Quantum Mechanics 2

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Perturbation Theory

Formalism

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Perturbation

Perturbations are small influences "on top" of a dominant force. There are very few quantum mechanical systems that are exactly solvable. However, there are a good number of cases in which the Hamiltonian may be expressed as

$$H = H_0 + H_I$$

where (a) the effects of H_I are much weaker than that of H_0, and (b) The eigenfunctions and eigenvalues of H_0 are exact, and have been solved.

In these cases, approximate eigenvalues and eigenfunctions for the full Hamiltonian H can be solved using Perturbation Theory.

Eigenenergy

Let $|n^{(0)}\rangle$ be the (known and exact) eigenkets of H_0, then

$$H_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle$$

$E_n^{(0)}$ are called the unperturbed eigenenergies, and $|n^{(0)}\rangle$ are the unperturbed states.

In order to keep track of the order of approximation, let us put a marker λ (or a parameter) beside the perturbation Hamiltonian H_I.

$$H = H_0 + \lambda H_I$$

We now make an ansatz that the eigenenergy can be expressed as a sum of successive correction terms of decreasing values

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

Eigenkets

Since the eigenkets $|n^{(0)}\rangle$ of H_0 are complete, we may use the expansion postulate to express the eigenkets $|n\rangle$ of H as linear combinations of the former

$$|n\rangle = N(\lambda)\left[|n^{(0)}\rangle + \sum_{k\neq n} C_{nk}(\lambda)|k^{(0)}\rangle\right]$$

If $\lambda = 0$, the Hamiltonian H reduces to the unperturbed Hamiltonian H_0. Thus, for consistency

$$N(\lambda = 0) = 1$$

$$C_{nk}(\lambda = 0) = 0$$

We likewise assume that the expansion coefficient can be expressed as a sum of correction terms

$$C_{nk}(\lambda) = \lambda C_{nk}^{(1)} + \lambda^2 C_{nk}^{(2)} + \cdots$$

Expansion

The eigenvalue equation

$$H|n\rangle = E_n|n\rangle$$

may then be expressed as

$$(H_0 + \lambda H_I)\left[\left|n^{(0)}\right\rangle + \lambda \sum_{k\neq n} C_{nk}^{(1)}\left|k^{(0)}\right\rangle + \lambda^2 \sum_{k\neq n} C_{nk}^{(2)}\left|k^{(0)}\right\rangle + \cdots\right]$$

$$= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots\ \right)\left[\left|n^{(0)}\right\rangle + \lambda \sum_{k\neq n} C_{nk}^{(1)}\left|k^{(0)}\right\rangle + \lambda^2 \sum_{k\neq n} C_{nk}^{(2)}\left|k^{(0)}\right\rangle + \cdots\right]$$

Orders

Equating terms of the same power of λ, we have for order zero,

$$H_0\left|n^{(0)}\right\rangle = E_n^{(0)}\left|n^{(0)}\right\rangle$$

For order one,

$$H_0\sum_{k\neq n} C_{nk}^{(1)}\left|k^{(0)}\right\rangle + H_I\left|n^{(0)}\right\rangle = E_n^{(0)}\sum_{k\neq n} C_{nk}^{(1)}\left|k^{(0)}\right\rangle + E_n^{(1)}\left|n^{(0)}\right\rangle \qquad \star$$

For order two,

$$H_0\sum_{k\neq n} C_{nk}^{(2)}\left|k^{(0)}\right\rangle + H_I\sum_{k\neq n} C_{nk}^{(1)}\left|k^{(0)}\right\rangle$$
$$= E_n^{(0)}\sum_{k\neq n} C_{nk}^{(2)}\left|k^{(0)}\right\rangle + E_n^{(1)}\sum_{k\neq n} C_{nk}^{(1)}\left|k^{(0)}\right\rangle + E_n^{(2)}\left|n^{(0)}\right\rangle \qquad \star\star$$

and so on

$$\vdots$$

First-Order Energy

If we take the inner product of the first-order expression with $\langle n^{(0)}|$

$$\sum_{k\neq n} C_{nk}^{(1)} \langle n^{(0)}|H_0|k^{(0)}\rangle + \langle n^{(0)}|H_I|n^{(0)}\rangle = E_n^{(0)} \sum_{k\neq n} C_{nk}^{(1)} \langle n^{(0)}|k^{(0)}\rangle + E_n^{(1)} \langle n^{(0)}|n^{(0)}\rangle$$

we have

$$\sum_{k\neq n} C_{nk}^{(1)} E_k^{(0)} \delta_{nk} + \langle n^{(0)}|H_I|n^{(0)}\rangle = E_n^{(0)} \sum_{k\neq n} C_{nk}^{(1)} \delta_{nk} + E_n^{(1)}$$

which yields the formula for the first-order correction for energy

$$\boxed{E_n^{(1)} = \langle n^{(0)}|H_I|n^{(0)}\rangle}$$

First-Order Eigenkets

If we take the inner product of the first-order expression with $\langle m^{(0)}|$, for $m \neq n$,

