CHAPTER 6

Many-Body Perturbation Theory

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**
>
> 6-1 so

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
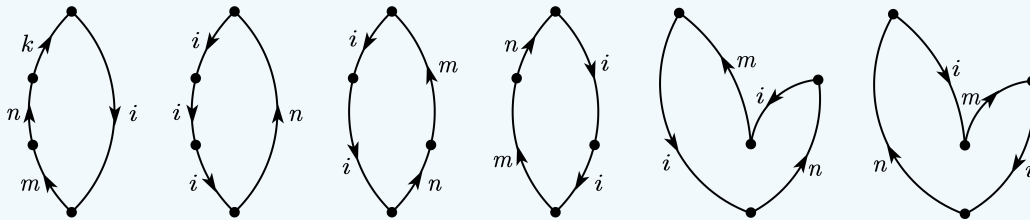>
>
>
> Figure 6.1: 1111
>
> where the indices m, n, k, ... exclude i. Using the approach of Section 6.1, obtain an algebraic expression for the fourth-order energy and compare it to the diagrammatic result.

> **Solution 6.2**
>
> 6-2 so
> fffff

6.2.3   Summation of Diagrams

6.3   Orbital Perturbation Theory: One-Particle Perturbations

Solution 6.3

6-3 so

Exercise 6.4

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

a. Show that

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

b. Show that

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

c. Show that

$$\begin{aligned}
\langle \Psi_a^r | \mathscr{V} | \Psi_b^s \rangle &= v_{rs} & \text{if } a = b \quad r \neq s, \\
&= -v_{ba} & \text{if } a \neq b \quad r = s, \\
&= \sum_c v_{cc} - v_{aa} + v_{rr} & \text{if } a = b \quad r = s, \\
&= 0 & \text{otherwise.}
\end{aligned}$$

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

6-4 so

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

6-5 so

Consider a cyclic polyene with $N = 4\nu + 2$, $\nu = 1, 2, \ldots$ 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
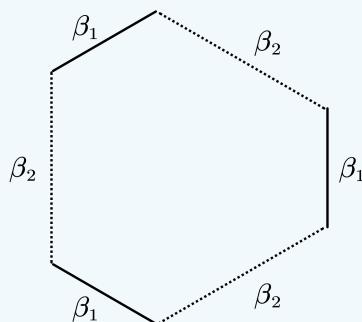

Figure 6.2: 1111

Now it can be shown that the exact energy for a cyclic polyene of this type is

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

(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

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

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

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

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
$$\mathcal{E}_0 = 6\alpha + 2(\beta_1 + \beta_2) - 4(\beta_1^2 + \beta_2^2 - \beta_1\beta_2)^{1/2}$$

    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

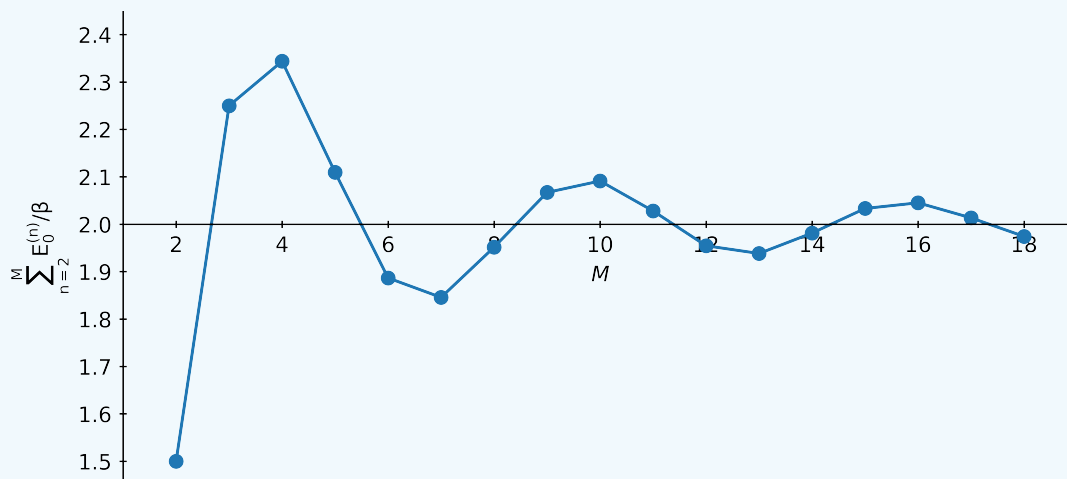$$(n + 1)E_0^{(n+1)} = (n - 1)E_0^{(n)} - (n - 2)E_0^{(n-1)}.$$

