Quantum Mechanics

Week 12

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Contents

Pre-Reading Note

Dear Students,

Welcome to the course on Quantum Mechanics. As part of your learning resources, I will prepare a series of educational materials and sheets designed to complement the lectures.

Please note that these materials are **abridged versions** of the content from the textbook ***"Introduction to Quantum Mechanics By David J. Griffiths"***. They have been tailored to align with the class schedule and topics, providing you with concise summaries and key points for each topic covered.

It's important to understand that these sheets are **not standalone resources**. They are intended to be used in conjunction with the class material. For a deeper understanding and a more comprehensive view of each topic, I strongly encourage you to refer to the mentioned textbook.

The book provides detailed explanations, examples, and insights that go beyond the scope of our summaries. It will be an invaluable resource for you to solidify your understanding of Quantum Mechanics.

I cannot guarantee neither correctness nor completeness of the script. Please report any mistake directly to me.

Have fun with Quantum Mechanics!

Best regards,

Mark Benazet Castells

1 Perturbation Theory

Perturbation theory is a pivotal tool in quantum mechanics, used primarily for analyzing complex systems where exact solutions are elusive. It allows for the approximation of such systems by introducing small modifications to simpler, solvable systems.

Fundamentally, this technique initiates with a quantum system characterized by a well-established Hamiltonian $\hat{H}^{(0)}$ and its corresponding solutions.

The essence of perturbation theory lies in its ability to bridge a complex problem to a more manageable one, already deciphered. This is achieved by formulating the new Hamiltonian as:

$$\hat{H}_{new} = \hat{H}^{(0)} + \lambda \cdot \hat{H}'$$

Here, $\hat{H}_{new}$ symbolizes the Hamiltonian for the intricate problem at hand, $\hat{H}^{(0)}$ represents the solvable Hamiltonian, λ functions as an adjustable parameter, and in cases where it is not explicitly specified, it is conventionally assumed to be one and $\hat{H}'$ signifies the perturbation.

Our objective is to resolve the equation $\hat{H}\psi_n = E_n\psi_n$, while drawing upon the solution of $\hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$.

In this framework, both energies and wavefunctions are articulated as second-order power series in λ:

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

1.1 Non-Degenerate Perturbation Theory

Non-Degenerate Perturbation Theory addresses quantum systems with distinct energy levels, especially when ${E_n}^{(0)} \neq {E_m}^{(0)}$. This method is used to approximate the effects of small perturbations on these systems.

The approach begins with an unperturbed Hamiltonian $\hat{H}^{(0)}$, for which the eigenvalues $E_n^{(0)}$ and eigenfunctions $\psi_n^{(0)}$ are known. A perturbation, denoted by the Hamiltonian $\hat{H}'$, is then introduced, resulting in the total Hamiltonian $\hat{H}_{new} = \hat{H}^{(0)} + \lambda\hat{H}'$. The objective is to find the new energy levels and eigenfunctions of $\hat{H}_{new}$.

The first-order energy correction, $E_n^{(1)}$, is determined by the expectation value of the perturbation Hamiltonian H' with the unperturbed eigenfunctions. It is mathematically expressed as:

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

This correction is critical as it quantifies the primary influence of the perturbation on the system's energy levels.

The first-order correction to the wavefunction, $\psi_n^{(1)}$, is expressible in terms of the basis $\psi_m^{(0)}$ since $\psi_n^{(0)}$ forms a complete set:

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

The term $m = n$ is excluded since $\psi_n^{(0)}$ is already included in ψ_n, which is defined as $\psi_n = \psi_n^{(0)} + \lambda \cdot \psi_n^{(1)} + \lambda^2 \cdot \psi_n^{(2)}$.

The second-order energy correction, $E_n^{(2)}$, involves a summation over all states except the state n itself and is given by:

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \psi_m^{(0)} | \hat{H}' \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \tag{3}$$

This correction considers the interactions between different energy levels under the perturbation, offering deeper insight into the system's behavior in response to the perturbation.

Remark: One could follow this procedure to derive the higher-order corrections but these expressions involve higher order sums over the unperturbed states and are not usually practical to use

Example

Consider an infinite square well with a perturbed constant potential. The potential $V(x)$ is defined as:

$$V(x) = \begin{cases} V_0, & 0 < x < \frac{a}{2}, \\ 0, & \frac{a}{2} < x < a, \end{cases}$$

where V_0 is the perturbation strength and a is the width of the well.

We can clearly see that the perturbation part of the Hamiltonian corresponds to V_0 in the region $0 < x < \frac{a}{2}$ and 0 elsewhere.
The unperturbed Hamiltonian eigenfunctions for an infinite square well are given by:

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

The first-order energy correction $E_n^{(1)}$ is the expectation value of the perturbation with these eigenfunctions:

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

Substituting the potential and the eigenfunctions, we get:

$$E_n^{(1)} = \int_0^{a/2} \left(\sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \right)^2 V_0 \, dx \tag{4}$$

$$= \frac{2}{a} \cdot V_0 \cdot \frac{a}{4} \tag{5}$$

$$= \frac{V_0}{2} \tag{6}$$

1.2 Degenerate Perturbation Theory

Degenerate Perturbation Theory is indispensable in quantum mechanics for systems where multiple eigenstates correspond to identical energy levels, resulting in degeneracy. Introduction of a perturbation to such a system can remove the degeneracy, leading to distinct energy levels and modified eigenstates.

Consider the degenerate eigenstates $\psi_a^{(0)}$ and $\psi_b^{(0)}$, both associated with the same eigenvalue $E^{(0)}$ and orthogonal to each other. Any linear combination of these states is also an eigenfunction of the unperturbed Hamiltonian $H^{(0)}$, posing a challenge to identify the correct combination that represents the system post-perturbation.

