Lecture Notes on Quantum Mechanics

1 Nondegenerate Perturbation Theory

Suppose we have an exact solution to the unperturbed Hamiltonian:

$$H^{(0)}\,\psi_n^{(0)} = E_n^{(0)}\,\psi_n^{(0)},$$

where the eigenfunctions $\psi_n^{(0)}$ are orthonormal:

$$\langle \psi_n^{(0)} | \psi_m^{(0)} \rangle = \delta_{nm}.$$

The perturbed Hamiltonian is given by:

$$H = H^{(0)} + \lambda\,H',$$

where H' is the perturbation term and λ is a small parameter. The goal of perturbation theory is to approximate the eigenvalues E_n and eigenfunctions ψ_n of the perturbed Hamiltonian based on the unperturbed solutions.

We assume the eigenfunctions and eigenvalues can be expanded in powers of λ:

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

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

Substituting these expansions into the Schrödinger equation $H\,\psi_n = E_n\,\psi_n$, we get:

$$(H^{(0)} + \lambda\,H')\left(\psi_n^{(0)} + \lambda\,\psi_n^{(1)} + \lambda^2\,\psi_n^{(2)} + \cdots\right) = \left(E_n^{(0)} + \lambda\,E_n^{(1)} + \lambda^2\,E_n^{(2)} + \cdots\right)\left(\psi_n^{(0)} + \lambda\,\psi_n^{(1)} + \lambda^2\,\psi_n^{(2)} + \cdots\right).$$

1.1 First-order energy correction

To find the first-order correction to the energy $E_n^{(1)}$, we take the inner product of the equation with the unperturbed eigenfunction $\psi_m^{(0)}$:

$$\langle \psi_m^{(0)} | H\,\psi_n \rangle = \langle \psi_m^{(0)} | E_n\,\psi_n \rangle.$$

Expanding both sides in powers of λ, we focus on the first-order terms:

$$\langle \psi_m^{(0)} | H^{(0)}\,\psi_n^{(1)} \rangle + \langle \psi_m^{(0)} | H'\,\psi_n^{(0)} \rangle = E_n^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle + E_n^{(1)} \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle. \quad (1)$$

Using the orthonormality condition $\langle \psi_m^{(0)} | \psi_n^{(0)} \rangle = \delta_{mn}$, we get:

$$\langle \psi_m^{(0)} | H^{(0)}\,\psi_n^{(1)} \rangle + \langle \psi_m^{(0)} | H'\,\psi_n^{(0)} \rangle = E_n^{(1)}\,\delta_{mn}.$$

For $m = n$, the equation simplifies to:

$$\langle \psi_n^{(0)} | H'\,\psi_n^{(0)} \rangle = E_n^{(1)}.$$

Thus, the first-order correction to the energy is:

$$E_n^{(1)} = \langle \psi_n^{(0)} | H' | \,\psi_n^{(0)} \rangle. \quad (2)$$

Summary

- **Unperturbed Hamiltonian**: $H^{(0)}\,\psi_n^{(0)} = E_n^{(0)}\,\psi_n^{(0)}$.
- **Perturbed Hamiltonian**: $H = H^{(0)} + \lambda\,H'$.
- **Eigenfunction Expansion**: $\psi_n = \psi_n^{(0)} + \lambda\,\psi_n^{(1)} + \lambda^2\,\psi_n^{(2)} + \cdots$.
- **Eigenvalue Expansion**: $E_n = E_n^{(0)} + \lambda\,E_n^{(1)} + \lambda^2\,E_n^{(2)} + \cdots$.
- **First-Order Energy Correction**: $E_n^{(1)} = \langle\psi_n^{(0)}|H'|\,\psi_n^{(0)}\rangle$.

Example 1. (The unperturbed Hamiltonian for a 1D infinite square well) 1. Unperturbed System: 1D Infinite Square Well

- **Wavefunctions:**

$$\psi_n^{(0)}(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\,\pi}{a}\,x\right), \quad n = 1, 2, 3, \ldots$$

- These are the eigenfunctions of the unperturbed system, where a is the width of the well.
  - **Energy levels:**

$$E_n^{(0)} = \frac{\hbar^2}{2\,m}\left(\frac{n\,\pi}{a}\right)^2, \quad n = 1, 2, 3, \ldots$$

- **Plane Wave Interpretation:**
  - The energy of a free particle is given by:

$$E = \frac{\hbar^2\,k^2}{2\,m}$$

- Quantization in the square well corresponds to:

$$k \rightarrow \frac{n\,\pi}{a}$$

First Perturbation: Constant Perturbation $H' = V_0$

- **Perturbation Hamiltonian:**

$$H' = V_0 \quad \text{(Constant)}$$

- **Solution:**
  - The first-order correction to the energy is given by:

$$E_n^{(1)} = \langle\psi_n^{(0)}|H'|\,\psi_n^{(0)}\rangle = \langle\psi_n^{(0)}|V_0|\,\psi_n^{(0)}\rangle = V_0\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle = V_0$$

