Approximate Methods in Quantum Chemistry
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Lecture 17
Perturbation Theory

Hello students! Welcome to this lecture. In the last few classes, we discussed the variational principle. We saw how we could use linear and non-linear variational methods and discuss chemical bonding. As applications of the linear variational principle, we discussed molecular orbital theory and valence bond theory. In this lecture, we will extend our discussion to another approximate method: the perturbation theory.

The key idea of variational principle is that if you have a system whose Hamiltonian is too difficult for an exact solution of the Schrödinger equation, you start with a trial function or a guess wave function (containing one or many variational parameters) and then use the variational principle to minimise the energy. By minimising the energy, you improve your trial function and finally estimate the true energy and true wave function. The critical bottleneck of this approach is that the best estimation of the energy and the wave function depends on the choice of the trail function. Furthermore, the application of the variational principle to the excited state was not straightforward. Keeping these two things in mind will now discuss the other approximate method that is the perturbation theory.

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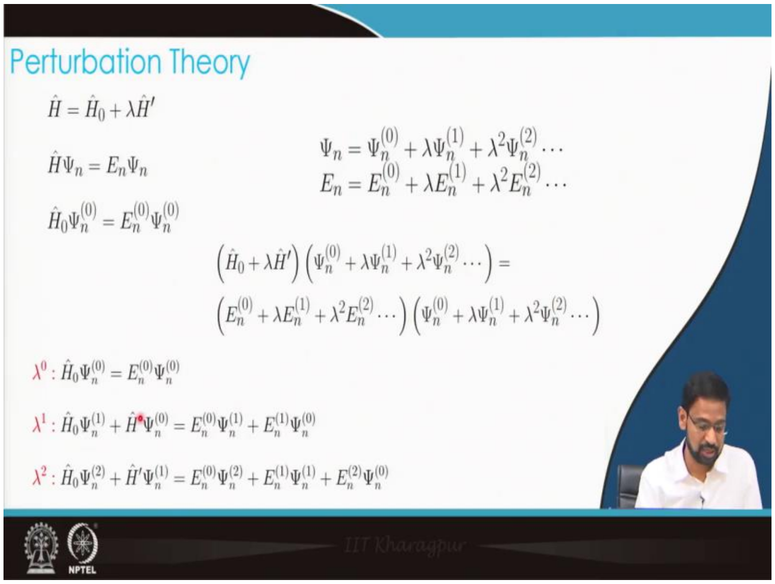

Perturbation Theory

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}'$$

$$\hat{H}\Psi_n = E_n\Psi_n$$

$$\hat{H}_0\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)}$$

$$\Psi_n = \Psi_n^{(0)} + \lambda\Psi_n^{(1)} + \lambda^2\Psi_n^{(2)} \cdots$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} \cdots$$

$$\left(\hat{H}_0 + \lambda\hat{H}'\right)\left(\Psi_n^{(0)} + \lambda\Psi_n^{(1)} + \lambda^2\Psi_n^{(2)} \cdots\right) =$$
$$\left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} \cdots\right)\left(\Psi_n^{(0)} + \lambda\Psi_n^{(1)} + \lambda^2\Psi_n^{(2)} \cdots\right)$$

$$\lambda^0 : \hat{H}_0\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)}$$

$$\lambda^1 : \hat{H}_0\Psi_n^{(1)} + \hat{H}'\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(1)} + E_n^{(1)}\Psi_n^{(0)}$$

$$\lambda^2 : \hat{H}_0\Psi_n^{(2)} + \hat{H}'\Psi_n^{(1)} = E_n^{(0)}\Psi_n^{(2)} + E_n^{(1)}\Psi_n^{(1)} + E_n^{(2)}\Psi_n^{(0)}$$

Within perturbation theory, the estimation of the true wave function and the true energy of a complicated system is obtained in a somewhat different way. The guiding principle in perturbation theory is to separate the complicated system into two parts, namely, the part that can be exactly solved (called the unperturbed part) and the remaining part that can not be solved exactly (the perturbation). For example, for a multi-electron atom or molecule, the two-body electron-electron interaction terms make the Schrödinger equation unsolvable. If we remove these terms, the remaining terms in the Hamiltonian are the sum of several 1-electron terms that can be solved exactly. Within perturbation theory, we would consider the electron-electron interaction terms are perturbation $(\widehat{H}^{'})$ to the non-interacting many-electron system $(\widehat{H_0})$.

