QM-23 Lecture Notes
Approximation Schemes for Time Independent Problems*
23.3 Perturbation theory for degenerate case

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§1 First order degenerate perturbation theory

The total hamiltonian H is split into two parts

$$H = H_0 + \lambda H' \tag{1}$$

Suppose we are looking for corrections to an energy eigenvalue E_n which is degenerate. Without loss of generality one may assume that the degeneracy is 2, the results derived can easily be generalized for any value of degeneracy. Thus assume that there are two linearly independent solutions $u_n^\alpha, \alpha = 1, 2$.

$$H_0 u_n^{(1)} = E_n u_n^{(1)} \tag{2}$$
$$H_0 u_n^{(2)} = E_n u_n^{(2)} \tag{3}$$

We assume that exact eigenvalue, W, and eigenfunctions, $\psi(x)$, have expansions in powers of λ

$$\psi = \psi_0 + \lambda\psi_1 + \lambda^2\psi_2 + \cdots \tag{4}$$
$$W = W_0 + \lambda W_1 + \lambda^2 W_2 + \cdots \tag{5}$$

First Order Energy Level Splitting Substituting the expansions of ψ and W from Eq.(4) and Eq.(5) in Eq.(1) we get

$$H_0\psi_0 = W_0\psi_0 \tag{6}$$
$$H_0\psi_1 + H'\psi_0 = W_0\psi_1 + W_1\psi_0 \tag{7}$$
$$H_0\psi_2 + H'\psi_1 = W_0\psi_2 + W_1\psi_1 + W_2\psi_0 \tag{8}$$

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To find the corrections to the unperturbed solutions of Eq.(2)-Eq.(3) we set $W_0 = E_n$ the most general expression for the unpertubed eigenfunction s ψ_0 is

$$\psi_0(x) = \alpha_1 u_n^{(1)} + \alpha_2 u_n^{(2)} \tag{9}$$

Taking the scalar product of Eq.(7) with $u_n^{(1)}$ and using $W_0 = E_n$, Eq.(2) we get

$$\begin{aligned} (u_n^{(1)}, H_0\psi_1) + (u_n^{(1)}, H'\psi_0) &= E_n(u_n^{(1)}, \psi_1) + W_1(u_n^{(1)}, \psi_0) && (10)\\ (u_n^{(1)}, H'\psi_0) &= W_1(u_n^{(1)}, \psi_0) && (11)\end{aligned}$$

Substiuting from Eq.(2) and Eq.(3) in Eq.(11) we get

$$(u_n^{(1)}, H'u_n(1))\alpha_1 + (u_n^{(1)}, H'u_n(2))\alpha_2 = W_1\alpha_1 \tag{12}$$

Similarly, taking the scalar product of Eq.(7) with $u_n^{[(2)}$ gives

$$(u_n^{(2)}, H'u_n(1))\alpha_1 + (u_n^{(2)}, H'u_n(2))\alpha_2 = W_1\alpha_2 \tag{13}$$

Now note that Eq.(12) and Eq.(13) can be rewritten in a matrix form

$$\begin{bmatrix}\langle n1|H'|n1\rangle & \langle n1|H'|n2\rangle\\ \langle n1|H'|n1\rangle & \langle n1|H'|n2\rangle\end{bmatrix}\begin{bmatrix}\alpha_1\\ \alpha_2\end{bmatrix} = W_1\begin{bmatrix}\alpha_1\\ \alpha_2\end{bmatrix} \tag{14}$$

This equation is recognised as an eigenvalue equation. Hence the first order correction, W_1, to the energy eigenvalue E_n is obtained by finding the eigenvalues of the matrix appearing in the left hand side of Eq.(14).

Note that the eigenvalues W_1 appearing in Eq.(14) will be distinct if either the off diagonal elements are nonzero

$$\langle n1|H'|n2\rangle \neq 0 \tag{15}$$

or if the diagonal elements are distinct,

$$\langle n1|H'|n1\rangle \neq \langle n2|H'|n2\rangle \tag{16}$$

If the eigenvalues are distinct,two sets of non-trivial values, one for each eigenvalue W_1, for the coefficients α_1, α_2 will can be found and Eq.(9) determines corresponding lowest order eigenfunctions,ψ_0. However, when the conditions in Eq.(15)-Eq.(16) are not satisfied, the constants α_1, α_2 remain undetermined and one must go to the second order perturbation theory to find the corrections to the energy levels and eigenfunctions.

We take the scalar product of Eq.(7) with u_k, with $k \neq n$, to get

$$(u_k, H_0\psi_1) + (u_k, H'\psi_0) = W_0(u_k, \psi_1) + W_1(u_k, \psi_0) \tag{17}$$

For $k \neq n$ $(u_k, \psi_0) = 0$ and

$$\begin{aligned} (u_k, H_0\psi_1) &= (H_0u_k, \psi_1) && (18)\\ &= E_k(u_k, \psi_1) && (19)\end{aligned}$$

Making use of Eq.(18)-Eq.(19) in Eq.(17) gives

$$\begin{aligned} E_k(u_k, \psi_1) + (u_k, H'\psi_0) &= E_n(u_k, \psi_1) && (20)\\ (u_k, \psi_1) &= \frac{(u_k, H'\psi_0)}{E_k - En} && (21)\end{aligned}$$