$$\sum_{k\neq n} C_{nk}^{(1)} \langle m^{(0)}|H_0|k^{(0)}\rangle + \langle m^{(0)}|H_I|n^{(0)}\rangle = E_n^{(0)} \sum_{k\neq n} C_{nk}^{(1)} \langle m^{(0)}|k^{(0)}\rangle + E_n^{(1)} \langle m^{(0)}|n^{(0)}\rangle$$

we have

$$\sum_{k\neq n} C_{nk}^{(1)} E_k^{(0)} \delta_{mk} + \langle m^{(0)}|H_I|n^{(0)}\rangle = E_n^{(0)} \sum_{k\neq n} C_{nk}^{(1)} \delta_{mk} + E_n^{(1)} \delta_{mn}$$

which reduces to

$$C_{nm}^{(1)} E_m^{(0)} + \langle m^{(0)}|H_I|n^{(0)}\rangle = E_n^{(0)} C_{nm}^{(1)}$$

Rearranging, we get the first order coefficient for the eigenkets

$$C_{nm}^{(1)} = \frac{\langle m^{(0)}|H_I|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}$$

Second-Order Energy

If we take the inner product of the second-order expression with $\langle n^{(0)}|$

$$\sum_{k\neq n} C_{nk}^{(2)}\langle n^{(0)}|H_0|k^{(0)}\rangle + \sum_{k\neq n} C_{nk}^{(1)}\langle n^{(0)}|H_I|k^{(0)}\rangle$$
$$= E_n^{(0)}\sum_{k\neq n} C_{nk}^{(2)}\langle n^{(0)}|k^{(0)}\rangle + E_n^{(1)}\sum_{k\neq n} C_{nk}^{(1)}\langle n^{(0)}|k^{(0)}\rangle + E_n^{(2)}\langle n^{(0)}|n^{(0)}\rangle$$

we have

$$\sum_{k\neq n} C_{nk}^{(2)}E_k^{(0)}\langle n^{(0)}|k^{(0)}\rangle + \sum_{k\neq n} C_{nk}^{(1)}\langle n^{(0)}|H_I|k^{(0)}\rangle = E_n^{(2)}$$

which yields the second-order correction to the energy

$$E_n^{(2)} = \sum_{k\neq n}\frac{\langle k^{(0)}|H_I|n^{(0)}\rangle}{E_n^{(0)}-E_k^{(0)}}\langle n^{(0)}|H_I|k^{(0)}\rangle = \sum_{k\neq n}\frac{\left|\langle n^{(0)}|H_I|k^{(0)}\rangle\right|^2}{E_n^{(0)}-E_k^{(0)}}$$

Second-Order Eigenkets

If we take the inner product of the second-order expression with $\langle m^{(0)}|$, for $m \neq n$,

$$\sum_{k\neq n} C_{nk}^{(2)}\langle m^{(0)}|H_0|k^{(0)}\rangle + \sum_{k\neq n} C_{nk}^{(1)}\langle m^{(0)}|H_I|k^{(0)}\rangle$$
$$= E_n^{(0)} \sum_{k\neq n} C_{nk}^{(2)} \langle m^{(0)}|k^{(0)}\rangle + E_n^{(1)} \sum_{k\neq n} C_{nk}^{(1)}\langle m^{(0)}|k^{(0)}\rangle + E_n^{(2)} \langle m^{(0)}|n^{(0)}\rangle$$

we have

$$\sum_{k\neq n} C_{nk}^{(2)} E_k^{(0)} \delta_{mk} + \sum_{k\neq n} C_{nk}^{(1)}\langle m^{(0)}|H_I|k^{(0)}\rangle = E_n^{(0)} \sum_{k\neq n} C_{nk}^{(2)} \delta_{mk} + E_n^{(1)} \sum_{k\neq n} C_{nk}^{(1)} \delta_{mk}$$

which reduces to

$$C_{nm}^{(2)} E_m^{(0)} + \sum_{k\neq n} C_{nk}^{(1)}\langle m^{(0)}|H_I|k^{(0)}\rangle = E_n^{(0)} C_{nm}^{(2)} + E_n^{(1)} C_{nm}^{(1)}$$

Second-Order Eigenkets

Rearranging, we have

$$C_{nm}^{(2)} = \sum_{k \neq n} \frac{C_{nk}^{(1)} \langle m^{(0)} | H_I | k^{(0)} \rangle - E_n^{(1)} C_{nm}^{(1)}}{E_n^{(0)} - E_m^{(0)}}$$

which yields the second-order coefficients for the eigenkets

$$C_{nm}^{(2)} = \sum_{k \neq n} \frac{\langle m^{(0)} | H_I | k^{(0)} \rangle \langle k^{(0)} | H_I | n^{(0)} \rangle}{\left(E_n^{(0)} - E_m^{(0)}\right)\left(E_n^{(0)} - E_k^{(0)}\right)} - \frac{\langle m^{(0)} | H_I | n^{(0)} \rangle \langle n^{(0)} | H_I | n^{(0)} \rangle}{\left(E_n^{(0)} - E_m^{(0)}\right)^2}$$