The first-order energy correction for degenerate states is computed using the formula:

$$E_{\pm}^{(1)} = \frac{1}{2}\left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4W_{ab}^2}\right], \tag{7}$$

where $W_{ij} = \langle \psi_i^{(0)} | H' | \psi_j^{(0)} \rangle$ with H' denoting the perturbation Hamiltonian. The W-matrix, composed of W_{ij}, elucidates the perturbation's impact on the degenerate states.

The phenomenon of degeneracy removal by a perturbation is depicted in the following figure:

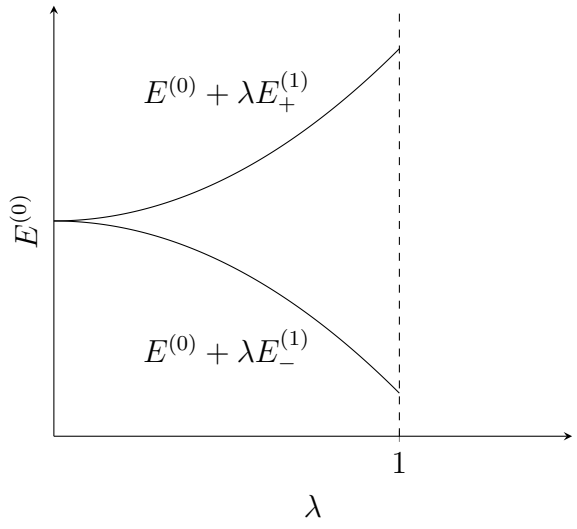

Figure 1: 'Lifting' of a degeneracy by a perturbation.

To ascertain the adjusted energy levels, one must diagonalize the W-matrix:

$$\begin{bmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{bmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \tag{8}$$

This procedure entails finding the matrix's eigenvalues, which correspond to the first-order corrections of the energy levels. If W_{ab} is non-zero, the matrix diagonalization process selects the appropriate linear combination of $\psi_a^{(0)}$ and $\psi_b^{(0)}$ that are 'proper' for use in the formulas akin to non-degenerate perturbation theory, hence lifting the degeneracy. Conversely, a zero W_{ab} implies that the perturbation fails to distinguish between the degenerate states, preserving the degeneracy.

2 Variational Principle

The Variational Principle is a foundational concept in quantum mechanics that provides a method for estimating the ground state energy of a quantum system. It is particularly useful when the system in question is too complex to solve analytically using the Schrödinger equation.

According to the Variational Principle, the ground state energy E_0 of a quantum system is the lowest possible expectation value of the Hamiltonian $\hat{H}$, and it can be approximated using a trial wave function ψ_{trial}. The principle states that for any normalized trial wave function, the expectation value of $\hat{H}$ is always greater than or equal to the true ground state energy:

$$E_{gs} \leq \langle \psi_{\text{trial}} | \hat{H} \psi_{\text{trial}} \rangle = E_{\text{approx}} \tag{9}$$

To apply the Variational Principle, one selects a suitable trial wave function, which may include one or more adjustable parameters. These parameters are then varied to minimize the expectation value of the Hamiltonian, providing an estimate for the ground state energy:

$$E_{\text{approx}} = \min_{\{\text{parameters}\}} \langle \psi_{\text{trial}} | \hat{H} \psi_{\text{trial}} \rangle \tag{10}$$

The trial wave function that yields the minimum expectation value is considered the best approximation for the ground state wave function, and the corresponding energy is the closest estimate to the actual ground state energy.

The Variational Principle not only gives an upper bound to the ground state energy but also provides a systematic approach for improving the accuracy of this bound. By judiciously choosing the trial wave function and optimizing the parameters, one can achieve remarkably close approximations to the true ground state energy of a quantum system.

Example

Consider the trial wave function for a particle in an infinite square well:

$$\psi_{\text{trial}}(x) = Ax(L - x), \tag{11}$$

which is not normalized. The variational principle is applied to estimate the system's ground state energy.

For an infinite square well, $\hat{H}$ is $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$. The trial energy is given by:

$$E_{\text{approx}} = \frac{\langle \psi_{\text{trial}} | \hat{H} \psi_{\text{trial}} \rangle}{\langle \psi_{\text{trial}} | \psi_{\text{trial}} \rangle}, \tag{12}$$

where the numerator and denominator represent the expectation value of the Hamiltonian and the normalization constant, respectively.

The numerator, after integrating, yields:

$$\langle\psi|\hat{H}\psi\rangle = \frac{\hbar^2}{m}\frac{L^3}{6}, \tag{13}$$

and the denominator is the normalization constant A^2:

$$A^2 = \frac{L^5}{30}. \tag{14}$$

Combining the numerator and denominator gives the trial energy:

$$E_{\text{approx}} = \frac{5\hbar^2}{mL^2}, \tag{15}$$

indicating that the energy of the ground state satisfies the inequality:

$$E_{gs} \leq \frac{5\hbar^2}{mL^2}. \tag{16}$$

Comparing it with the known solution for the ground state of the Infinite Square Well $E_{gs} = \frac{\hbar^2\pi^2}{2mL^2}$, we take the ratio:

$$\frac{E_{\text{trial}}}{E_{gs}} = \frac{\frac{5\hbar^2}{mL^2}}{\frac{\hbar^2\pi^2}{2mL^2}} = \frac{10}{\pi^2}$$

Since $\pi^2 \approx 9.87$, the ratio is:

$$\frac{10}{\pi^2} < 5$$

Thus, we consider it to be a "good" guess.