Perturbation Theory in Quantum Mechanics

BIRMD

The Time Independent Perturbation Theory

Non-Degenerate Rayleigh - Schrödinger Perturbation Theory

- **Given:** Hamiltonian
$$\hat{H} = \hat{H}_0 + \delta \hat{H}$$
where $\hat{H}_0$ is exactly solvable and it's energy spectrum is
$$\hat{H}_0 \left|\phi_n\right\rangle = \epsilon_n \left|\phi_n\right\rangle$$
Now we need to find the energy spectrum of complete $\hat{H}$ such that
$$\hat{H} \left|\psi_n\right\rangle = E_n \left|\psi_n\right\rangle$$

- **Assume:**
  - ◇ $\hat{H} = \hat{H}_0 + \lambda\, \delta \hat{H}$
  - ◇ $E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots = \sum_{i=0}^{\infty} \lambda^i E_n^{(i)}$
  - ◇ $\left|\psi_n\right\rangle = \left|\psi_n^{(0)}\right\rangle + \lambda \left|\psi_n^{(1)}\right\rangle + \lambda^2 \left|\psi_n^{(2)}\right\rangle + \cdots = \sum_{i=0}^{\infty} \lambda^i \left|\psi_n^{(i)}\right\rangle$

- Substituting this in Schrödinger equation and comparing powers of λ will give
  - ◇ $\lambda^0 \,:\, \hat{H}_0 \left|\psi_n^{(0)}\right\rangle = E_n^{(0)} \left|\psi_n^{(0)}\right\rangle$; and
  - ◇ $\lambda^m \,:\, \hat{H}_0 \left|\psi_n^{(m)}\right\rangle + \delta\hat{H} \left|\psi_n^{(m-1)}\right\rangle = \sum_{j=0}^{m} E_n^{(j)} \left|\psi_n^{(m-j)}\right\rangle$, for $\forall\, m \in \mathbb{N}$ $\star$

- **Zeroth Order Correction:** Comparing this with Schrödinger equation for $\hat{H}_0$ will give
$$E_n^{(0)} = \epsilon_n \quad \& \quad \left|\psi_n^{(0)}\right\rangle = \left|\phi_n\right\rangle$$

- **First Order Correction:** We know
$$\hat{H}_0 \left|\psi_n^{(1)}\right\rangle + \delta\hat{H} \left|\psi_n^{(0)}\right\rangle = E_n^{(0)} \left|\psi_n^{(1)}\right\rangle + E_n^{(1)} \left|\psi_n^{(0)}\right\rangle$$

Act by $\langle\phi_m|$ on both side will give

$$\langle\phi_m|\hat{H}_0\left|\psi_n^{(1)}\right\rangle + \langle\phi_m|\delta\hat{H}|\phi_n\rangle = \langle\phi_m|\epsilon_n\left|\psi_n^{(1)}\right\rangle + \langle\phi_m|E_n^{(1)}|\phi_n\rangle$$

$\hat{H}_0$ can act on $\langle\phi_n|$ as it's hermitian and this state is its eigenstate. Thus we get

$$\epsilon_m\left\langle\phi_m|\psi_n^{(1)}\right\rangle + \langle\phi_m|\delta\hat{H}|\phi_n\rangle = \epsilon_n\left\langle\phi_m|\psi_n^{(1)}\right\rangle + E_n^{(1)}\delta_{m,n}$$

1) For $m = n$, we get

$$\boxed{E_n^{(1)} = \langle\phi_n|\delta\hat{H}|\phi_n\rangle}$$

2) For $m \neq n$, we get

$$\left\langle\phi_m|\psi_n^{(1)}\right\rangle = \frac{\langle\phi_m|\delta\hat{H}|\phi_n\rangle}{\epsilon_n - \epsilon_m}$$

which will give

$$\boxed{\left|\psi_n^{(1)}\right\rangle = \left\langle\phi_n|\psi_n^{(1)}\right\rangle|\phi_n\rangle + \sum_{m\neq n}\frac{\langle\phi_m|\delta\hat{H}|\phi_n\rangle}{\epsilon_n - \epsilon_m}|\phi_m\rangle}$$

