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.

$$(-1)^{4+1}\frac{V_{11}^3 V_{12}V_{21}}{(E_1^{(0)} - E_2^{(0)})^4} \qquad (-1)^{3+1}\frac{V_{11}^2 V_{12}V_{21}V_{22}}{(E_1^{(0)} - E_2^{(0)})^4} \qquad (-1)^{3+1}\frac{V_{11}^2 V_{12}V_{21}V_{22}}{(E_1^{(0)} - E_2^{(0)})^4} \qquad (-1)^{3+1}\frac{V_{11}^2 V_{12}V_{21}V_{22}}{(E_1^{(0)} - E_2^{(0)})^4}$$

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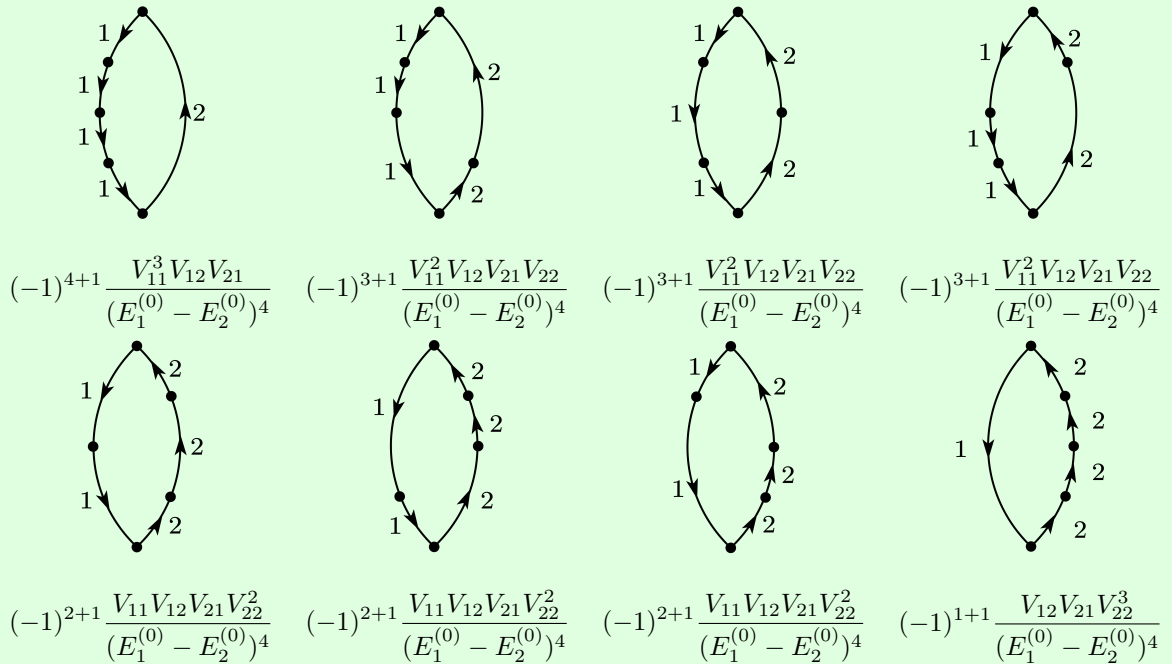
Figure 6.1: All fifth-order diagrams, which have the property that an imaginary horizontal line crosses only one hole and one particle line, and their mathematical expressions.

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
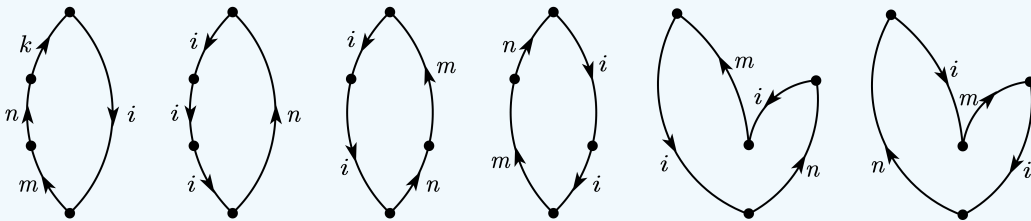
where the indices $m, n, k, \ldots$ exclude i. Using the approach of Section 6.1, obtain an algebraic expression for the fourth-order energy and compare it to the diagrammatic result.

