Stationary State Perturbation Theory

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The subsequent notes are intended to *complement* rather than *supplant* the exposition on Stationary Perturbation Theory in standard texts on Quantum Mechanics.

We want to solve

$$\big[H_0 + \lambda H'\big]\,|n\rangle = E_n\,|n\rangle\,, \tag{1}$$

using our (as complete as necessary/desired) knowledge of

$$H_0\,|n;0\rangle = E_n^{(0)}\,|n;0\rangle\,, \tag{2}$$

of which we assume that $n \neq m \Leftrightarrow E_n^{(0)} \neq E_m^{(0)}$, *i.e.*, the spectrum of H_0 has no degeneracy. In turn, however, n, m are formal labels, both representing possibly several counters the range of which may include both discrete (finite or infinite) and continuous values. Accordingly, summation over n, m may well include integration with an appropriate measure. We also assume that:

$$E_n = \sum_{k=0} \lambda^k E_n^{(k)}, \qquad |n\rangle = \sum_{k=0}^{\infty} \lambda^k\,|n;k\rangle = \sum_{k=0}^{\infty} \lambda^k \sum_{m=0}^{\infty} |m;0\rangle\,\langle m;0|n;k\rangle, \tag{3}$$

that is, that the *perturbation* $H_0 \to H_0 + \lambda H'$ is small/mild enough, so that E_n and $|n\rangle$ are analytic functions of λ, with $E_n^{(0)}$ and $|n;0\rangle$, respectively, the initial, $\lambda = 0$ terms. Finally, we choose the normalization:

$$\langle n;0|n\rangle = 1, \qquad \Rightarrow \qquad \langle n;0|n,k\rangle = \delta_{k,0}, \quad \text{and} \quad \langle n;k|m;k\rangle = \delta_{n,m}. \tag{4}$$

Substituting (3) into (1), we have:

$$\big[H_0 + \lambda H'\big]\Big[\sum_{k=0}^{\infty} \lambda^k\,|n;k\rangle\Big] = \Big[\sum_{i=0}^{\infty} \lambda^i E_n^{(i)}\Big]\Big[\sum_{j=0}^{\infty} \lambda^j\,|n;j\rangle\Big],$$

$$H_0\,|n;0\rangle + \sum_{k=1}^{\infty} \lambda^k\,\big[H_0\,|n;k\rangle + H'\,|n;k-1\rangle\,\big] = \sum_{k=0}^{\infty}\;\sum_{i=0}^{k} \lambda^i\,E_n^{(i)}\,|n;k{-}i\rangle\,, \tag{5a}$$

or, by equating like powers of λ:

$$\lambda^0: \qquad H_0\,|n;0\rangle = E_n^{(0)}\,|n;0\rangle\,, \tag{5b}$$

$$\lambda^1: \qquad H_0\,|n;1\rangle + H'\,|n;0\rangle = E_n^{(0)}\,|n;1\rangle + E_n^{(1)}\,|n;0\rangle\,, \tag{5c}$$

$$\lambda^2: \qquad H_0\,|n;2\rangle + H'\,|n;1\rangle = E_n^{(0)}\,|n;2\rangle + E_n^{(1)}\,|n;1\rangle + E_n^{(2)}\,|n;0\rangle\,, \tag{5d}$$

$$\vdots \qquad\qquad \vdots \qquad \vdots$$

$$\lambda^k: \qquad H_0\,|n;k\rangle + H'\,|n;k{-}1\rangle = \sum_{i=0}^{k} E_n^{(i)}\,|n;k{-}i\rangle\,, \qquad k > 0. \tag{5e}$$

From here, upon acting with $\langle n;0|$, we have:

$$\langle n;0|\, H'\, |n;k{-}1\rangle = E_n^{(k)}, \qquad k>0, \tag{6}$$

with no other contributions on either side. Thus, to compute $E_n^{(k)}$, we first need to know $|n;k{-}1\rangle$.

Next, we use that $\{\, |n;k\rangle\,,\ n=0,1,2,\cdots\}$ is a complete set of eigenstates for every k, so that

$$|n;k\rangle = \sum_m c_{mn}^{(k)}\, |m;0\rangle\,, \qquad c_{mn}^{(k)} = \langle m;0|n;k\rangle, \tag{7}$$

where

$$c_{mn}^{(0)} = \delta_{m,n}, \qquad \text{and} \qquad c_{nn}^{(k)} = \delta_{k,0}. \tag{8}$$

Eq. (6) then becomes

$$E_n^{(k)} = \sum_{m\neq n} c_{mn}^{(k)}\langle n;0|H'|m;0\rangle, \tag{9}$$

so that, by determining the coefficients $c_{mn}^{(k)}$, Eqs. (7) and (9), respectively, give the k^{th} correction to the state and the energy.