- **Overlap of $|\phi_n\rangle$ and $\left|\psi_n^{(s\geq 1)}\right\rangle$:**
  - **Intermediate Normalization:**

$$\left\langle\phi_n|\psi_n^{(s\geq 1)}\right\rangle = 0$$

  - **Conventional Normalization:**

$$\langle\psi_n|\psi_n\rangle = 1 \quad \Rightarrow \quad \sum_{i,j}\lambda^{i+j}\left\langle\psi_n^{(i)}|\psi_n^{(j)}\right\rangle = 1$$

rewriting this

$$\sum_i \lambda^i\left(\sum_j\left\langle\psi_n^{(j)}|\psi_n^{(i-j)}\right\rangle\right) = \sum_i \lambda^i\delta_{i,0}$$

Thus

$$\boxed{\sum_j\left\langle\psi_n^{(j)}|\psi_n^{(i-j)}\right\rangle = \delta_{i,0}}$$

So for $i = 0$, we have

$$\left\langle\phi_n|\psi_n^{(1)}\right\rangle + \left\langle\psi_n^{(1)}|\phi_n\right\rangle = 0$$

And so on...

- **Second Order Correction:** Again, we know that

$$\hat{H}_0\left|\psi_n^{(2)}\right\rangle + \delta\hat{H}\left|\psi_n^{(1)}\right\rangle = E_n^{(0)}\left|\psi_n^{(2)}\right\rangle + E_n^{(1)}\left|\psi_n^{(1)}\right\rangle + E_n^{(2)}\left|\psi_n^{(0)}\right\rangle$$

Act by $\langle\phi_m|$ on both side will give

$$\langle\phi_m|\hat{H}_0\left|\psi_n^{(2)}\right\rangle + \langle\phi_m|\delta\hat{H}\left|\psi_n^{(1)}\right\rangle = \langle\phi_m|\epsilon_n\left|\psi_n^{(2)}\right\rangle + \langle\phi_m|E_n^{(1)}\left|\psi_n^{(1)}\right\rangle + \langle\phi_m|E_n^{(2)}|\phi_n\rangle$$

This will simplify into following

$$(\epsilon_m - \epsilon_n) \left\langle \phi_m | \psi_n^{(2)} \right\rangle + \langle \phi_m | \delta\hat{H} \left| \psi_n^{(1)} \right\rangle = E_n^{(1)} \left\langle \phi_m | \psi_n^{(1)} \right\rangle + E_n^{(2)} \delta_{m,n}$$

1) For $m = n$, we get

$$E_n^{(2)} = \langle \phi_m | \delta\hat{H} \left| \psi_n^{(1)} \right\rangle - E_n^{(1)} \left\langle \phi_n | \psi_n^{(1)} \right\rangle$$

The term in red can't be determined using perturbation theory. But we don't need that. We can use resolution of identity:

$$E_n^{(2)} = \langle \phi_n | \delta\hat{H} \left(\sum_m |\phi_m\rangle \langle \phi_m| \right) \left| \psi_n^{(1)} \right\rangle - E_n^{(1)} \left\langle \phi_m | \psi_n^{(1)} \right\rangle$$

This will simplify into following

$$E_n^{(2)} = \sum_{m \neq n} \langle \phi_n | \delta\hat{H} | \phi_m \rangle \left\langle \phi_m | \psi_n^{(1)} \right\rangle + \left(\langle \phi_n | \delta\hat{H} | \phi_n \rangle - E_n^{(1)} \right) \left\langle \phi_n | \psi_n^{(1)} \right\rangle$$

The term in red goes to zero and we can substitute the term in blue from an expression above in first order correction part, which will give us following result

$$\boxed{E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \phi_m | \delta\hat{H} | \phi_n \rangle|^2}{\epsilon_n - \epsilon_m}}$$