Figure 6.3: 1111

6.4   Diagrammatic Representation of Orbital Perturbation Theory

Exercise 6.7

Find the fourth-order energy for a closed-shell cyclic polyene.

    a. Show that

and

so that

$$E_0^{(4)} = \frac{N\beta}{64}$$

Thus the resonance energy calculated for a cyclic polyene with $N > 6$ up to fourth order is $(1/4 + 1/64)N\beta = 0.2656N\beta$, which compares very favorably with the asymptotically exact value of 0.2732β (i.e., 97%).

b. For benzene, show that the diagrammatic result for the fourth-order energy agrees with the independently calculated result found in Exercise 6.6.

Solution 6.7

6-7 so

6.5   Perturbation Expansion of the Correlation Energy

Exercise 6.8

Derive Eqs.(6.73) and (6.74) starting with Eq.(6.72).

Solution 6.8

6-8 so

Exercise 6.9

Derive Eqs.(6.77) and (6.78) from Eq.(6.76).

Solution 6.9

6-9 so

6.6   The N-Dependence of the RS Perturbation Expansion

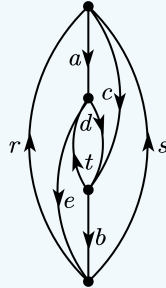**Exercise 6.10**

Derive Eqs.(6.80b) and (6.90).

Solution 6.10

6-10 so

6.7 Diagrammatic Representation of the Perturbation Expansion of the Correlation Energy

6.7.1 Hugenholtz Diagrams

Show that the fourth-order diagram

is equal to

$$-\frac{1}{2} \sum_{abcderst} \frac{\langle rs\|ac\rangle\langle at\|de\rangle\langle dc\|tb\rangle\langle eb\|rs\rangle}{(\varepsilon_a + \varepsilon_c - \varepsilon_r - \varepsilon_s)(\varepsilon_c + \varepsilon_d + \varepsilon_e - \varepsilon_r - \varepsilon_t - \varepsilon_s)(\varepsilon_b + \varepsilon_e - \varepsilon_r - \varepsilon_s)}.$$
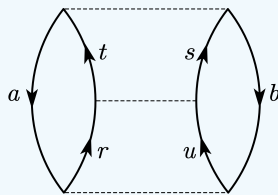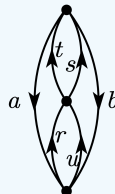
Solution 6.11

6-11 so

6.7.2 Goldstone Diagrams

Exercise 6.12

We stated that the Goldstone diagrams in Table 6.2 can be obtained by "pulling apart" the second- and third-order Hugenholtz diagrams. This is quite tricky to see but the converse is much easier. For example, if we push

together, it is clear that we obtain

Push all third-order diagrams in Table 6.2 together in a similar way and, thus, find which Goldstone diagram comes from which Hugenholtz diagram. For the above Hugenholtz diagram, verify that its mathematical value is indeed the sum of the values of the corresponding Goldstone diagrams.

Solution 6.12

6-12 so

6.7.3 Summation of Diagrams

6.7.4 What Is the Linked Cluster Theorem?

Exercise 6.13

Calculate $E_0^{(3)}$ for a supermolecule consisting of N non-interacting minimal basis H_2 molecules by evaluating the Goldstone diagrams in Table 6.2. Compare your result with that of Eq.(6.92), which was obtained algebraically by explicitly cancelling terms proportional to N^2.

Hint: Simply show that the value of each Goldstone diagram for the supermolecule in N times the result for a single molecule.

Solution 6.13

6-13 so

6.8 Some Illustrative Calculations