Solution 6.2

Firstly, all fourth-order diagrams and their mathematical expressions are listed in Fig 6.2.

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

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

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

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

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

$$(-1)^{2+1}\sum_{mn}{}' \frac{V_{in}V_{ni}V_{im}V_{mi}}{(2E_i^{(0)}-E_m^{(0)}-E_n^{(0)})(E_i^{(0)}-E_n^{(0)})^2}$$
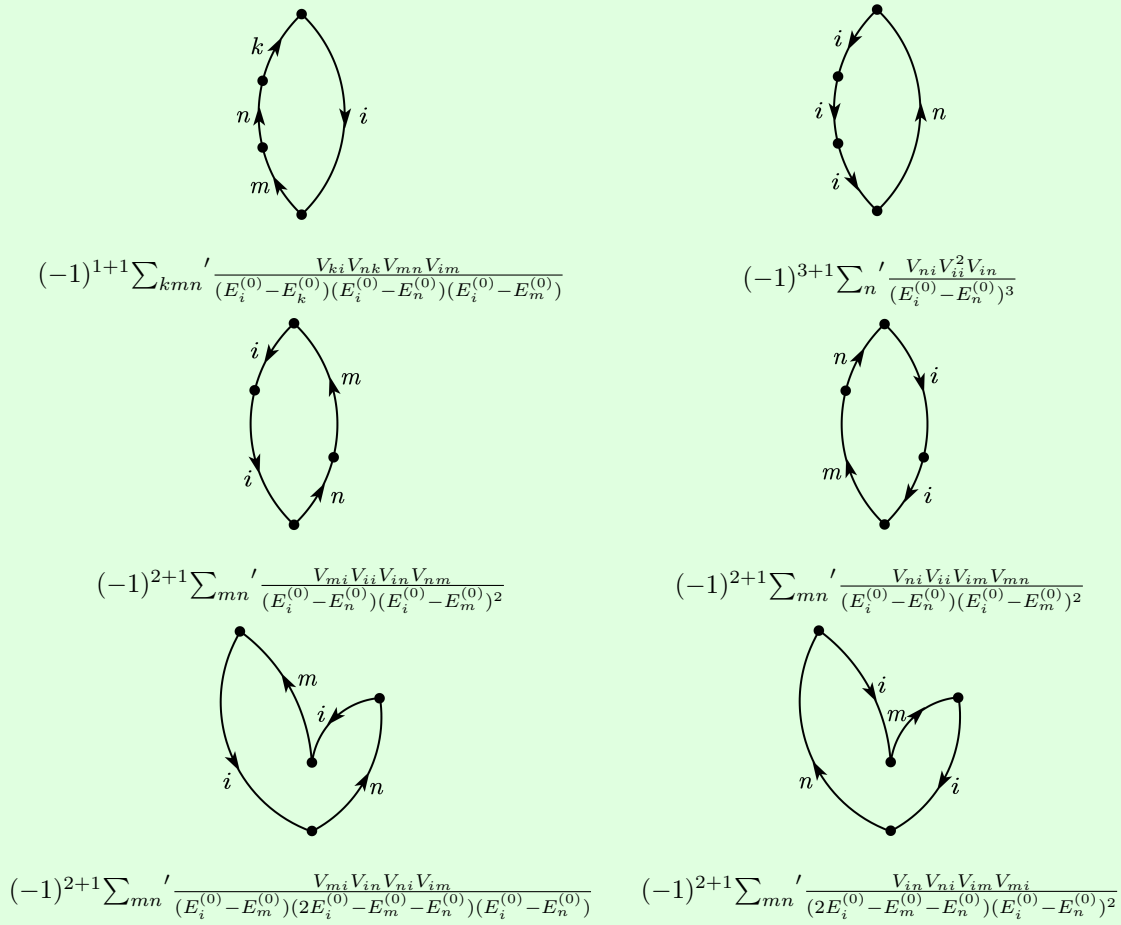
Figure 6.2: All fourth-order diagrams and their mathematical expressions.