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}'$$

$$\hat{H}\Psi_n = E_n \Psi_n$$

$$\hat{H}_0 \Psi_n^{(0)} = E_n^{(0)} \Psi_n^{(0)}$$

The term λ is a book-keeping perturbation parameter that controls the strength of the perturbation $(0 \geq \lambda \leq 1)$. The ultimate goal of the exercise is to find $\Psi_n and\ E_n$, while at the beginning of the exercise, we only know $\Psi_n^{(0)} and\ E_n^{(0)}$. We express $\Psi_n and\ E_n$ as,

$$\Psi_n = \Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} \cdots$$
$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} \cdots$$

Here, $\Psi_n^{(1)} and\ E_n^{(1)}$ are the first order correction to the wave function and energy, respectively. The above expressions are truncated after second-order corrections. We can use these expressions in the Schrodinger equation and obtain

$$\left(\hat{H}_0 + \lambda \hat{H}'\right)\left(\Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} \cdots\right) =$$
$$\left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} \cdots\right)\left(\Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} \cdots\right)$$

Next, we collect the terms with equal powers of λ $(\lambda^n, n = 0, 1, 2\ \ldots)$ s to obtain:

$$\lambda^0 : \hat{H}_0\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)}$$

$$\lambda^1 : \hat{H}_0\Psi_n^{(1)} + \hat{H}'\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(1)} + E_n^{(1)}\Psi_n^{(0)}$$

$$\lambda^2 : \hat{H}_0\Psi_n^{(2)} + \hat{H}'\Psi_n^{(1)} = E_n^{(0)}\Psi_n^{(2)} + E_n^{(1)}\Psi_n^{(1)} + E_n^{(2)}\Psi_n^{(0)}$$

The first expression is the solution of the unperturbed system.

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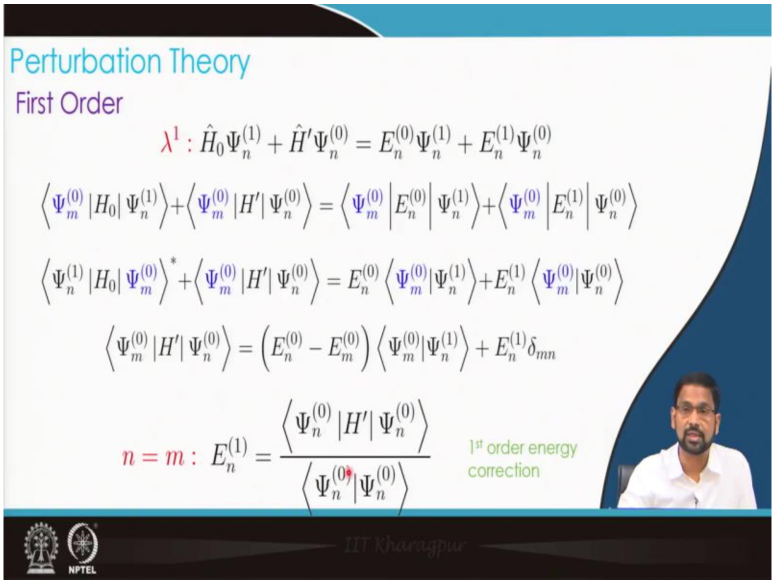

Perturbation Theory

First Order

$$\lambda^1 : \hat{H}_0\Psi_n^{(1)} + \hat{H}'\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(1)} + E_n^{(1)}\Psi_n^{(0)}$$

$$\left\langle \Psi_m^{(0)} \left| H_0 \right| \Psi_n^{(1)} \right\rangle + \left\langle \Psi_m^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle = \left\langle \Psi_m^{(0)} \left| E_n^{(0)} \right| \Psi_n^{(1)} \right\rangle + \left\langle \Psi_m^{(0)} \left| E_n^{(1)} \right| \Psi_n^{(0)} \right\rangle$$

$$\left\langle \Psi_n^{(1)} \left| H_0 \right| \Psi_m^{(0)} \right\rangle^* + \left\langle \Psi_m^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle = E_n^{(0)} \left\langle \Psi_m^{(0)} | \Psi_n^{(1)} \right\rangle + E_n^{(1)} \left\langle \Psi_m^{(0)} | \Psi_n^{(0)} \right\rangle$$

$$\left\langle \Psi_m^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle = \left(E_n^{(0)} - E_m^{(0)} \right) \left\langle \Psi_m^{(0)} | \Psi_n^{(1)} \right\rangle + E_n^{(1)}\delta_{mn}$$

$$n = m : \; E_n^{(1)} = \frac{\left\langle \Psi_n^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle}{\left\langle \Psi_n^{(0)} | \Psi_n^{(0)} \right\rangle}$$