Rewrite (5e) as

$$\big[H_0 - E_n^{(0)}\big]\,|n;k\rangle = \big[E_n^{(1)} - H'\big]\,|n;k{-}1\rangle + \sum_{i=2}^{k} E_n^{(i)}\,|n;k{-}i\rangle\,, \qquad k>0 \tag{10}$$

Substituting (7) into (10) gives:

$$\sum_{m'} c_{m'n}^{(k)}\big(E_{m'}^{(0)} - E_n^{(0)}\big)\,|m';0\rangle = \big[E_n^{(1)} - H'\big]\,|n;k{-}1\rangle + \sum_{i=2}^{k} E_n^{(i)}\,|n;k{-}i\rangle\,, \qquad k>0, \tag{11}$$

from which, upon applying $\langle m;0|$, we have:

$$c_{mn}^{(k)}\big(E_m^{(0)} - E_n^{(0)}\big) = E_n^{(1)} c_{mn}^{(k-1)} - \langle m;0|H'|n;k{-}1\rangle + \sum_{i=2}^{k} E_n^{(i)} c_{mn}^{(k-i)}, \qquad k>0, \tag{12}$$

or, case-by-case:

$$k=1: \qquad c_{mn}^{(1)}\big(E_m^{(0)} - E_n^{(0)}\big) = E_n^{(1)} c_{mn}^{(0)} - \langle m;0|H'|n;0\rangle, \tag{13}$$

$$m=n: \qquad 0 = E_n^{(1)} - \langle n;0|H'|n;0\rangle, \tag{14}$$

so that

$$\boxed{E_n^{(1)} = \langle n;0|H'|n;0\rangle.} \tag{15}$$

On the other hand,

$$m\neq n: \quad c_{mn}^{(1)}\big(E_m^{(0)} - E_n^{(0)}\big) = -\langle m;0|H'|n;0\rangle,$$

produces:

$$\boxed{c_{mn}^{(1)} = -\frac{\langle m;0|H'|n;0\rangle}{\big(E_m^{(0)} - E_n^{(0)}\big)},} \tag{16}$$

and

$$|n;1\rangle = -\sum_{m\neq n} \frac{\langle m;0|H'|n;0\rangle}{(E_m^{(0)} - E_n^{(0)})}\,|m;0\rangle\,. \tag{17}$$

$$k=2: \qquad c_{mn}^{(2)}\big(E_m^{(0)} - E_n^{(0)}\big) = E_n^{(1)} c_{mn}^{(1)} - \langle m;0|H'|n;1\rangle + E_n^{(2)} c_{mn}^{(0)}, \tag{18}$$

$$m=n: \qquad 0 = -\langle n;0|H'|n;1\rangle + E_n^{(2)}, \tag{19}$$

so that

$$\begin{aligned} E_n^{(2)} &= \langle n;0|H'|n;1\rangle, \\ &= -\sum_{m\neq n} \frac{\langle m;0|H'|n;0\rangle}{E_m^{(0)} - E_n^{(0)}} \langle n;0|H'|m;0\rangle, \end{aligned} \tag{20}$$

where the initial formula agrees with (6), and simplifies to:

$$\boxed{E_n^{(2)} = -\sum_{m\neq n} \frac{|\langle m;0|H'|n;0\rangle|^2}{E_m^{(0)} - E_n^{(0)}}.} \tag{21}$$

