Contents

6.1 Rayleigh-Schrödinger (RS) Perturbation Theory

*6.2 Diagrammatic Representation of RS Perturbation Theory

6.2.1 Diagrammatic Perturbation Theory for Two States

> **Exercise 6.1**
>
> Write down and evaluate all fifth-order diagrams that have the property that an imaginary horizontal line crosses only one hole and one particle line. Show that the sum of such diagrams is
>
> $$\frac{V_{12}V_{21}(V_{22}-V_{11})^3}{(E_1^{(0)}-E_2^{(0)})^4}$$
>
> *Hint*: There are eight such diagrams, and they can be generated by adding three dots to the second-order diagram in all positive ways.

> **Solution 6.1**
>
> The final results are listed below firstly.
>
>
>
> $$(-1)^{4+1}\frac{V_{11}^3 V_{12}V_{21}}{(E_1^{(0)}-E_2^{(0)})^4} \qquad (-1)^{3+1}\frac{V_{11}^2 V_{12}V_{21}V_{22}}{(E_1^{(0)}-E_2^{(0)})^4} \qquad (-1)^{3+1}\frac{V_{11}^2 V_{12}V_{21}V_{22}}{(E_1^{(0)}-E_2^{(0)})^4} \qquad (-1)^{3+1}\frac{V_{11}^2 V_{12}V_{21}V_{22}}{(E_1^{(0)}-E_2^{(0)})^4}$$
>
> $$(-1)^{2+1}\frac{V_{11} V_{12}V_{21}V_{22}^2}{(E_1^{(0)}-E_2^{(0)})^4} \qquad (-1)^{2+1}\frac{V_{11} V_{12}V_{21}V_{22}^2}{(E_1^{(0)}-E_2^{(0)})^4} \qquad (-1)^{2+1}\frac{V_{11} V_{12}V_{21}V_{22}^2}{(E_1^{(0)}-E_2^{(0)})^4} \qquad (-1)^{1+1}\frac{V_{12}V_{21}V_{22}^3}{(E_1^{(0)}-E_2^{(0)})^4}$$
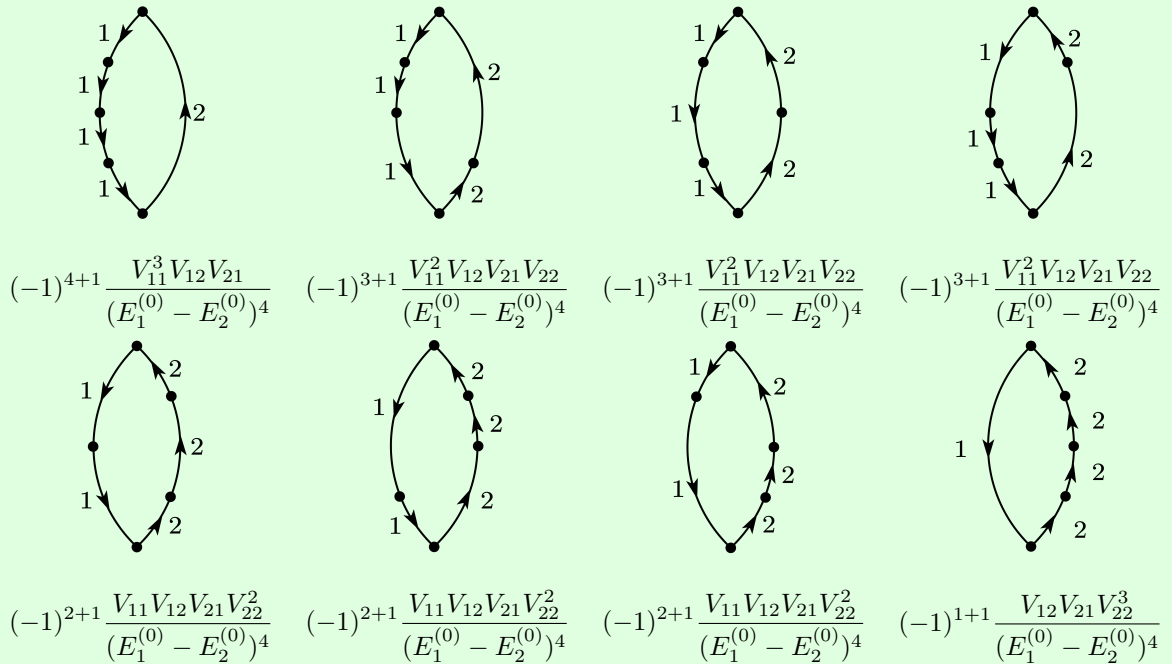>
> Figure 6.1: All fifth-order diagrams, which have the property that an imaginary horizontal line crosses only one hole and one particle line, and their mathematical expressions.
>
> Note that the diagrams, which have the property that an imaginary horizontal line crosses only one hole

and one particle line, have no pair of hole/particle lines whose overlap is nonempty. For any pair of hole/particle lines which connect the dots m_1 and n_1, m_2 and n_2, where $n_1 > m_1$ and $n_2 > m_2$, their overlap will be

- $[\max\{m_1, m_2\}, \min\{n_1, n_2\}]$, if $\min\{n_1, n_2\} > \max\{m_1, m_2\}$;

- empty, otherwise.