1st order energy correction

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Let us consider the terms containing λ^1 and multiply $< \Psi_m^{(0)}|$ in each term,

$$\left\langle \Psi_m^{(0)} \left| H_0 \right| \Psi_n^{(1)} \right\rangle + \left\langle \Psi_m^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle = \left\langle \Psi_m^{(0)} \left| E_n^{(0)} \right| \Psi_n^{(1)} \right\rangle + \left\langle \Psi_m^{(0)} \left| E_n^{(1)} \right| \Psi_n^{(0)} \right\rangle$$

Using the facts that H_0 is Hermitian, and $\Psi_m^{(0)}, \Psi_n^{(0)} \ldots$ are orthogonal functions (eigenfunctions of Hermitian operator H_0), we get

$$\left\langle \Psi_m^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle = \left(E_n^{(0)} - E_m^{(0)} \right) \left\langle \Psi_m^{(0)} | \Psi_n^{(1)} \right\rangle + E_n^{(1)}\delta_{mn}$$

For $m = n$, upon rearrangement, we obtain:

$$\boxed{E_n^{(1)} = \frac{\left\langle \Psi_n^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle}{\left\langle \Psi_n^{(0)} | \Psi_n^{(0)} \right\rangle}}$$

The first order energy correction requires evaluation of two integrals. One, (in the numerator of the above expression) is evaluation of the expectation value of the perturbation Hamiltonian when the state of the system is defined as the unperturbed wave function $\Psi_n^{(0)}$. The second integral to be evaluated is equivalent to the normalization of $\Psi_n^{(0)}$. Please note, this correction is for the n^{th} state of the unperturbed system. To get energy correction of other states, similar procedure can be obtained.

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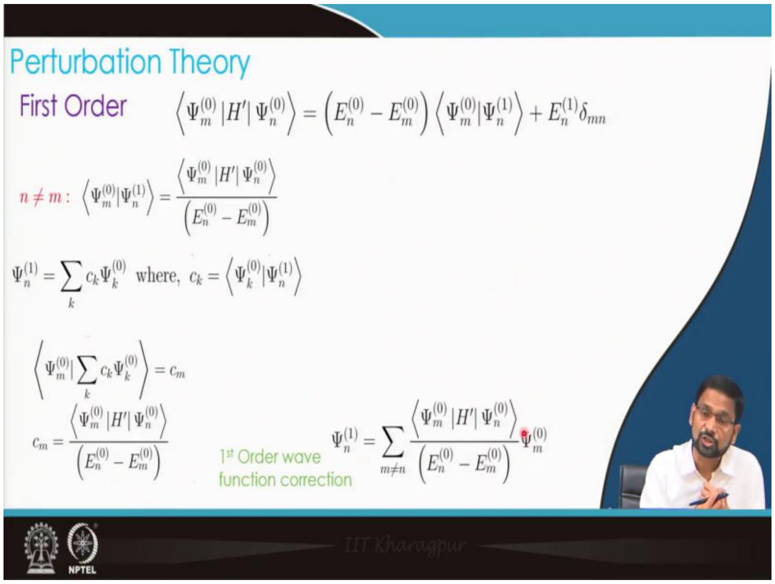

Perturbation Theory

First Order $\left\langle \Psi_m^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle = \left(E_n^{(0)} - E_m^{(0)} \right) \left\langle \Psi_m^{(0)} | \Psi_n^{(1)} \right\rangle + E_n^{(1)} \delta_{mn}$

$$n \neq m: \left\langle \Psi_m^{(0)} | \Psi_n^{(1)} \right\rangle = \frac{\left\langle \Psi_m^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)}$$

$$\Psi_n^{(1)} = \sum_k c_k \Psi_k^{(0)} \text{ where, } c_k = \left\langle \Psi_k^{(0)} | \Psi_n^{(1)} \right\rangle$$

$$\left\langle \Psi_m^{(0)} \left| \sum_k c_k \Psi_k^{(0)} \right. \right\rangle = c_m$$

$$c_m = \frac{\left\langle \Psi_m^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)}$$

1st Order wave function correction

$$\Psi_n^{(1)} = \sum_{m \neq n} \frac{\left\langle \Psi_m^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)} \Psi_m^{(0)}$$