- **Remarks**
  - The energy of perturbed Hamiltonian upto second order correction is

$$\boxed{E_n \approx \epsilon_n + \delta\hat{H}_{nn} + \sum_{m \neq n} \frac{|\delta\hat{H}_{mn}|^2}{\epsilon_n - \epsilon_m}}$$

    where $\delta\hat{H}_{mn} = \langle \phi_m | \delta\hat{H} | \phi_n \rangle$.
  - The second order correction is important if: (i) The first order correction vanishes; or (ii) There is an energy level very close to ϵ_n.
  - For the ground state, the second order energy correction is always negative.
  - The indeterminacy in the first order correction of the wave function $\left(\left| \psi_n^{(1)} \right\rangle \right)$ does not affect the value of $E_n^{(2)}$.

- If we act by $\langle \phi_n |$ on both side of $\star$, it'll give

$$E_n^{(m)} = \langle \phi_n | \delta\hat{H} \left| \psi_n^{(m-1)} \right\rangle - \sum_{j=1}^{m-1} E_n^{(j)} \left\langle \phi_n | \psi_n^{(m-j)} \right\rangle$$

It seems that for knowing m-th order energy correction, we need previous $m - 1$ energy correction, but that is not the case.

- **$2s+1$ Rule:** If we know energy and eigenstate correction up to s-th order, then using them, we can find energy correction up to $(2s+1)$-th order.

  We can re-write the $\star$ equation as

$$(\hat{H}_0 - \epsilon_n)\left|\psi_n^{(m)}\right\rangle + (\delta\hat{H} - E_n^{(1)})\left|\psi_n^{(m-1)}\right\rangle = \sum_{j=2}^{m} E_n^{(j)}\left|\psi_n^{(m-j)}\right\rangle$$

  Using this, we can find an expression for $\left\langle\psi_n^{(p)}\right|(\delta\hat{H} - E_n^{(1)})$ and act it on $\left|\psi_n^{(q)}\right\rangle$, which will give

$$\left\langle\psi_n^{(p)}\right|(\delta\hat{H} - E_n^{(1)})\left|\psi_n^{(q)}\right\rangle = \left\langle\psi_n^{(p+1)}\right|(\epsilon_n - \hat{H}_0)\left|\psi_n^{(q)}\right\rangle + \sum_{j=2}^{p+1} E_n^{(j)}\left\langle\psi_n^{(p+1-j)}|\psi_n^{(q)}\right\rangle$$

  Now again previous expression, we can expand the blue term in this equation and can arrive at following formula

$$\left\langle\psi_n^{(p)}\right|(\delta\hat{H} - E_n^{(1)})\left|\psi_n^{(q)}\right\rangle = \left\langle\psi_n^{(p+1)}\right|(\delta\hat{H} - E_n^{(1)})\left|\psi_n^{(q-1)}\right\rangle - \sum_{j=2}^{q} E_n^{(j)}\left\langle\psi_n^{(p+1)}|\psi_n^{(q-j)}\right\rangle + \sum_{j=2}^{p+1} E_n^{(j)}\left\langle\psi_n^{(p+1-j)}|\psi_n^{(q)}\right\rangle$$

  Using this formula, we can find energy correction up to $2s+1$ order.

  ◇ **Third Order Correction:**

$$E_n^{(3)} = \left\langle\psi_n^{(1)}\right|(\delta\hat{H} - E_n^{(1)})\left|\psi_n^{(1)}\right\rangle$$

  ◇ **Fourth Order Correction:**

$$E_n^{(4)} = \left\langle\psi_n^{(1)}\right|(\delta\hat{H} - E_n^{(1)})\left|\psi_n^{(2)}\right\rangle + E_n^{(2)}\left\langle\psi_n^{(2)}|\phi_n\right\rangle$$

  ◇ **Fifth Order Correction:**

$$E_n^{(5)} = \left\langle\psi_n^{(1)}\right|(\delta\hat{H} - E_n^{(1)})\left|\psi_n^{(2)}\right\rangle - E_n^{(2)}\left(\left\langle\psi_n^{(1)}|\psi_n^{(2)}\right\rangle + \left\langle\psi_n^{(2)}|\psi_n^{(1)}\right\rangle\right)$$