rangle. \tag{17}$$

Since the states $|n,r\rangle$, $r = 1,2,\dots,g_n$ all are eigenstates of H_0 with the same eigenvalue E_n^0, see eq. (2), the states $|n,i\rangle$, $i = 1,2,\dots,g_n$ are also eigenstates of H_0 with eigenvalue E_n^0.

If the operator F also commutes with the perturbation V, and thus the total Hamiltonian H, there also exist simultaneous eigenstates of F and H,

$$H|\psi_{n\alpha}\rangle = E_{n\alpha}|\psi_{n\alpha}\rangle, \tag{18}$$
$$F|\psi_{n\alpha}\rangle = f_\alpha|\psi_{n\alpha}\rangle, \tag{19}$$

with $\alpha = 1,2,\dots,g_n$, where we focus on one specific level n and therefore denote the eigenvalue of F only by f_α. Multiplying the latter equation by $\langle n,i|$ from the left, we get

$$\begin{aligned}\langle n,i|F|\psi_{n\alpha}\rangle &= \langle\psi_{n\alpha}|F|n,i\rangle^* \\ &= f_\alpha\langle n,i|\psi_{n\alpha}\rangle = f_i^*\langle n,i|\psi_{n\alpha}\rangle \\ \Rightarrow (f_\alpha - f_i)\langle n,i|\psi_{n\alpha}\rangle &= 0,\end{aligned} \tag{20}$$

where we have used $f_i = f_i^*$ for eigenvalues of a Hermitian operator. If *all* the eigenvalues f_i are distinct within a level n,

$$f_i \neq f_j \text{ if } i \neq j, \tag{21}$$

there are only two ways of satisfying eq. (20). (i) Either $f_\alpha = f_i$, or (ii) $\langle n,i|\psi_{n\alpha}\rangle = 0$ if $f_\alpha \neq f_i$. Hence, the states $|n,i\rangle$ and $|\psi_{n\alpha}\rangle$ are orthogonal if $i \neq \alpha$ since they then have different eigenvalues of F. This should hold for any λ, and therefore also in the limit $\lambda \to 0$, meaning that $\langle n,i|\psi_{n\alpha}^{(0)}\rangle = 0$ if $i \neq \alpha$. However, if $i = \alpha$ the states $|\psi_{n\alpha}^{(0)}\rangle$ and $|n,\alpha\rangle$ have the same eigenvalue f_α (and E_n^0), and since all degenerate states with energy E_n^0 have distinct eigenvalues of F, we must have

$$|\psi_{n\alpha}^{(0)}\rangle = |n,\alpha\rangle. \tag{22}$$

We now multiply the Schrödinger equation (1), with the notation from eqs. (3) and (4), by $\langle n,i|$ from the left,

$$\begin{aligned}E_{n\alpha}\langle n,i|\psi_{n\alpha}\rangle &= \langle n,i|H|\psi_{n\alpha}\rangle = \langle\psi_{n\alpha}|H_0+\lambda V|n,i\rangle^* \\ &= E_n^0\langle n,i|\psi_{n\alpha}\rangle + \lambda\langle n,i|V|\psi_{n\alpha}\rangle \\ \Rightarrow \quad \langle n,i|V|\psi_{n\alpha}\rangle &= \frac{E_{n\alpha}-E_n^0}{\lambda}\delta_{i\alpha} \\ &= \delta_{i\alpha}\left[E_{n\alpha}^{(1)} + \lambda E_{n\alpha}^{(2)} + \dots\right].\end{aligned} \tag{23}$$

Hence, $\langle n,i|V|\psi_{n\alpha}\rangle$ is nonzero only if $i = \alpha$. This should hold also in the limit $\lambda \to 0$, meaning that we have

$$\langle n,i|V|\psi_{n\alpha}^{(0)}\rangle = \langle n,i|V|n,\alpha\rangle = 0 \text{ if } i \neq \alpha, \tag{24}$$

and

$$E_{n\alpha}^{(1)} = \langle n,\alpha|V|n,\alpha\rangle. \tag{25}$$

Therefore, we have arrived at the following theorem:

> If we can identify a Hermitian operator F which commutes with both H_0 and V, and find degenerate unperturbed energy eigenstates $|n,\alpha\rangle$, $\alpha = 1,2,\dots,g_n$ which are also eigenstates of F with **distinct** eigenvalues, we get
>
> $$\langle n,\alpha|V|n,\beta\rangle = 0 \text{ if } \alpha \neq \beta,$$
>
> allowing us to use non-degenerate perturbation theory directly, with the first-order energy corrections
>
> $$E_{n\alpha}^{(1)} = \langle n,\alpha|V|n,\alpha\rangle.$$
>
> The states $|n,\alpha\rangle$ are the "good" or "limit" states.

In some cases the operator F will be a product[1] of multiple Hermitian operators which all separately commute with H_0 and V, but do not have distinct eigenvalues by themselves. As an example, assume that the orbital angular momentum operators $\mathbf{L}^2$ and L_z commute with H_0 and V_0, but that the degenerate states $|\psi_{nlm}\rangle$ of the hydrogen atom for a level n do not all have distinct eigenvalues of the operators separately,

$$\mathbf{L}^2|\psi_{nlm}\rangle = \hbar^2 l(l+1)|\psi_{nlm}\rangle, \tag{26}$$
$$L_z|\psi_{nlm}\rangle = \hbar m|\psi_{nlm}\rangle, \tag{27}$$

since the first equation does not distinguish between the $2l+1$ possible values of m for a given l, and the latter does not distinguish between different possibilities of l with the same value m. However, the operator $F = \mathbf{L}^2 L_z$ does have distinct eigenvalues,

$$\mathbf{L}^2 L_z|\psi_{nlm}\rangle = \hbar^3 l(l+1)m|\psi_{nlm}\rangle, \tag{28}$$

and the states $|\psi_{nlm}\rangle$ are therefore "good" states to use in perturbation theory.

[1] Thanks to the student who pointed this out.