BYJU'S EXAM PREP

Study Notes On Perturbation Theory

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Perturbation Method

It is one of the Approximate methods.
Let's derive the equation for a first-order correction to the energy. The problem that we wish to solve is

$$\hat{H}\Psi_n = E_n\Psi_n \qquad ...(1)$$

where

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} \qquad ...(2)$$

And where the problem, $\hat{H}^{(0)}\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)}$ ...(3)

has been solved exactly, so that the $\Psi_n^{(0)}$ and $E_n^{(0)}$ are known. In order to keep track of the order of our perturbation expansion, it is convenient to introduce a parameter λ into the Hamiltonian operator:

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{H}^{(1)} \qquad ...(4)$$

The factor λ is simply a bookkeeping device that will help us identify to what order our resultant perturbation equations are valid. We shall see that terms linear in λ give us what we call first-order corrections, terms in λ^2 give us second-order corrections, and so on. At the end of the problem, once we have calculated corrections to the desired order, we shall simply set λ = 1.

The fact that $\hat{H}$ in $\hat{H}\Psi_n = E_n\Psi_n$ is of the form $\hat{H}^{(0)} + \lambda\hat{H}^{(1)}$ means that Ψ_n and E_n will depend upon λ. We assume that we can express the Ψ_n and E_n in $\hat{H}\Psi_n = E_n\Psi_n$ as power series in λ, so that

$$\Psi_n = \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \ldots \qquad ...(5)$$

and

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots \qquad ...(6)$$

If Equations (5) and (6) are to be useful, successive terms in their series must grow progressively less important and we can obtain good approximations to Ψ_n and E_n with just a few terms.
We substitute Equations 5 and 6 into 1 to obtain-

$$(\hat{H}^{(0)} + \lambda\hat{H}^{(1)})(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \ldots) = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots)$$
$$\times(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \ldots)$$

Each side of this equation is an expansion in λ, which can be written as-

$$(\hat{H}^{(0)}\psi_n^{(0)} - E_n^{(0)}\psi_n^{(0)}) + \hat{H}^{(0)}\psi_n^{(1)} + \hat{H}^{(1)}\psi_n^{(0)} - E_n^{(0)}\psi_n^{(1)} - E_n^{(1)}\psi_n^{(0)})\lambda$$
$$+ (\hat{H}^{(0)}\psi_n^{(2)} + \hat{H}^{(1)}\psi_n^{(1)} - E_n^{(0)}\psi_n^{(2)} - E_n^{(1)}\psi_n^{(1)} - E_n^{(2)}\psi_n^{(0)}\lambda^2 + O(\lambda^3) = 0 \qquad ...(7)$$

where $O(\lambda^3)$ means terms of order λ^3 and higher. Notice that both terms in the first set of parentheses, the coefficient of λ^0, are of zero order, all four terms in the second set of parentheses, the coefficient of λ^1, are of first order, and so on.
Because λ is an arbitrary parameter, the coefficients of each power of λ must be equal to zero separately for Equation 7 to hold. The terms in the first set of parentheses, the coefficient of λ^0 cancel because of Equation 3.
Let's look at the coefficient of λ^1:

$$\hat{H}^{(0)}\psi_n^{(1)} + \hat{H}^{(1)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)} \qquad ...(8)$$

Equation 8 can be simplified considerably by multiplying both sides from the left by $\psi_n^{(0)*}$ integrating over all space. By doing this and then rearranging slightly, we get-

$$\int \psi_n^{(0)*}(\hat{H}^{(0)} - E_n^{(0)})\psi_n^{(1)} d\tau + \int \psi_n^{(0)*}(\hat{H}^{(1)}\psi_n^{(0)} d\tau = E_n^{(1)} \int \psi_n^{(0)*}\psi_n^{(0)} d\tau \qquad ...(9)$$

It is convenient (and economical) at this stage to use the bracket notation and write Equation 9 as

$$\left\langle \psi_n^{(0)} \,|\, \hat{H}^{(0)} - E_n^{(0)} \,|\, \psi_n^{(1)} \right\rangle + \left\langle \psi_n^{(0)} \,|\, (\hat{H}^{(1)} \,|\, \psi_n^{(0)} \right\rangle = E_n^{(1)} \left\langle \psi_n^{(0)} \,|\, \psi_n^{(0)} \right\rangle \qquad ...(10)$$

The integral in the last term in Equation 10 is unity because we take $\psi_n^{(0)}$ to be normalized. More importantly, however, the first term on the left side is equal to zero.
To see this, remember that $\hat{H}^{(0)} - E^{(0)}$ is Hermitian, and so we have

$$\left\langle \psi_n^{(0)} \,|\, \hat{H}^{(0)} - E_n^{(0)} \,|\, \psi_n^{(1)} \right\rangle = \left\langle (\hat{H}^{(0)} - E_n^{(0)})\psi_n^{(0)} \,|\, \psi_n^{(1)} \right\rangle = 0$$

because of Equation 3.

Thus, Equation 10 becomes

$$E_n^{(1)} = \left\langle \psi_n^{(0)} \,|\, \hat{H}^{(1)} \,|\, \psi_n^{(0)} \right\rangle = \int d\tau\, \psi_n^{(0)*} H^{(1)}\, \psi_n^{(0)} \qquad ...(11)$$

Equation 11 gives $E_n^{(1)}$, the first-order correction to $E_n^{(0)}$. Through first order, then, the energy is given by

$$E_n = E_n^{(0)} + E_n^{(1)} = E_n^{(0)} + \left\langle \psi_n^{(0)} \,|\, \hat{H}^{(1)} \,|\, \psi_n^{(0)} \right\rangle \quad \text{(first order)} \qquad ...(12)$$

Second Order Perturbation

It is the correction to the energy i.e. based on the function that is modified during 1st order perturbation energy.
For the second order perturbation, the energy state can never be equal. The energy correction for second order is-

$$E_n^2 = \sum_{m \neq n} \frac{\langle \phi_m \,|\, W \,|\, \phi_n \rangle^2}{E_n^0 - E_m^0}$$

If $n = m$ then the value becomes zero.