Before the formal algebraic derivation, we should obtain some useful intermediate results. From (6.7d), multiplying by $\langle n|$, where $n \neq i$, we find that

$$E_n^{(0)}\langle n|\Psi_i^{(3)}\rangle + \langle n|\mathscr{V}|\Psi_i^{(2)}\rangle = E_i^{(0)}\langle n|\Psi_i^{(3)}\rangle + E_i^{(1)}\langle n|\Psi_i^{(2)}\rangle + E_i^{(1)}\langle n|\Psi_i^{(2)}\rangle,$$

and thus

$$\langle n|\Psi_i^{(3)}\rangle = \frac{1}{E_i^{(0)}-E_n^{(0)}}\left[\langle n|\mathscr{V}|\Psi_i^{(2)}\rangle - E_i^{(1)}\langle n|\Psi_i^{(2)}\rangle - E_i^{(1)}\langle n|\Psi_i^{(2)}\rangle\right].$$

Moreover, (6.8b), (6.10), (6.12), and (6.14) are used in the formal derivation. The fourth-order perturbation energy $E_i^{(4)}$ can be divided into 3 terms, viz.,

$$E_i^{(4)} = \langle i|\mathscr{V}|\Psi_i^{(3)}\rangle = \sum_n{}'\langle i|\mathscr{V}|n\rangle\langle n|\Psi_i^{(3)}\rangle = \sum_n{}' V_{in}\frac{\langle n|\mathscr{V}|\Psi_i^{(2)}\rangle - E_i^{(1)}\langle n|\Psi_i^{(2)}\rangle - E_i^{(2)}\langle n|\Psi_i^{(1)}\rangle}{E_i^{(0)}-E_n^{(0)}}$$

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

The first term is

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

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

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

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

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

$$= \sideset{}{'}\sum_{mnk} \frac{V_{in}V_{nm}V_{mk}}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_m^{(0)})} \frac{V_{ki}}{E_i^{(0)}-E_k^{(0)}} - \sideset{}{'}\sum_{mn} \frac{V_{ii}V_{in}V_{nm}}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_m^{(0)})} \frac{V_{mi}}{E_i^{(0)}-E_m^{(0)}}$$

$$= \sideset{}{'}\sum_{mnk} \frac{V_{in}V_{nm}V_{mk}V_{ki}}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_m^{(0)})(E_i^{(0)}-E_k^{(0)})} - \sideset{}{'}\sum_{mn} \frac{V_{ii}V_{in}V_{nm}V_{mi}}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_m^{(0)})^2}$$

$$= \sideset{}{'}\sum_{mnk} \frac{V_{im}V_{mn}V_{nk}V_{ki}}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_m^{(0)})(E_i^{(0)}-E_k^{(0)})} - \sideset{}{'}\sum_{mn} \frac{V_{ii}V_{in}V_{nm}V_{mi}}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_m^{(0)})^2}.$$

It is evident that the first part of the first term correspond to the first subdiagram and the second part of the first term correspond to the third subdiagram.

The second term is

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

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

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

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

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

$$= -\sideset{}{'}\sum_{mn} \frac{V_{ii}V_{in}V_{nm}}{(E_i^{(0)}-E_n^{(0)})^2}\frac{\langle m|\mathscr{V}|i\rangle}{E_i^{(0)}-E_m^{(0)}} + \sideset{}{'}\sum_n \frac{V_{ii}^2V_{in}}{(E_i^{(0)}-E_n^{(0)})^2}\frac{\langle n|\mathscr{V}|i\rangle}{E_i^{(0)}-E_n^{(0)}}$$

$$= -\sideset{}{'}\sum_{mn} \frac{V_{ii}V_{in}V_{nm}V_{mi}}{(E_i^{(0)}-E_n^{(0)})^2(E_i^{(0)}-E_m^{(0)})} + \sideset{}{'}\sum_n \frac{V_{ii}^2V_{in}V_{ni}}{(E_i^{(0)}-E_n^{(0)})^3}$$

$$= -\sideset{}{'}\sum_{mn} \frac{V_{ii}V_{im}V_{mn}V_{ni}}{(E_i^{(0)}-E_m^{(0)})^2(E_i^{(0)}-E_n^{(0)})} + \sideset{}{'}\sum_n \frac{V_{ii}^2V_{in}V_{ni}}{(E_i^{(0)}-E_n^{(0)})^3}.$$

It is evident that the first part of the second term correspond to the fourth subdiagram and the second part of the second term correspond to the second subdiagram.