For example, if there is a pair of hole lines, one connecting the dot 1 and 3, and the other connecting 2 and 5, their overlap will be $[2, 3]$. Take an another example, if there is a pair of particle lines, one connecting the dot 5 and 4, and the other connecting 2 and 1, their overlap will be empty.

Thus, there are four cases.

- Four hole lines and one particle line. There is only one method, hole lines are $(1, 2)$, $(2, 3)$, $(3, 4)$, $(4, 5)$ and the only particle line is $(5, 1)$, as the first subdiagram in Fig 6.1.

- Three hole lines and two particle lines. There are three methods as follows.

    - Hole lines are $(1, 2)$, $(2, 3)$, and $(3, 5)$ while particle lines are $(5, 4)$, $(4, 1)$.
    - Hole lines are $(1, 2)$, $(2, 4)$, and $(4, 5)$ while particle lines are $(5, 3)$, $(3, 1)$.
    - Hole lines are $(1, 3)$, $(3, 4)$, and $(4, 5)$ while particle lines are $(5, 2)$, $(2, 1)$.

    They correspond to the second, third, fourth subdiagram in Fig 6.1.

- Two hole lines and three particle lines. There are three methods as follows.

    - Hole lines are $(1, 3)$, $(3, 5)$ while particle lines are $(5, 4)$, $(4, 2)$, and $(2, 1)$.
    - Hole lines are $(1, 4)$, $(4, 5)$ while particle lines are $(5, 3)$, $(3, 2)$, and $(2, 1)$.
    - Hole lines are $(1, 2)$, $(2, 5)$ while particle lines are $(5, 4)$, $(4, 3)$, and $(3, 1)$.

    They correspond to the fifth, sixth, seventh subdiagram in Fig 6.1.

- One hole line and four particle lines. There is only one method, the only hole line is $(1, 5)$ and particle lines are $(5, 4)$, $(4, 3)$, $(3, 2)$, and $(2, 1)$, as the eighth subdiagram in Fig 6.1.

Thus, the sum of such diagrams is

$$-\frac{V_{12}V_{21}\left(V_{11}^3 - 3V_{11}^2 V_{22} + 3V_{11}V_{22} - V_{22}^3\right)}{(E_1^{(0)} - E_2^{(0)})^4} = -\frac{V_{12}V_{21}\left(V_{11} - V_{22}\right)^3}{(E_1^{(0)} - E_2^{(0)})^4} = \frac{V_{12}V_{21}\left(V_{22} - V_{11}\right)^3}{(E_1^{(0)} - E_2^{(0)})^4}.$$

In fact, as the textbook says, these eight diagrams can be generated by adding three dots to the second-order diagram in all positive ways. In fact, any pair of hole/particle lines in them has also empty overlap. I think the calculation of the overlap is much direct than inspecting the property of lines.