- Since $\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle = 1$ (normalized wavefunctions), the total energy up to the first-order correction is:

$$E_n = E_n^{(0)} + E_n^{(1)} = E_n^{(0)} + V_0$$

Second Perturbation: Spatially Dependent Perturbation

- **Perturbation Hamiltonian:**

$$H'(x) = \begin{cases} V_0, & 0 \le x \le \frac{a}{2} \\ 0, & \text{otherwise} \end{cases}$$

- **Solution:**
  - The first-order correction to the energy is given by:

$$E_n^{(1)} = \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle = \int d\,x\ \psi_n^{(0)}(x)\, H'(x)\, \psi_n^{(0)}(x)$$

- For $H'(x)$, the integral becomes:

$$E_n^{(1)} = \int_0^{a/2} d\,x\ V_0 \left(\sqrt{\frac{2}{a}} \sin\left(\frac{n\,\pi}{a} x \right) \right)^2$$

$$E_n^{(1)} = V_0 \int_0^{a/2} \frac{2}{a} \sin^2\left(\frac{n\,\pi}{a} x \right) d\,x$$

- Using the identity $\sin^2(x) = \frac{1 - \cos(2\,x)}{2}$:

$$\int_0^{a/2} \sin^2\left(\frac{n\,\pi}{a} x \right) d\,x = \frac{a}{4} \quad \text{(for odd } n\text{)}$$

$$\int_0^{a/2} \sin^2\left(\frac{n\,\pi}{a} x \right) d\,x = \frac{a}{4} - \frac{a}{2\,\pi\,n} \quad \text{(for even } n\text{)}$$

- Therefore:

$$E_n^{(1)} = V_0 \cdot \frac{1}{2} \quad \text{(for odd } n\text{)}$$

$$E_n^{(1)} = V_0 \left(\frac{1}{2} - \frac{1}{\pi\,n} \right) \quad \text{(for even } n\text{)}$$

Completeness of Wavefunctions

- The completeness relation for the wavefunctions is:

$$\int d\,x\, |x\rangle \langle x| = \hat{1}$$

$$\sum_n |n\rangle \langle n| = \hat{1}$$

- This ensures that the set of eigenfunctions $\{\psi_n(x)\}$ forms a complete basis in the Hilbert space.

Harmonic Oscillator

- The lecture also briefly mentions the harmonic oscillator, which is another important system in quantum mechanics.

1.2 First-order correction to the wave function $\psi_n^{(1)}$

Rewrite (1) into

$$\left[H^0 - E_n^{(0)}\right]\psi_n^{(1)} = -\left[H' - E_n^{(1)}\right]\psi_n^{(0)}$$

Since $(H^{(0)} - E_n^{(0)})\,\psi_n^{(0)} = 0$, the equation becomes:

$$(H^{(0)} - E_n^{(0)})\,\psi_n^{(1)} = -H'\,\psi_n^{(0)}$$

Projecting onto $\psi_m^{(0)}$:

$$\langle\psi_m^{(0)}|(H^{(0)} - E_n^{(0)})\,\psi_n^{(1)}\rangle = -\langle\psi_m^{(0)}|H'\,\psi_n^{(0)}\rangle$$

Using the orthogonality of the unperturbed wave functions:

$$\langle\psi_m^{(0)}|\psi_n^{(1)}\rangle\,(H^{(0)} - E_n^{(0)})\,\delta_{mn} = -\langle\psi_m^{(0)}|H'\,\psi_n^{(0)}\rangle$$

For $m = n$:

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

Since $\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle = 0$ (orthogonality):

$$0 = -\langle\psi_n^{(0)}|H'\,\psi_n^{(0)}\rangle$$

Thus, the first-order correction to the wave function is obtained by solving:

$$\psi_n^{(1)} = \sum_{m \neq n} C_m\,\psi_m^{(0)}$$

where the coefficients C_m are determined by:

$$C_m = \frac{\langle\psi_m^{(0)}|H'|\,\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}.$$

1.3 Second-order energy correction

Second-Order Correction: The second-order correction to the energy is given by

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle\psi_m^{(0)}|H'|\,\psi_n^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

Derivation from the Schrödinger Equation: To derive this, we use the fact that the perturbed state satisfies the Schrödinger equation:

$$H|\psi_n\rangle = E_n|\psi_n\rangle$$

Substituting the expansions for H, $|\psi_n\rangle$, and E_n, and collecting terms at $\mathcal{O}(\lambda^2)$, we get:

$$H_0|\psi_n^{(2)}\rangle + H'|\psi_n^{(1)}\rangle = E_n^{(2)}|\psi_n^{(0)}\rangle + E_n^{(0)}|\psi_n^{(2)}\rangle + E_n^{(1)}|\psi_n^{(1)}\rangle$$