The third term is

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

$$= -\left(\sideset{}{'}\sum_m \frac{V_{im}V_{mi}}{(E_i^{(0)}-E_m^{(0)})}\right)\sideset{}{'}\sum_n \frac{V_{in}V_{ni}}{(E_i^{(0)}-E_n^{(0)})^2} = -\sideset{}{'}\sum_{mn} \frac{V_{im}V_{mi}V_{in}V_{ni}}{(E_i^{(0)}-E_m^{(0)})(E_i^{(0)}-E_n^{(0)})^2}.$$

It seems that it does not directly correspond to any subdiagram in Fig 6.2. However, we can find that the sum of the mathematical expressions of the fifth and sixth subdiagram is

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

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

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

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

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

which is the third term exactly. Thus we can conclude that the results obtained by algebraic methods is the same as that by diagrammatic techniques. The mathematical expression of the fourth-order perturbation energy $E_i^{(4)}$ is

$$E_i^{(4)} = \sum_{mnk}' \frac{V_{im}V_{mn}V_{nk}V_{ki}}{(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})(E_i^{(0)} - E_k^{(0)})} - \sum_{mn}' \frac{V_{ii}V_{in}V_{nm}V_{mi}}{(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})^2}$$

$$- \sum_{mn}' \frac{V_{ii}V_{im}V_{mn}V_{ni}}{(E_i^{(0)} - E_m^{(0)})^2(E_i^{(0)} - E_n^{(0)})} + \sum_{n}' \frac{V_{ii}^2 V_{in}V_{ni}}{(E_i^{(0)} - E_n^{(0)})^3} - \sum_{mn}' \frac{V_{im}V_{mi}V_{in}V_{ni}}{(E_i^{(0)} - E_m^{(0)})(E_i^{(0)} - E_n^{(0)})^2}.$$

6.2.3 Summation of Diagrams

6.3 Orbital Perturbation Theory: One-Particle Perturbations

Exercise 6.3

Derive

$$E_0^{(2)} = \sum_{ar} \frac{v_{ar}v_{ra}}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}}$$

starting with the general expression for the second-order energy (Eq.(6.12)) applied to an N-electron system,

$$E_0^{(2)} = \sum_{n}' \frac{\left| \langle \Psi_0 | \sum_i v(i) | n \rangle \right|^2}{E_0^{(0)} - E_n^{(0)}}$$

where the sum runs over all states of the system except the ground state.

Hint: The states $|n\rangle$ must be single excitations of the type

$$|\Psi_a^r\rangle = |\chi_1^{(0)} \cdots \chi_{a-1}^{(0)} \chi_r^{(0)} \chi_{a+1}^{(0)} \cdots \chi_N^{(0)}\rangle.$$

Solution 6.3

Note that (6.31) states that $\mathcal{V} = \sum_i v(i)$ only connects two Slater determinants whose different occupied orbitals should be no more than one, thus we obtain that

$$E_0^{(2)} = \sum_{n}' \frac{|\langle \Psi_0 | \sum_i v(i) | n \rangle|^2}{E_0^{(0)} - E_n^{(0)}} = \sum_{ar} \frac{|\langle \Psi_0 | \mathcal{V} | \Psi_a^r \rangle|^2}{E_0^{(0)} - (E_0^{(0)} + \varepsilon_r^{(0)} - \varepsilon_a^{(0)})} = \sum_{ar} \frac{v_{ar}v_{ra}}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}}. \tag{6.3-1}$$

Exercise 6.4

Calculate the third-order energy $E_0^{(3)}$ using the general expression given in Eq.(6.15).

