Time-Independent Perturbation Theory

Assume that for a quantum system there exists a Hamiltonian $\mathcal{H}_\circ$ for which eigenfunctions $\{\phi_i\}$ and eigenvalues $\{\epsilon_i\}$ are known. If some other contribution to the total energy is discovered or created by external means, then another term must be added to the Hamiltonian,

$$\mathcal{H} = \mathcal{H}_\circ + V. \tag{1}$$

If the new operator V represents an energy contribution which is small compared to the original energy ϵ_i of state ϕ_i, then V is said to be a perturbation to the original Hamiltonian $\mathcal{H}_\circ$.

The existence of a perturbation leads to a description of the system in terms of a new set of wavefunctions $\{\psi_i\}$. We can describe the transformation of a particular function $\phi_a \to \psi_a$ in terms of an operator P, such that

$$\psi_a(\vec{r}) = P(V)\phi_a(\vec{r}). \tag{2}$$

Presumably, ψ_a differs only slightly from ϕ_a, and that difference can be expressed as a linear combination of elements of the complete set $\{\psi_i\}$,

$$\psi_a = \phi_a + \sum_i c_{ia}\phi_i. \tag{3}$$

The perturbation operator P can be expanded in a series of terms dependent upon V to some order. Since V is assumed to be much smaller that $\mathcal{H}_\circ$ in an operator sense, terms of order V^n should become less significant as n increases. Usually, only effects up to order 2, that is, dependent upon V^2, need be considered. Thus,

$$P = 1 + P^{(1)} + P^{(2)} + \cdots . \tag{4}$$

The set of coefficients $\{c_{ia}\}$ is determined by projecting each component

$$O_k\psi_a = |k\rangle\langle k|\psi_a\rangle = \sum_i c_{ia}\langle k|i\rangle|k\rangle = c_{ka}\phi_k = c_{ka}|k\rangle, \tag{5}$$

and

$$c_{ka} = \langle k|\psi_a\rangle = \langle k|P|\phi_a\rangle. \tag{6}$$

So, each coefficient is a sum over a series of terms of increasing order in V

$$c_{ka} = \delta_{ka} + \langle k|P^{(1)}|\phi_a\rangle + \langle k|P^{(2)}|\phi_a\rangle + \cdots . \tag{7}$$

To develop the operator P, begin with the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi = \mathcal{H}\psi \to i\hbar P\frac{\partial}{\partial t}\phi = (\mathcal{H}_\circ + V)P\phi, \tag{8}$$

where the subscript a is supressed. Using

$$i\hbar\frac{\partial}{\partial t}\phi = \mathcal{H}_\circ\phi, \tag{9}$$

we find that

$$P\mathcal{H}_\circ = (\mathcal{H}_\circ + V)P. \tag{10}$$

Expanding P,

$$(1 + P^{(1)} + P^{(2)} + \cdots)\mathcal{H}_\circ = (\mathcal{H}_\circ + V)(1 + P^{(1)} + P^{(2)} + \cdots). \tag{11}$$

Collecting terms of equal order in the perturbation V, we arrive at the set of equations

$$\mathcal{H}_\circ = \mathcal{H}_\circ \tag{12}$$

$$P^{(1)}\mathcal{H}_\circ = \mathcal{H}_\circ P^{(1)} + V \tag{13}$$

$$P^{(2)}\mathcal{H}_\circ = \mathcal{H}_\circ P^{(2)} + VP^{(1)} \tag{14}$$

$$\vdots \tag{15}$$

Evaluating one matrix element of the first-order equation yields

$$\langle k|P^{(1)}\mathcal{H}_\circ|a\rangle = \langle k|\mathcal{H}_\circ P^{(1)}|a\rangle + \langle k|V|a\rangle. \tag{16}$$

Operating to the left or right with the operator $\mathcal{H}_\circ$ yields

$$\langle k|P^{(1)}|a\rangle\epsilon_a = \epsilon_k\langle k|P^{(1)}|a\rangle + \langle k|V|a\rangle. \tag{17}$$