Now, we will look at the wave function correction. Starting from the expression,

$$\left\langle \Psi_m^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle = \left(E_n^{(0)} - E_m^{(0)} \right) \left\langle \Psi_m^{(0)} | \Psi_n^{(1)} \right\rangle + E_n^{(1)} \delta_{mn}$$

and considering $m \neq n$, we get

$$n \neq m: \left\langle \Psi_m^{(0)} | \Psi_n^{(1)} \right\rangle = \frac{\left\langle \Psi_m^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)}$$

Now, we can express the unknown function $\Psi_n^{(1)}$ in the basis of orthonormal, complete set of functions $\{\Psi_m^{(0)}\}$ as

$$\Psi_n^{(1)} = \sum_k c_k \Psi_k^{(0)} \quad \text{where,} \quad c_k = \left\langle \Psi_k^{(0)} | \Psi_n^{(1)} \right\rangle$$

With some rearrangements, we obtain

$$\Psi_n^{(1)} = \sum_{m \neq n} \frac{\left\langle \Psi_m^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)} \Psi_m^{(0)}$$

To obtain the first order wave function correction for the n^{th} state, we need to evaluate integrals $\langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \rangle$ for all values of $m \neq n$. This summation is over *all* the states of the complete set of eigenfunctions of the unperturbed Hamiltonian (H_0). Hence, the cost of obtaining first order wave function correction is quite high, because, in principle, we have to calculate infinite number of integrals.

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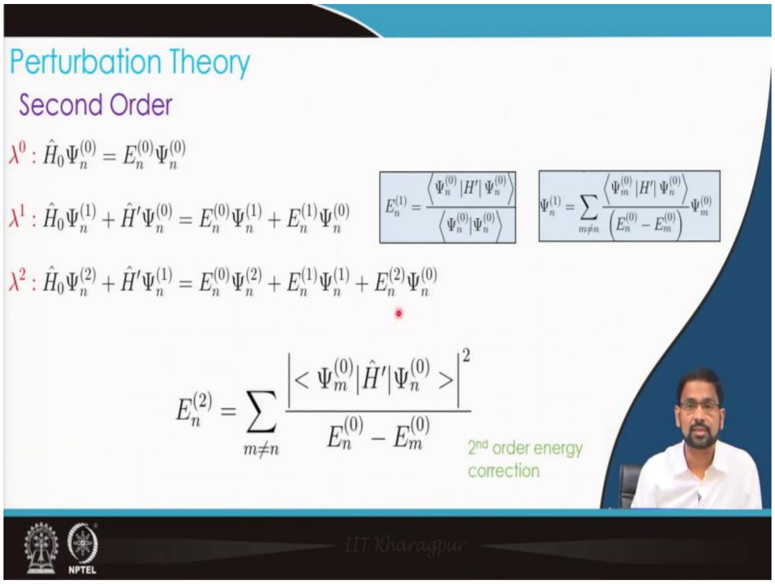

Perturbation Theory

Second Order

$$\lambda^0 : \hat{H}_0 \Psi_n^{(0)} = E_n^{(0)} \Psi_n^{(0)}$$

$$\lambda^1 : \hat{H}_0 \Psi_n^{(1)} + \hat{H}' \Psi_n^{(0)} = E_n^{(0)} \Psi_n^{(1)} + E_n^{(1)} \Psi_n^{(0)}$$

$$\boxed{E_n^{(1)} = \frac{\left\langle \Psi_n^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle}{\left\langle \Psi_n^{(0)} | \Psi_n^{(0)} \right\rangle}} \qquad \boxed{\Psi_n^{(1)} = \sum_{m \neq n} \frac{\left\langle \Psi_m^{(0)} \left| H' \right| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)} \Psi_m^{(0)}}$$

$$\lambda^2 : \hat{H}_0 \Psi_n^{(2)} + \hat{H}' \Psi_n^{(1)} = E_n^{(0)} \Psi_n^{(2)} + E_n^{(1)} \Psi_n^{(1)} + E_n^{(2)} \Psi_n^{(0)}$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{\left| < \Psi_m^{(0)} | \hat{H}' | \Psi_n^{(0)} > \right|^2}{E_n^{(0)} - E_m^{(0)}}$$

2nd order energy correction

So far, we have obtained first-order wave function and energy corrections. By doing a similar exercise, we can obtain the second order energy correction (shown above). Careful observation would show that the terms appearing in the 2nd order wave function correction are already present in the 1st order wave function correction. Hence, the cost of obtaining second-order energy correction is equivalent to the cost of getting the first-order wave function corrections.