On the other hand,

$$m\neq n: \quad c_{mn}^{(2)}\big(E_m^{(0)} - E_n^{(0)}\big) = E_n^{(1)} c_{mn}^{(1)} - \langle m;0|H'|n;1\rangle,$$

from which:

$$c_{mn}^{(2)} = \frac{E_n^{(1)} c_{mn}^{(1)} - \langle m;0|H'|n;1\rangle}{(E_m^{(0)} - E_n^{(0)})}, \tag{22}$$

$$\boxed{c_{mn}^{(2)} = \bigg(\sum_{\ell\neq n} \frac{\langle m;0|H'|\ell;0\rangle}{(E_m^{(0)} - E_n^{(0)})} \frac{\langle \ell;0|H'|n;0\rangle}{(E_\ell^{(0)} - E_n^{(0)})} - \langle n;0|H'|n;0\rangle \frac{\langle m;0|H'|n;0\rangle}{(E_m^{(0)} - E_n^{(0)})^2}\bigg),} \tag{23}$$

is… well, less than compact. Nevertheless, Eq. (6) produces

$$E_n^{(3)} = \langle n;0|H'|n;2\rangle,$$

$$\boxed{E_n^{(3)} = \sum_{\ell,m\neq n} \frac{\langle n;0|H'|m;0\rangle\langle m;0|H'|\ell;0\rangle\langle \ell;0|H'|n;0\rangle}{(E_m^{(0)} - E_n^{(0)})(E_\ell^{(0)} - E_n^{(0)})} - E_n^{(1)} \sum_{m\neq n} \frac{\big|\langle m;0|H'|n;0\rangle\big|^2}{(E_n^{(0)} - E_m^{(0)})^2}.} \tag{24}$$

Churning out further corrections in this manner is clearly doable, but does seem… arduous, rather bewildering and quite unilluminating in the present notation and for the general case…

As it turns out, the above derivation, adapting from Ballentine **[**1**]**, in fact follows Messiah **[**2, p. 685–689, 694–695**]**. Adapting from there, define

$$\widehat{\Pi}_n^{\alpha} := \sum_{m\neq n} \frac{|m;0\rangle\,\langle m;0|}{(E_n^{(0)} - E_m^{(0)})^{\alpha}}, \qquad \text{so that} \qquad \widehat{\Pi}_n^{\alpha}\,\widehat{\Pi}_n^{\beta} = \widehat{\Pi}_n^{\alpha+\beta}, \tag{25}$$

and the subscript of $\widehat{\Pi}_n^{\alpha}$ in fact really is a power. Using this notation, Eqs. (6) and (10) may be written equivalently in a compact recursive form, in several variously convenient ways:

$$|n;k\rangle = \widehat{\Pi}_n^{1}\Big(H'\,|n;k-1\rangle - \sum_{i=1}^{k-1} E_n^{(i)}\,|n;k-i\rangle\Big), \qquad k>0, \tag{26a}$$

$$= (\widehat{\Pi}^1_n\, H')^k\, |n;0\rangle - \text{all "extractions"}^{1}; \qquad k \geqslant 0, \tag{26b}$$

$$E^{(k)}_n = \langle n;0 \big| H' \big| n;k{-}1\rangle. \tag{26c}$$

The first few iterations of these are as follows:

$$E^{(1)}_n = \langle n;0|H'|n;0\rangle, \tag{27a}$$

$$|n;1\rangle = \widehat{\Pi}^1_n\, H'\, |n;0\rangle\,, \tag{27b}$$

$$E^{(2)}_n = \langle n;0 \big| H'\, \widehat{\Pi}^1_n\, H' \big| n;0\rangle \tag{27c}$$

$$\begin{aligned}
|n;2\rangle &= \widehat{\Pi}^1_n (H' - E^{(1)}_n)\, |n;1\rangle\,,\\
&= \widehat{\Pi}^1_n \big(H' - \langle n;0 \big| H' \big| n;0\rangle\big)\, \widehat{\Pi}^1_n\, H'\, |n;0\rangle\,,\\
&= \widehat{\Pi}^1_n\, H'\, \widehat{\Pi}^1_n\, H'\, |n;0\rangle - \widehat{\Pi}^1_n\, \widehat{\Pi}^1_n\, H'\, |n;0\rangle\, \langle n;0 \big| H' \big| n;0\rangle,\\
&= \big[\, \widehat{\Pi}^1_n\, H'\, \widehat{\Pi}^1_n - \widehat{\Pi}^2_n\, H'\, |n;0\rangle\, \langle n;0|\, \big]\, H'\, |n;0\rangle\,,
\end{aligned} \tag{27d}$$