The quantity $\langle k|P^{(1)}|a\rangle$ can be expressed in a very useful form by observing that

$$\langle k|P^{(1)}|a\rangle = \frac{\langle k|V|a\rangle}{\epsilon_a - \epsilon_k} = \langle k|[\epsilon_a - \epsilon_k]^{-1}V|a\rangle = \langle k|[\epsilon_a - \mathcal{H}_\circ]^{-1}V|a\rangle. \tag{18}$$

Thus, the operator $P^{(1)}$ is defined as

$$P^{(1)} = [\epsilon_a - \mathcal{H}_\circ]^{-1}V. \tag{19}$$

Evaluating one matrix element of the second-order equation yields

$$\langle k|P^{(2)}\mathcal{H}_\circ|a\rangle = \langle k|\mathcal{H}_\circ P^{(2)}|a\rangle + \langle k|VP^{(1)}|a\rangle. \tag{20}$$

Operating to the left or right with the operator $\mathcal{H}_\circ$ and using the expression for $P^{(1)}$ yields

$$\langle k|P^{(2)}|a\rangle\epsilon_a = \epsilon_k\langle k|P^{(2)}|a\rangle + \langle k|V[\epsilon_a - \mathcal{H}_\circ]^{-1}V|a\rangle. \tag{21}$$

The quantity $\langle k|P^{(1)}|a\rangle$ can be expressed in the very useful form

$$\langle k|P^{(2)}|a\rangle = \frac{\langle k|V[\epsilon_a - \mathcal{H}_\circ]^{-1}V|a\rangle}{\epsilon_a - \epsilon_k} = \langle k|[\epsilon_a - \epsilon_k]^{-1}V[\epsilon_a - \mathcal{H}_\circ]^{-1}V|a\rangle = \langle k|[\epsilon_a - \mathcal{H}_\circ]^{-1}V[\epsilon_a - \mathcal{H}_\circ]^{-1}V|a\rangle. \tag{22}$$

The operator $P^{(2)}$ is defined as

$$P^{(2)} = [\epsilon_a - \mathcal{H}_\circ]^{-1}V[\epsilon_a - \mathcal{H}_\circ]^{-1}V. \tag{23}$$

Generalizing,

$$P^{(n)} = ([\epsilon_a - \mathcal{H}_\circ]^{-1}V)^n. \tag{24}$$

The perturbative corrections to an initial function ϕ_a can now be written.

$$\psi_a = \phi_a + \sum_{k \neq a} c_{ka} \phi_k \tag{25}$$

$$c_{ka} = \sum_n c_{ka}^{(n)} \tag{26}$$

$$c_{ka}^{(n)} = \langle k | P^{(n)} | a \rangle = \langle k | ([\epsilon_a - \mathcal{H}_\circ]^{-1} V)^n | a \rangle. \tag{27}$$

To evaluate one of these terms, it is useful to "insert a complete set of states" in between pairs of $[\epsilon_a - \mathcal{H}_\circ]^{-1} V$ operators. This action is mathematically based on the identity operator $\sum_m O_m = I$, where $O_m = |m\rangle\langle m|$ is the mth projection operator. The rationale for doing this lies in the simple interpretation of a complex integral in terms of products of integrals involving only V. The second order coefficient becomes

$$c_{ka}^{(2)} = \langle k | [\epsilon_a - \mathcal{H}_\circ]^{-1} V [\epsilon_a - \mathcal{H}_\circ]^{-1} V | a \rangle = \langle k | [\epsilon_a - \mathcal{H}_\circ]^{-1} V \sum_m O_m [\epsilon_a - \mathcal{H}_\circ]^{-1} V | a \rangle. \tag{28}$$

$$= \sum_m \langle k | [\epsilon_a - \mathcal{H}_\circ]^{-1} V | m \rangle \langle m | [\epsilon_a - \mathcal{H}_\circ]^{-1} V | a \rangle. \tag{29}$$

$$= \frac{\sum_m \langle k | V | m \rangle \langle m | V | a \rangle}{(\epsilon_a - \epsilon_k)(\epsilon_a - \epsilon_m)}. \tag{30}$$