    a. Show that

$$B_0^{(3)} = -E_0^{(1)} \sum_{n}' \frac{|\langle \Psi_0 | \mathcal{V} | n \rangle|^2}{(E_0^{(0)} - E_n^{(0)})^2} = -\sum_{abr} \frac{v_{aa}v_{rb}v_{br}}{(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})^2}.$$

    b. Show that

$$A_0^{(3)} = \sum_{nm}' \frac{\langle \Psi_0 | \mathcal{V} | n \rangle \langle n | \mathcal{V} | m \rangle \langle m | \mathcal{V} | \Psi_0 \rangle}{(E_0^{(0)} - E_n^{(0)})(E_0^{(0)} - E_m^{(0)})} = \sum_{abrs} \frac{v_{ar}v_{sb}\langle \Psi_a^r | \mathcal{V} | \Psi_b^s \rangle}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_s^{(0)})}.$$

c. Show that

$$
\begin{aligned}
\langle \Psi_a^r | \mathscr{V} | \Psi_b^s \rangle &= v_{rs} & &\text{if } a = b \quad r \neq s, \\
&= -v_{ba} & &\text{if } a \neq b \quad r = s, \\
&= \sum_c v_{cc} - v_{aa} + v_{rr} & &\text{if } a = b \quad r = s,
\end{aligned}
$$

and zero otherwise.

d. Finally, combine the two terms to obtain

$$
E_0^{(3)} = A_0^{(3)} + B_0^{(3)} = \sum_{ars} \frac{v_{ar} v_{rs} v_{sa}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} - \sum_{abr} \frac{v_{ra} v_{ab} v_{br}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})}.
$$

e. Show that for a chosed-shell system

$$
E_0^{(3)} = 2 \sum_{ars}^{N/2} \frac{v_{ar} v_{rs} v_{sa}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} - 2 \sum_{abr}^{N/2} \frac{v_{ra} v_{ab} v_{br}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})}.
$$

Solution 6.4

a. Similar to Exercise 6.3, it is evident that

$$
\begin{aligned}
B_0^{(3)} &= -E_0^{(1)} \sideset{}{'}\sum_n \frac{|\langle \Psi_0 | \mathscr{V} | n \rangle|^2}{(E_0^{(0)} - E_n^{(0)})^2} = -\left(\sum_a v_{aa} \right) \sum_{br} \frac{v_{rb} v_{br}}{[E_0^{(0)} - (E_n^{(0)} + \varepsilon_r^{(0)} - \varepsilon_b^{(0)})]^2} \\
&= -\sum_{abr} \frac{v_{aa} v_{rb} v_{br}}{(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})^2}.
\end{aligned}
$$

b. In the same way, we obtain that

$$
\begin{aligned}
A_0^{(3)} &= \sideset{}{'}\sum_{nm} \frac{\langle \Psi_0 | \mathscr{V} | n \rangle \langle n | \mathscr{V} | m \rangle \langle m | \mathscr{V} | \Psi_0 \rangle}{(E_0^{(0)} - E_n^{(0)})(E_0^{(0)} - E_m^{(0)})} \\
&= \sum_{ar} \sum_{bs} \frac{\langle \Psi_0 | \mathscr{V} | \Psi_a^r \rangle \langle \Psi_a^r | \mathscr{V} | \Psi_b^s \rangle \langle \Psi_b^s | \mathscr{V} | \Psi_0 \rangle}{[E_0^{(0)} - (E_0^{(0)} + \varepsilon_r^{(0)} - \varepsilon_a^{(0)})][E_0^{(0)} - (E_0^{(0)} + \varepsilon_s^{(0)} - \varepsilon_b^{(0)})]} \\
&= \sum_{abrs} \frac{v_{ar} v_{sb} \langle \Psi_a^r | \mathscr{V} | \Psi_b^s \rangle}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_s^{(0)})}.
\end{aligned}
$$

c. Using the conclusion of Exercise 2.13, at once we get

$$
\begin{aligned}
\langle \Psi_a^r | \mathscr{V} | \Psi_b^s \rangle &= v_{rs} & &\text{if } a = b \quad r \neq s, \\
&= -v_{ba} & &\text{if } a \neq b \quad r = s, \\
&= \sum_c v_{cc} - v_{aa} + v_{rr} & &\text{if } a = b \quad r = s,
\end{aligned}
$$

and zero otherwise.