$$\begin{aligned}
E^{(3)}_n &= \langle n;0 \big| H' \big| n;2\rangle\\
&= \langle n;0|\, H' \big[\, \widehat{\Pi}^1_n\, H'\, \widehat{\Pi}^1_n - \widehat{\Pi}^2_n\, H'\, |n;0\rangle\, \langle n;0|\, \big]\, H'\, |n;0\rangle\\
&= \langle n;0|\, H'\, \widehat{\Pi}^1_n\, H'\, \widehat{\Pi}^1_n\, H'\, |n;0\rangle - \langle n;0|\, H'\, \widehat{\Pi}^2_n\, H'\, |n;0\rangle\, \langle n;0|H'|n;0\rangle\\
&= \langle n;0|\, H' \big(\, \widehat{\Pi}^1_n\, H'\big)^2\, |n;0\rangle - \langle n;0|\, H'\, \widehat{\Pi}^2_n\, H'\, |n;0\rangle\, \langle n;0|H'|n;0\rangle,
\end{aligned} \tag{27e}$$

$$\begin{aligned}
|n;3\rangle &= \widehat{\Pi}^1_n \big((H' - E^{(1)}_n)\, |n;2\rangle - E^{(2)}_n\, |n;1\rangle\, \big),\\
&= \widehat{\Pi}^1_n\, H'\, |n;2\rangle - \widehat{\Pi}^1_n\, |n;2\rangle\, \langle n;0 \big| H' \big| n;0\rangle - \widehat{\Pi}^1_n\, |n;1\rangle\, \langle n;0 \big| H'\, \widehat{\Pi}^1_n\, H' \big| n;0\rangle,\\
&= \widehat{\Pi}^1_n\, H' \big[\, \widehat{\Pi}^1_n\, H'\, \widehat{\Pi}^1_n - \widehat{\Pi}^2_n\, H'\, |n;0\rangle\, \langle n;0|\, \big]\, H'\, |n;0\rangle\\
&\quad - \widehat{\Pi}^1_n\, \big[\, \widehat{\Pi}^1_n\, H'\, \widehat{\Pi}^1_n - \widehat{\Pi}^2_n\, H'\, |n;0\rangle\, \langle n;0|\, \big]\, H'\, |n;0\rangle\, \langle n;0 \big| H' \big| n;0\rangle\\
&\quad - \widehat{\Pi}^1_n\, \widehat{\Pi}^1_n\, H'\, |n;0\rangle\, \langle n;0 \big| H'\, \widehat{\Pi}^1_n\, H' \big| n;0\rangle,\\
&= \widehat{\Pi}^1_n\, H'\, \widehat{\Pi}^1_n\, H'\, \widehat{\Pi}^1_n\, H'\, |n;0\rangle - \widehat{\Pi}^1_n\, H'\, \widehat{\Pi}^2_n\, H'\, |n;0\rangle\, \langle n;0|H'|n;0\rangle\\
&\quad - \widehat{\Pi}^1_n\, \widehat{\Pi}^1_n\, H'\, \widehat{\Pi}^1_n\, H'\, |n;0\rangle\, \langle n;0|H'|n;0\rangle - \widehat{\Pi}^1_n\, \widehat{\Pi}^2_n\, H'\, |n;0\rangle\, \langle n;0|H'|n;0\rangle^2\\
&\quad - \widehat{\Pi}^1_n\, \widehat{\Pi}^1_n\, H'\, |n;0\rangle\, \langle n;0 \big| H'\, \widehat{\Pi}^1_n\, H' \big| n;0\rangle,\\
&= \widehat{\Pi}^1_n\, H'\, \widehat{\Pi}^1_n\, H'\, \widehat{\Pi}^1_n\, H'\, |n;0\rangle - \widehat{\Pi}^2_n\, H'\, \widehat{\Pi}^1_n\, H'\, |n;0\rangle\, \langle n;0|H'|n;0\rangle\\
&\quad - \widehat{\Pi}^1_n\, H'\, \widehat{\Pi}^2_n\, H'\, |n;0\rangle\, \langle n;0|H'|n;0\rangle - \widehat{\Pi}^2_n\, H'\, |n;0\rangle\, \langle n;0 \big| H'\, \widehat{\Pi}^1_n\, H' \big| n;0\rangle\\
&\quad - \widehat{\Pi}^3_n\, H'\, |n;0\rangle\, \langle n;0|H'|n;0\rangle^2, \quad \textit{etc.}
\end{aligned} \tag{27f}$$

The above expressions, while more compact than the likes of (24), are still bewilderingly repetitive and less than intuitive.