6.2.2   Diagrammatic Perturbation Theory for N States

Exercise 6.2

Use diagrammatic techniques to obtain the fourth-order perturbation energy of a particular state (say, i) of an N-state system. That is, evaluate the diagrams
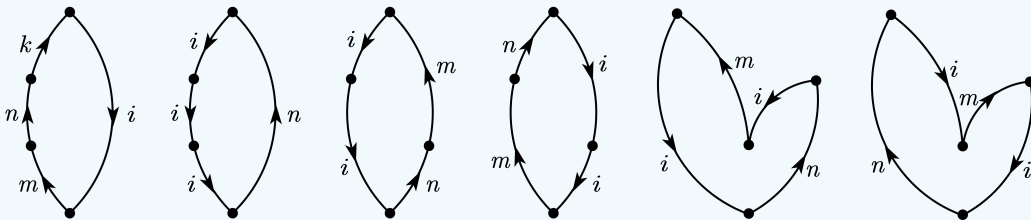
where the indices m, n, k, ... exclude i. Using the approach of Section 6.1, obtain an algebraic expression for the fourth-order energy and compare it to the diagrammatic result.
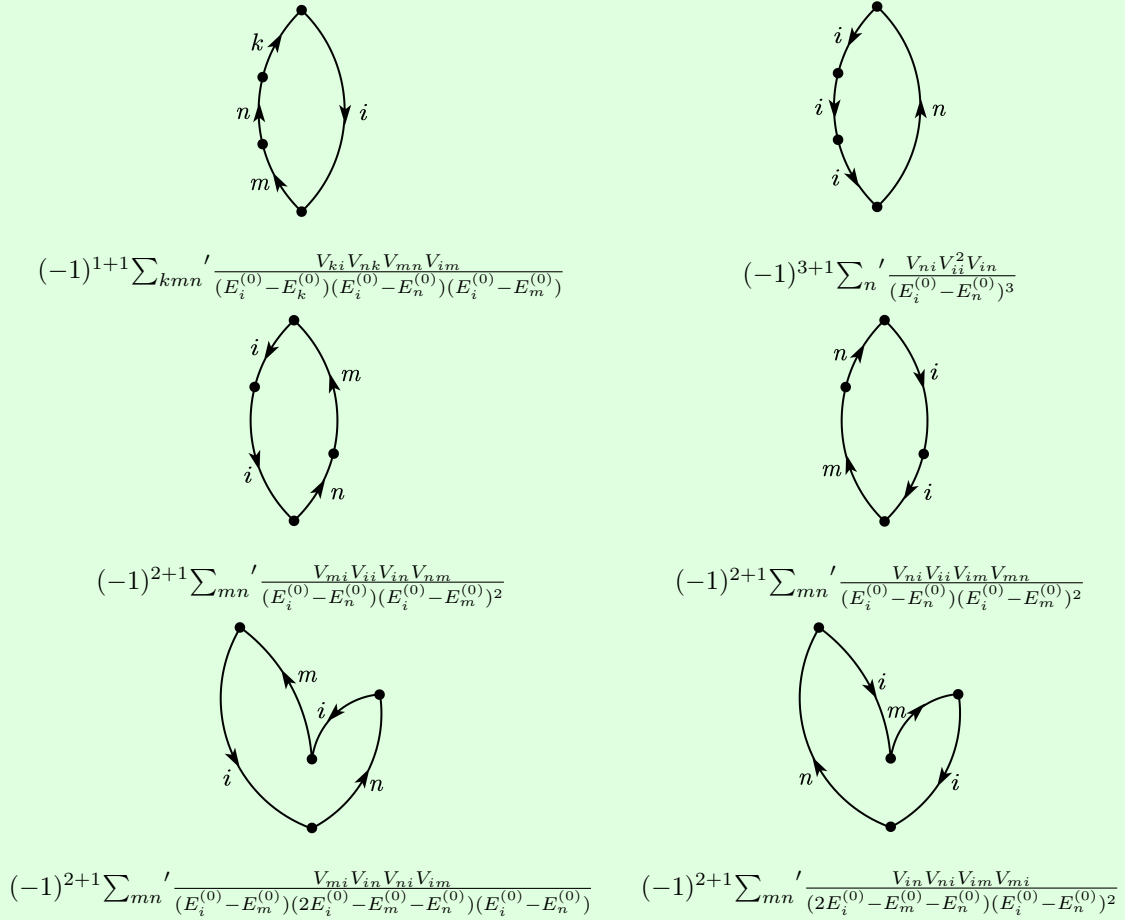
Solution 6.2

$(-1)^{1+1}\sum_{kmn}'\frac{V_{ki}V_{nk}V_{mn}V_{im}}{(E_i^{(0)}-E_k^{(0)})(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_m^{(0)})}$

$(-1)^{3+1}\sum_n'\frac{V_{ni}V_{ii}^2 V_{in}}{(E_i^{(0)}-E_n^{(0)})^3}$

$(-1)^{2+1}\sum_{mn}'\frac{V_{mi}V_{ii}V_{in}V_{nm}}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_m^{(0)})^2}$

$(-1)^{2+1}\sum_{mn}'\frac{V_{ni}V_{ii}V_{im}V_{mn}}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_m^{(0)})^2}$

$(-1)^{2+1}\sum_{mn}'\frac{V_{mi}V_{in}V_{ni}V_{im}}{(E_i^{(0)}-E_m^{(0)})(2E_i^{(0)}-E_m^{(0)}-E_n^{(0)})(E_i^{(0)}-E_n^{(0)})}$

$(-1)^{2+1}\sum_{mn}'\frac{V_{in}V_{ni}V_{im}V_{mi}}{(2E_i^{(0)}-E_m^{(0)}-E_n^{(0)})(E_i^{(0)}-E_n^{(0)})^2}$

Figure 6.2: All fourth-order diagrams and their mathematical expressions.