d. Thus, we simplify $A_0^{(3)}$ as follows.

$$
\begin{aligned}
A_0^{(3)} &= \sum_{abrs} \frac{v_{ar} v_{sb} \langle \Psi_a^r | \mathscr{V} | \Psi_b^s \rangle}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_s^{(0)})} \\
&= \sum_{ar} \frac{v_{ar} v_{ra}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2} \left(\sum_c v_{cc} - v_{aa} + v_{rr} \right) + \sum_{\substack{ar \\ s \neq r}} \frac{v_{ar} v_{sa} v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} \\
&\quad + \sum_{\substack{ar \\ b \neq a}} \frac{v_{ar} v_{rb}(-v_{ba})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})}
\end{aligned}
$$

$$= \sum_{ar} \frac{v_{ar}v_{ra}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2} \left(\sum_b v_{bb} \right) - v_{aa} \sum_{ar} \frac{v_{ar}v_{ra}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2} + v_{rr} \sum_{ar} \frac{v_{ar}v_{ra}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2}$$

$$+ \sum_{\substack{ar \\ s \neq r}} \frac{v_{ar}v_{sa}v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} - \sum_{\substack{ar \\ b \neq a}} \frac{v_{ar}v_{rb}v_{ba}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})}$$

$$= \left(\sum_a v_{aa} \right) \sum_{br} \frac{v_{br}v_{rb}}{(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})^2} + \sum_{ars} \frac{v_{ar}v_{sa}v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} - \sum_{abr} \frac{v_{ar}v_{rb}v_{ba}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})}$$

$$= \sum_{abr} \frac{v_{aa}v_{br}v_{rb}}{(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})^2} + \sum_{ars} \frac{v_{ar}v_{sa}v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} - \sum_{abr} \frac{v_{ar}v_{rb}v_{ba}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})}.$$

Finally,

$$E_0^{(3)} = A_0^{(3)} + B_0^{(3)}$$

$$= \sum_{abr} \frac{v_{aa}v_{br}v_{rb}}{(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})^2} + \sum_{ars} \frac{v_{ar}v_{sa}v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})}$$

$$- \sum_{abr} \frac{v_{ar}v_{rb}v_{ba}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})} - \sum_{abr} \frac{v_{aa}v_{rb}v_{br}}{(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})^2}$$

$$= \sum_{ars} \frac{v_{ar}v_{sa}v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} - \sum_{abr} \frac{v_{br}v_{ra}v_{ab}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})}.$$

e. Since a matrix element $v_{ij} = \langle i|v|j \rangle$ is nonzero only if both spin orbitals i and j have the same spin, thus only $v_{ar}v_{sa}v_{rs}$ and $v_{\bar{a}\bar{r}}v_{\bar{s}\bar{a}}v_{\bar{r}\bar{s}}$ contribute, and so $v_{br}v_{ra}v_{ab}$ and $v_{\bar{b}\bar{r}}v_{\bar{r}\bar{a}}v_{\bar{a}\bar{b}}$ do $v_{br}v_{ra}v_{ab}$. Besides, the denominators is invariant regardless of spin up or down. In this way, we obtain that

$$E_0^{(3)} = \sum_{ars}^{N/2} \frac{v_{ar}v_{sa}v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} + \sum_{\bar{a}\bar{r}\bar{s}}^{N/2} \frac{v_{\bar{a}\bar{r}}v_{\bar{s}\bar{a}}v_{\bar{r}\bar{s}}}{(\varepsilon_{\bar{a}}^{(0)} - \varepsilon_{\bar{r}}^{(0)})(\varepsilon_{\bar{a}}^{(0)} - \varepsilon_{\bar{s}}^{(0)})}$$

$$- \sum_{abr}^{N/2} \frac{v_{br}v_{ra}v_{ab}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})} - \sum_{\bar{a}\bar{b}\bar{r}}^{N/2} \frac{v_{\bar{b}\bar{r}}v_{\bar{r}\bar{a}}v_{\bar{a}\bar{b}}}{(\varepsilon_{\bar{a}}^{(0)} - \varepsilon_{\bar{r}}^{(0)})(\varepsilon_{\bar{b}}^{(0)} - \varepsilon_{\bar{r}}^{(0)})}$$

$$= 2\sum_{ars}^{N/2} \frac{v_{ar}v_{sa}v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} - 2\sum_{abr}^{N/2} \frac{v_{br}v_{ra}v_{ab}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})}.$$

Exercise 6.5

Show that the second term in Eq.(6.52) is equal to $\frac{3}{8}\beta$ for benzene.