However, the reordering of terms in the last of these expressions reveals a simple algorithmic rule for the numerous subtractions as they occur in (26):

1. write the initial term in (26b)—and thereupon also (26c), and
2. subtract all possible nonzero *extractions*,
   which are obtained from the initial term as follows:

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[1] See the definition 1 of *extraction* and the discussion including Eqs. (29)–(33).

Definition 1 (Extraction) *Let $\mathcal{O}_1 \cdots \mathcal{O}_\alpha |n;0\rangle$ be the "initial term". All its* extractions *are of the form:*

$$\begin{aligned}
&\mathcal{O}_1 \cdots \underline{[\mathcal{O}_\beta \cdots \mathcal{O}_{\beta+\gamma}]} \cdots \underline{[\mathcal{O}_\delta \cdots \mathcal{O}_{\delta+\epsilon}]} \cdots \mathcal{O}_\alpha |n;0\rangle \\
&:= \mathcal{O}_1 \cdots \underbrace{(\mathcal{O}_\beta \cdots \mathcal{O}_{\beta+\gamma})}_{omit} \cdots \underbrace{(\mathcal{O}_\delta \cdots \mathcal{O}_{\delta+\epsilon})}_{omit} \cdots \mathcal{O}_\alpha |n;0\rangle \\
&\quad \times \langle n;0|\mathcal{O}_\beta \cdots \mathcal{O}_{\beta+\gamma}|n;0\rangle \langle n;0|\mathcal{O}_\delta \cdots \mathcal{O}_{\delta+\epsilon}|n;0\rangle,
\end{aligned} \tag{28}$$

extracting the two subsequences $(\mathcal{O}_\beta \cdots \mathcal{O}_{\beta+\gamma})$ and $(\mathcal{O}_\delta \cdots \mathcal{O}_{\delta+\epsilon})$. In general, "all possible extractions" includes ***all*** *numbers of* ***all*** *subsequences of the sequence $\mathcal{O}_1 \cdots \mathcal{O}_\alpha$ from the initial term.*

Here is a simple but non-trivial example:

$$\begin{aligned}
|n;3\rangle &= \widehat{\Pi}^1_n H' \widehat{\Pi}^1_n H' \widehat{\Pi}^1_n H' |n;0\rangle \\
&\quad - \widehat{\Pi}^1_n \underline{[H']} \widehat{\Pi}^1_n H' \widehat{\Pi}^1_n H' |n;0\rangle - \widehat{\Pi}^1_n H' \widehat{\Pi}^1_n \underline{[H']} \widehat{\Pi}^1_n H' |n;0\rangle \\
&\quad - \widehat{\Pi}^1_n \underline{[H' \widehat{\Pi}^1_n H']} \widehat{\Pi}^1_n H' |n;0\rangle - \widehat{\Pi}^1_n \underline{[H']} \widehat{\Pi}^1_n \underline{[H']} \widehat{\Pi}^1_n H' |n;0\rangle
\end{aligned} \tag{29}$$

where *extracting* the underlined-bracketed factors is done as follows:

$$\widehat{\Pi}^1_n \underline{[H']} \widehat{\Pi}^1_n H' \widehat{\Pi}^1_n H' |n;0\rangle = \widehat{\Pi}^1_n \, \widehat{\Pi}^1_n H' \widehat{\Pi}^1_n H' |n;0\rangle \, \langle n;0|H'|n;0\rangle, \tag{30a}$$

$$\widehat{\Pi}^1_n \underline{[H' \widehat{\Pi}^1_n H']} \widehat{\Pi}^1_n H' |n;0\rangle = \widehat{\Pi}^1_n \, \widehat{\Pi}^1_n H' |n;0\rangle \, \langle n;0|H' \widehat{\Pi}^1_n H'|n;0\rangle, \quad etc. \tag{30b}$$

Note that only factors of the form $(H' \widehat{\Pi}^\alpha_n \cdots \widehat{\Pi}^\beta_n H')$ can have non-vanishing expectation values in the unperturbed, original state $|n;0\rangle$, only such factors can be so *extracted*. Also, *extracting* the rightmost factor of H' from the initial term in (29) vanishes always:

$$\widehat{\Pi}^1_n H' \widehat{\Pi}^1_n H' \widehat{\Pi}^1_n \underline{[H']} |n;0\rangle = \widehat{\Pi}^1_n H' \widehat{\Pi}^1_n H' \underbrace{\widehat{\Pi}^1_n |n;0\rangle}_{=0} \langle n;0|H'|n;0\rangle, \tag{31a}$$