1. **Projection onto Unperturbed States**: To isolate $E_n^{(2)}$, project the above equation onto $\langle\psi_n^{(0)}|$:

$$\langle\psi_n^{(0)}|H_0|\,\psi_n^{(2)}\rangle + \langle\psi_n^{(0)}|H'|\,\psi_n^{(1)}\rangle = E_n^{(2)}\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle + E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(2)}\rangle + E_n^{(1)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle$$

Using the orthogonality of the unperturbed eigenstates, $\langle\psi_n^{(0)}|\psi_m^{(0)}\rangle = \delta_{n,m}$, and the fact that $\langle\psi_n^{(0)}|H_0|\,\psi_n^{(2)}\rangle = E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(2)}\rangle$, the equation simplifies to:

$$\langle\psi_n^{(0)}|H'|\,\psi_n^{(1)}\rangle = E_n^{(2)}$$

1. **Expression for $|\psi_n^{(1)}\rangle$**: From the first-order perturbation theory, the first-order correction to the state is:

$$|\psi_n^{(1)}\rangle = \sum_{m\neq n} \frac{\langle\psi_m^{(0)}|H'|\,\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}|\psi_m^{(0)}\rangle$$

Substituting this into the expression for $E_n^{(2)}$, we get:

$$E_n^{(2)} = \langle\psi_n^{(0)}|H'|\,\psi_n^{(1)}\rangle = \sum_{m\neq n} \frac{\langle\psi_n^{(0)}|H'|\,\psi_m^{(0)}\rangle\,\langle\psi_m^{(0)}|H'|\,\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}$$

This simplifies to:

$$E_n^{(2)} = \sum_{m\neq n} \frac{|\langle\psi_m^{(0)}|H'|\,\psi_n^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

Final Result

The second-order correction to the energy is:

$$\boxed{E_n^{(2)} = \sum_{m\neq n} \frac{|\langle\psi_m^{(0)}|H'|\,\psi_n^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}}}$$

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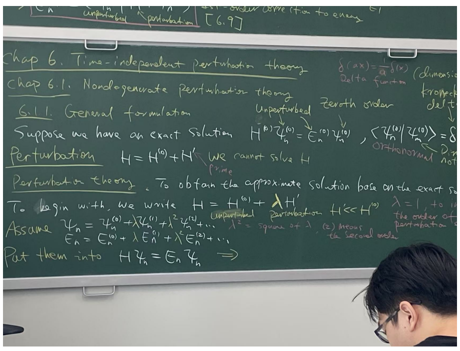
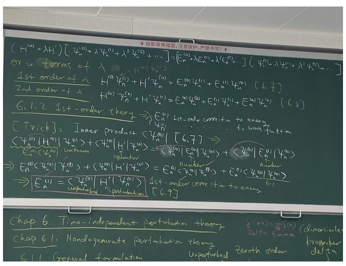
32B> 



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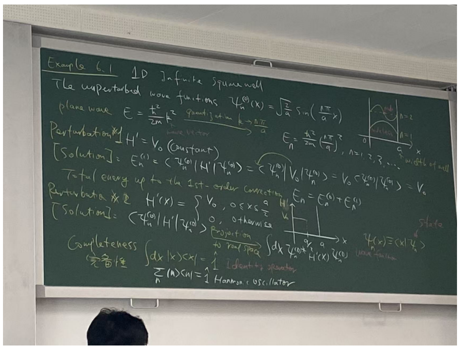
32B> 

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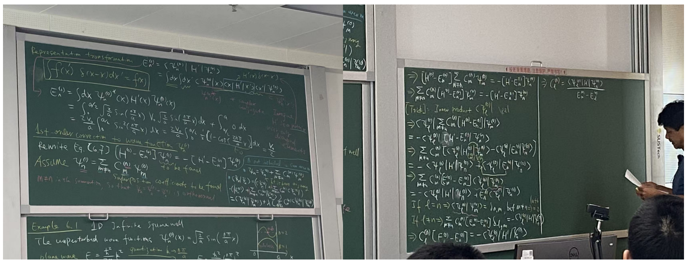
32B> 

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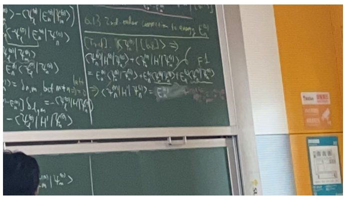
Equation 6.7 is

$\langle \psi_m^{(0)} | H^{(0)} \psi_n^{(1)} \rangle + \langle \psi_m^{(0)} | H' \psi_n^{(0)} \rangle = E_n^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle + E_n^{(1)} \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle$

The key is how First-order correction to the wave function $\psi_n^{(1)}$ is derived

32B> 

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The key is how 2nd-order correction to the energy function $E_n^{(2)}$ is derived.

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