Solution 6.5

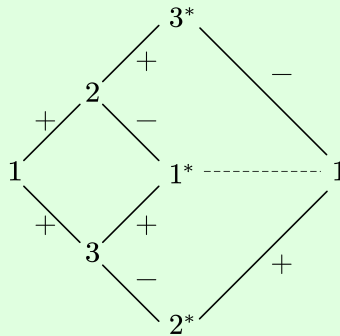The pictorial representation of the second term in $E_0^{(3)}$ can be seen in Fig 6.3.

Figure 6.3: Pictorial representation of the second term in $E_0^{(3)}$, where the order is v_{ij}, v_{jk^*} and v_{k^*i} from the left to the right. The plus and minus signs indicate whether the matrix elements between the two orbitals is $\pm\frac{\beta}{2}$.

With the high symmetry, it is

$$-2 \times \frac{1}{(2\beta)^2} \sum_{i=1}^{3} [v_{12}v_{23*}v_{3*1} + v_{13}v_{32*}v_{2*1}] = -\frac{3}{2\beta^2} \left[\frac{\beta}{2} \times \frac{\beta}{2} \times \left(-\frac{\beta}{2}\right) + \frac{\beta}{2} \times \left(-\frac{\beta}{2}\right) \times \frac{\beta}{2} \right] = \frac{3}{8\beta}.$$

(6.5-1)

Exercise 6.6

Consider a cyclic polyene with $N = 4\nu + 2$, $\nu = 1, 2, ...$ carbons. Instead of assuming that all the bonds are identical, suppose they alternate in length. In the context of Hückel theory this means that the resonance integrals between adjacent carbons are not all equal to β but alternate between $\beta_1 1$ and β_2. For example, for benzene we have
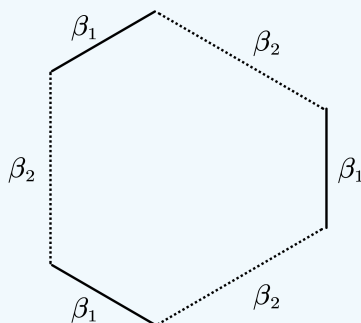
Now it can be shown that the exact energy for a cyclic polyene of this type is

$$\mathscr{E}_0 = N\alpha - 2 \sum_{j=-\nu}^{\nu} \left(\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos \frac{2j\pi}{2\nu+1} \right)^{1/2}$$

(see for example, L. Salem, *Molecular Orbital Theory of Conjugated Systems*, Benjamin, New York, 1966, pp.498-500). Note that when $\beta_1 = \beta_2 = \beta$, since $2\cos^2 \theta = (1 + \cos 2\theta)$ and β is negative, we recover

$$\mathscr{E}_0 = N\alpha + 4\beta \sum_{j=-\nu}^{\nu} \cos \frac{j\pi}{2\nu+1}$$

which is the result quoted in Subsection 5.3.2. Also note that when $\beta_1 = \beta$ but $\beta_2 = 0$, we have

$$\mathscr{E}_0 = N\alpha + N\beta$$

which is just the total energy of the polyene using the localized ethylenic description. The purpose of this exercise is to obtain the perturbation expansion for the resonance energy by expanding the exact energy in powers of β_2/β_1.

a. Show that for benzene ($\nu = 1$) the exact ground state energy in the alternating short and long bond model is
$$\mathscr{E}_0 = 6\alpha + 2(\beta_1 + \beta_2) - 4(\beta_1^2 + \beta_2^2 - \beta_1\beta_2)^{1/2}$$