$$\widehat{\Pi}^1_n H' \widehat{\Pi}^1_n H' \underline{[\widehat{\Pi}^1_n H']} |n;0\rangle = \widehat{\Pi}^1_n H' \widehat{\Pi}^1_n H' |n;0\rangle \underbrace{\langle n;0| \widehat{\Pi}^1_n}_{=0} H' |n;0\rangle, \tag{31b}$$

$$\widehat{\Pi}^1_n H' \widehat{\Pi}^1_n \underline{[H' \widehat{\Pi}^1_n H']} |n;0\rangle = \widehat{\Pi}^1_n H' \underbrace{\widehat{\Pi}^1_n |n;0\rangle}_{=0} \langle n;0|H' \widehat{\Pi}^1_n H'|n;0\rangle, \qquad etc., \tag{31c}$$

owing to the fact that

$$\widehat{\Pi}^1_n |n;0\rangle = \sum_{m \neq n} \frac{|m;0\rangle \langle m;0|}{E^{(0)}_n - E^{(0)}_m} |n;0\rangle = \sum_{m \neq n} \frac{1}{E^{(0)}_n - E^{(0)}_m} |m;0\rangle \underbrace{\langle m;0|n;0\rangle}_{=0 \ (\because \ m \neq n)}. \tag{32}$$

Using this *extraction* notation, Eq. (27e) becomes:

$$E^{(3)}_n = \langle n;0|H' \widehat{\Pi}^1_n H' \widehat{\Pi}^1_n H'|n;0\rangle - \langle n;0|H' \widehat{\Pi}^1_n \underline{[H']} \widehat{\Pi}^1_n H'|n;0\rangle, \tag{33}$$

and we note that no other non-vanishing extractions exist.

This Messiah-inspired $\widehat{\Pi}_n^k$-notation (26) becomes very efficient when we know that the energy corrections vanish up through the $(k-1)^{\text{st}}$ order. In this case the results at the k^{th} order are particularly simple, since then *all* the *extractions* vanish:

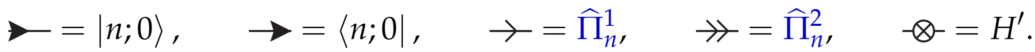
$$E_n^{(k)} = \langle n;0|H'|n;k-1\rangle = \langle n;0|H'\left(\widehat{\Pi}_n^1 H'\right)^{k-1}|n;0\rangle, \tag{34}$$

$$|n;k\rangle = \widehat{\Pi}_n^1 H'\,|n;k-1\rangle \quad = \left(\widehat{\Pi}_n^1 H'\right)^k |n;0\rangle\,. \tag{35}$$

These are then the lowest non-vanishing perturbative corrections—which is often of interest.

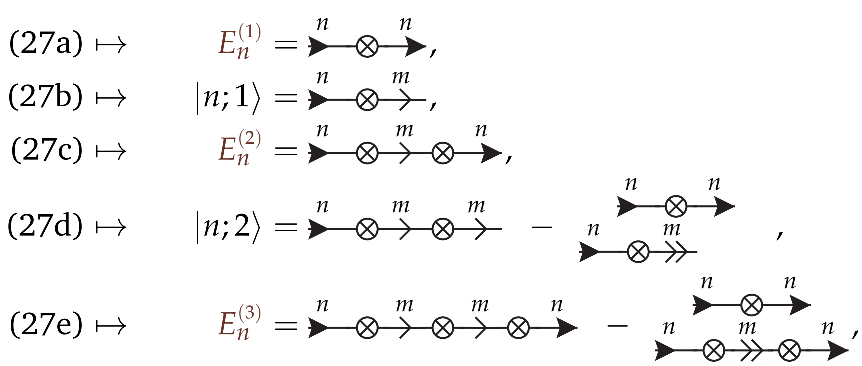
— ⋆ —

The results (26) may be represented graphically, by drawing



(36)

Then



(37)
(38)
(39)
(40)
(41)

and so on, where stacked diagrams represent products of corresponding factors. In many ways, tese diagrams resemble (and were inspired by) Feynman diagrams for self-energy in field teory.

References

[1] L. E. Ballentine, *Quantum Mechanics*, 2nd ed., World Scientific Publishing Co. Inc., 1998.

[2] A. Messiah, *Quantum Mechanics*, Vol. 2, John Wiley & Sons Inc., 1958.