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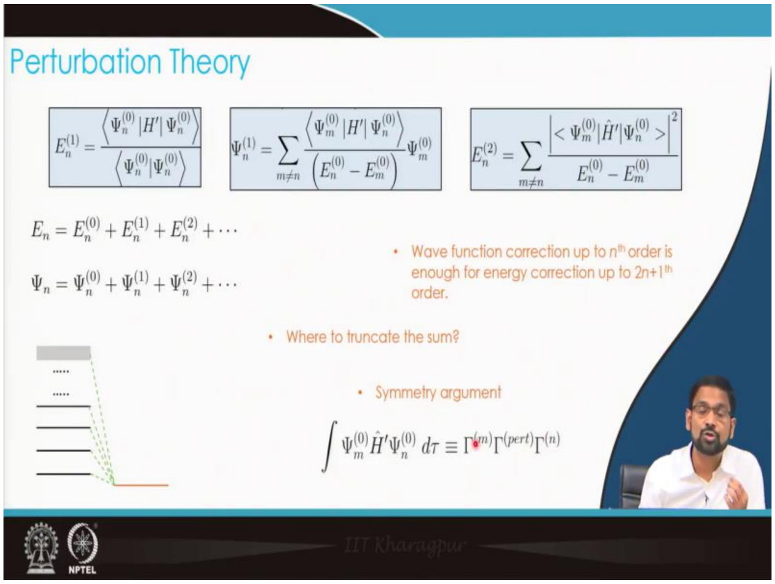

Perturbation Theory

$$E_n^{(1)} = \frac{\left\langle \Psi_n^{(0)} \middle| H' \middle| \Psi_n^{(0)} \right\rangle}{\left\langle \Psi_n^{(0)} \middle| \Psi_n^{(0)} \right\rangle}$$

$$\Psi_n^{(1)} = \sum_{m \neq n} \frac{\left\langle \Psi_m^{(0)} \middle| H' \middle| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)} \Psi_m^{(0)}$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{\left| < \Psi_m^{(0)} | \hat{H}' | \Psi_n^{(0)} > \right|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \cdots$$

$$\Psi_n = \Psi_n^{(0)} + \Psi_n^{(1)} + \Psi_n^{(2)} + \cdots$$

- Wave function correction up to n^{th} order is enough for energy correction up to $2n+1^{th}$ order.
- Where to truncate the sum?
- Symmetry argument

$$\int \Psi_m^{(0)} \hat{H}' \Psi_n^{(0)} \, d\tau \equiv \Gamma^{(m)} \Gamma^{(pert)} \Gamma^{(n)}$$

Using the corrections in the energy and wave functions, we can obtain the final form of the energy and wave functions as shown above. We can obtain higher-order corrections, but they come with huge additional cost with a marginal increase in accuracy.

We already saw that the cost of obtaining first-order wave function correction and second-order energy correction are similar. In fact, it can be shown that if we have n^{th} order wave function correction, we can estimate $(2n+1)^{\text{th}}$ order energy corrections. So, in principle, if I have first-order wave function correction, I can easily evaluate up to the third energy correction.

For 1st order wave function correction (and also 2nd order energy correction), we noticed that the number of integrals to be evaluated is, in principle, infinite. In practice, we need to truncate it somewhere. Suppose I want 1st order correction for $n = 1$. We can immediately see that $|E_m - E_1|$ becomes very large for states that are far in energy from E_1. Hence, their contribution to the 1st order wave function correction is low. Hence, the perturbation correction for a state of choice is dominant from those states that lie close in energy to the state of interest. Thus, we can truncate the series to a few nearby states.

Additionally, we can also use symmetry to decide which states can contribute to the correction of the state of choice.

$$\int \Psi_m^{(0)} \hat{H}' \Psi_n^{(0)} \, d\tau \equiv \Gamma^{(m)} \Gamma^{(pert)} \Gamma^{(n)}$$

It can be shown that only those states (m) have a non-zero contribution, for which the right-hand side of the above equation contains the totally symmetric irreducible representation. In such a case, we need to evaluate contributions from a fewer number of states that satisfy the symmetry requirement.

In the next lecture, we will discuss a few examples of perturbation theory.

Thank you for your attention.