Do this first by using the general expression and then by setting up the Hückel matrix, diagonalizing it and adding up the occupied orbital energies. Note that when $\beta_1 = \beta_2 = \beta$ we recover our old result, $6\alpha + 8\beta$.

b. Setting $\beta_1 = \beta$ and $\beta_2/\beta_1 = x$ show that the resonance energy of benzene can be written as

$$E_R = 4\beta(\frac{1}{2}x - 1 + (1 - x + x^2)^{1/2})$$

Note that when $x = 0$, $E_R = 0$ and when $x = 1$, $E_R = 2\beta$ which is exact.

c. Using the relation

$$(1+y)^{1/2} = 1 + \frac{1}{2}y - \frac{1}{8}y^2 + \frac{1}{16}y^3 - \frac{5}{128}y^4 + \cdots, \quad |y| < 1$$

expand E_R to fourth order in x and thus show that

$$E_R = \beta\left(\frac{3}{2}x^2 + \frac{3}{4}x^3 + \frac{3}{32}x^4 + \cdots\right)$$

Identifying the coefficient of x^n with the nth-order perturbation result (i.e., $E^{(n)}{}_0$), we have

$$E_0^{(2)} = \frac{3}{2}\beta,$$

$$E_0^{(3)} = \frac{3}{4}\beta,$$

$$E_0^{(4)} = \frac{3}{32}\beta.$$

Note that $E_0^{(2)}$ and $E_0^{(3)}$ agree with our previously calculated values. This derivation provides some insight into the poor convergence of the perturbation expansion of the resonance energy of benzene. Basically, the perturbation expansion converges rapidly when x is small. However, for our problem x is equal to unity.

The resonance energy calculated up to Mth-order as a function of M is shown below. Note the oscillatory convergence towards the exact value to 2β. The method used above to obtain $E_0^{(n)}$ for $n = 2, 3, 4$ becomes extremely laborious for larger n. The results below were calculated by first showing that $E_0^{(n)} = 4\beta C_n^{-1/2}(1/2)$, where $C_n^{-1/2}(x)$ is a Gegenbauer polynomial of degree n and order $-\frac{1}{2}$, and then using the recursive properties of these polynomials, to show that

$$(n+1)E_0^{(n+1)} = (n-1)E_0^{(n)} - (n-2)E_0^{(n-1)}.$$
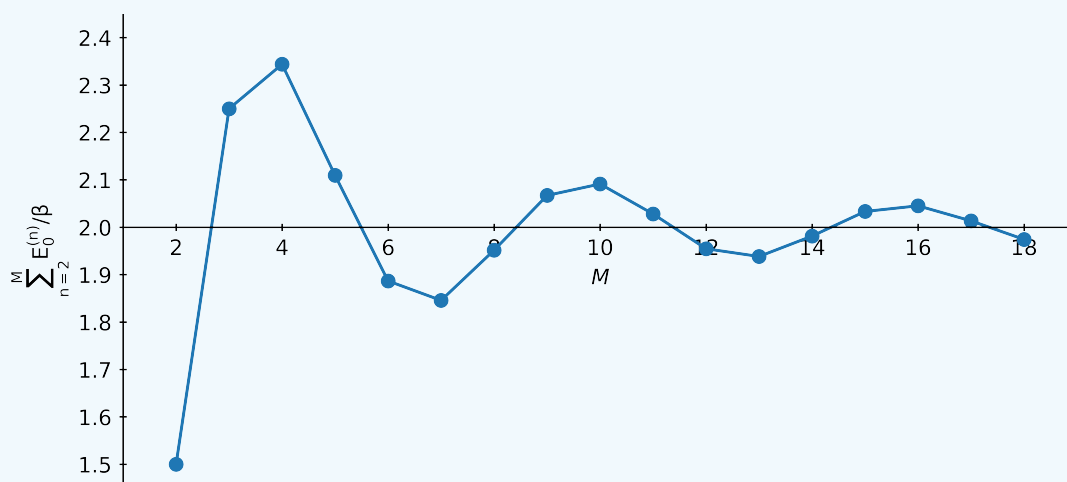
Solution 6.6

6-6 so
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6.4 Diagrammatic Representation of Orbital Perturbation Theory