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$$E_i^{(4)} = \langle i|\mathscr{V}|\Psi_i^{(3)}\rangle = \sum_n' \langle i|\mathscr{V}|n\rangle\langle n|\Psi_i^{(3)}\rangle$$

$$= \sum_n' \frac{V_{in}}{E_i^{(0)}-E_n^{(0)}}\left[\langle n|\mathscr{V}|\Psi_i^{(2)}\rangle - E_i^{(1)}\langle n|\Psi_i^{(2)}\rangle - E_i^{(2)}\langle n|\Psi_i^{(1)}\rangle\right]$$

$$= \sum_n' \frac{V_{in}\langle n|\mathscr{V}|\Psi_i^{(2)}\rangle}{E_i^{(0)}-E_n^{(0)}} - E_i^{(1)}\sum_n'\frac{V_{in}\langle n|\Psi_i^{(2)}\rangle}{E_i^{(0)}-E_n^{(0)}} - E_i^{(2)}\sum_n'\frac{V_{in}\langle n|\Psi_i^{(1)}\rangle}{E_i^{(0)}-E_n^{(0)}}$$

$$= \sum_{mn}' \frac{V_{in}\langle n|\mathscr{V}|m\rangle\langle m|\Psi_i^{(2)}\rangle}{E_i^{(0)}-E_n^{(0)}} - E_i^{(1)}\sum_n'\frac{V_{in}}{E_i^{(0)}-E_n^{(0)}}\langle n|\Psi_i^{(2)}\rangle - E_i^{(2)}\sum_{mn}'\frac{V_{in}\langle n|\mathscr{V}|m\rangle\langle m|\Psi_i^{(1)}\rangle}{E_i^{(0)}-E_n^{(0)}}$$

$$= \sum_{mn}' \frac{V_{in}V_{nm}}{E_i^{(0)}-E_n^{(0)}}\langle m|\Psi_i^{(2)}\rangle - \sum_n'\frac{V_{ii}V_{in}}{E_i^{(0)}-E_n^{(0)}}\langle n|\Psi_i^{(2)}\rangle - \left(\sum_k'\frac{V_{ik}V_{ki}}{E_i^{(0)}-E_k^{(0)}}\right)\sum_{mn}'\frac{V_{in}V_{nm}\langle m|\Psi_i^{(1)}\rangle}{E_i^{(0)}-E_n^{(0)}}$$

$$= \sum_{mn}' \frac{V_{in}V_{nm}}{E_i^{(0)}-E_n^{(0)}}\frac{\langle m|\mathscr{V}|\Psi_i^{(1)}\rangle - E_i^{(1)}\langle m|\Psi_i^{(1)}\rangle}{E_i^{(0)}-E_m^{(0)}} - \sum_n'\frac{V_{ii}V_{in}}{E_i^{(0)}-E_n^{(0)}}\frac{\langle n|\mathscr{V}|\Psi_i^{(1)}\rangle - E_i^{(1)}\langle n|\Psi_i^{(1)}\rangle}{E_i^{(0)}-E_n^{(0)}}$$

$$\quad - \left(\sum_k'\frac{V_{ik}V_{ki}}{E_i^{(0)}-E_k^{(0)}}\right)\sum_{mn}'\frac{V_{in}V_{nm}}{E_i^{(0)}-E_n^{(0)}}\langle m|\Psi_i^{(1)}\rangle$$

$$= \sum_{mn}' \frac{V_{in}V_{nm}}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_m^{(0)})}\left[\sum_k'\langle m|\mathscr{V}|k\rangle\langle k|\Psi_i^{(1)}\rangle - E_i^{(1)}\langle m|\Psi_i^{(1)}\rangle\right]$$

$$\quad - \sum_n'\frac{V_{ii}V_{in}}{(E_i^{(0)}-E_n^{(0)})^2}\left[\sum_m'\langle n|\mathscr{V}|m\rangle\langle m|\Psi_i^{(1)}\rangle - E_i^{(1)}\langle n|\Psi_i^{(1)}\rangle\right] - \sum_{mnk}'\frac{V_{ik}V_{ki}V_{in}V_{nm}\langle m|\Psi_i^{(1)}\rangle}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_k^{(0)})}$$

$$= \sideset{}{'}\sum_{mnk} \frac{V_{in}V_{nm}V_{mk}}{(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})} \langle k|\Psi_i^{(1)}\rangle - \sideset{}{'}\sum_{mn} \frac{V_{ii}V_{in}V_{nm}}{(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})} \langle m|\Psi_i^{(1)}\rangle$$

$$- \sideset{}{'}\sum_{mn} \frac{V_{ii}V_{in}V_{nm}}{(E_i^{(0)} - E_n^{(0)})^2} \langle m|\Psi_i^{(1)}\rangle + \sideset{}{'}\sum_{n} \frac{V_{ii}^2 V_{in}}{(E_i^{(0)} - E_n^{(0)})^2} \langle n|\Psi_i^{(1)}\rangle - \sideset{}{'}\sum_{mnk} \frac{V_{ik}V_{ki}V_{in}V_{nm}\langle m|\Psi_i^{(1)}\rangle}{(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_k^{(0)})}$$

6.2.3   Summation of Diagrams

6.3   Orbital Perturbation Theory: One-Particle Perturbations