To determine ψ_1 we expand it in terms of the unperturbed solutions and write

$$\begin{aligned} \psi_1 &= \sum d_k u_k && (22)\\ &= d_n^{(1)}u_n^{(1)} + d_n^{(2)}u_n^{(2)} + \sum_{k\neq n} d_k u_k && (23)\end{aligned}$$

and the coefficients $d_n, n \neq k$ are just the constants given by $d_k = (u_k, \psi_1)$ and hence

$$\psi_1 = d_n^{(1)}u_n^{(1)} + d_n^{(2)}u_n^{(2)} + \sum_{k\neq n}\frac{(u_k, H'\psi_0)}{E_k - En}u_k \tag{24}$$

In case the matrix appearing in Eq.(14) is a multiple of identity then α_1, α_2 are not determined and one has to go to the next order of perturbation theory.

§2 Second order degenerate perturbation theory

In all the cases of realistic applications of degenerate perturbation theory one is interested in the splitting of the levels due to the perturbation term. In case the degeneracy is not removed in the first order one must go for a second order computation. In such a case the lowest order calculation does not lead to information on the wave function because α_1, α_2 remain undetermined. The change in energy W_2 and the constants α_1, α_2 must then be fixed by the second order perturbation theory.

Upto the second order in the perturbation Hamiltonian the wave function is

$$\psi = \psi_0 + \lambda\psi_1 + \lambda^2\psi_2 \tag{25}$$

$$= \alpha_1 u_n^{(1)} + \alpha_2 u_n^{(2)} + \lambda\psi_1 + \lambda^2\psi_2 \tag{26}$$

Without loss of generality, we may assume that ψ_1 and ψ_2 are orthogonal to the unperturbed eigenfunctions $u_n^{(1)}, u_n^{(2)}$. Demanding this amounts to changing, as yet unknown, parameters α_1, α_2. We start with the equation,

$$H_0\psi_2 + H'\psi_1 = W_0\psi_2 + W_1\psi_1 + W_2\psi_0 \tag{27}$$

Taking scalar product with $u_n^{(1)}$, we get

$$(u_n^{(1)}, H_0\psi_2) + (u_n^{(1)}, H'\psi_1) = W_0(u_n^{(1)}, \psi_2) + W_1(u_n^{(1)}, \psi_1) + W_2(u_n^{(1)}, \psi_0) \tag{28}$$

The first two terms on the right hand side are zero due the orthogonality of ψ_1, ψ_2 to $u_n^{(1)}$. The first term on the left hand side also vanishes on using the hermiticity of H_0

$$(u_n^{(1)}, H_0\psi_2) = (H_0 u_n^{(1)}, \psi_2) \tag{29}$$

$$= E_n(u_n^{(1)}, \psi_2) \tag{30}$$

$$= 0$$

Also Eq.(28) we get,

$$(u_n^{(1)}, H'\psi_1) = W_2(u_n^{(1)}, \psi_0) \tag{31}$$

$$= \alpha_1 W_2 \tag{32}$$

On using for ψ_1 we get

$$\sum_{k\neq n} \frac{\langle k|H'|\psi_0\rangle}{E_k - E_n} = W_2\alpha_1 \tag{33}$$

Substituting for ψ_0 from (9) in Eq.(33) we get

$$\sum_{k\neq n} \frac{\langle k|H'|n1\rangle\langle n1|H'|k\rangle}{E_k - E_n}\alpha_1 + \sum_{k\neq n} \frac{\langle k|H'|n2\rangle\langle n1|H'|k\rangle}{E_k - E_n}\alpha_2 = W_2\,\alpha_1 \tag{34}$$

Similarly, taking scalar product with $u_n^{(2)}$ gives another equation

$$\sum_{k\neq n} \frac{\langle k|H'|n1\rangle\langle n2|H'|k\rangle}{E_k - E_n}\alpha_1 + \sum_{k\neq n} \frac{\langle k|H'|n2\rangle\langle n2|H'|k\rangle}{E_k - E_n}\alpha_2 = W_2\,\alpha_2 \tag{35}$$

The above equations can be put in a matrix form

$$\begin{bmatrix} \sum_{k\neq n} \frac{\langle n1|H'|k\rangle\langle k|H'|n1\rangle}{E_k - E_n} & \sum_{k\neq n} \frac{\langle n1|H'|k\rangle\langle k|H'|n2\rangle}{E_k - E_n} \\ \sum_{k\neq n} \frac{\langle n2|H'|k\rangle\langle k|H'|n1\rangle}{E_k - E_n} & \sum_{k\neq n} \frac{\langle n2|H'|k\rangle\langle k|H'|n2\rangle}{E_k - E_n} \end{bmatrix} \begin{bmatrix} \alpha_1 \\ \alpha_2 \end{bmatrix} = W_2 \begin{bmatrix} \alpha_1 \\ \alpha_2 \end{bmatrix} \tag{36}$$

The two eigenvalues, for W_2, give the second order corrections and the eigenvectors give the values of α_1, α_2 which determines the lowest order wave function ψ_0. It must be remembered that the above formula apply only in case the degeneracy is not removed to the first order in λ.

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