

# Modern Quantum Chemistry, Szabo & Ostlund

## HW

WSF

July 6, 2020

## Contents

<b>6</b>	<b>Many-body Perturbation Theory</b>	<b>2</b>
6.1	RS Perturbation Theory	2
6.2	Diagrammatic Representation of RS Perturbation Theory	2
6.2.1	Diagrammatic Perturbation Theory for Two States	2
	Ex 6.1	2
6.2.2	Diagrammatic Perturbation Theory for $N$ States	3
	Ex 6.2	3
6.2.3	Summation of Diagrams	4
6.3	Orbital Perturbation Theory: One-Particle Perturbations	4
	Ex 6.3	4
	Ex 6.4	4
	Ex 6.5	6
	Ex 6.6	6
6.4	Diagrammatic Representation of Orbital Perturbation Theory	7
	Ex 6.7	7
6.5	Perturbation Expansion of the Correlation Energy	9
	Ex 6.8	9
	Ex 6.9	9
6.6	The $N$ -dependence of the RS Perturbation Expansion	9
	Ex 6.10	9
6.7	Diagrammatic Representation of the Perturbation Expansion of the Correlation Energy	10
6.7.1	Hugenholtz Diagrams	10
	Ex 6.11	10
6.7.2	Goldstone Diagrams	10
	Ex 6.12	10
6.7.3	Summation of Diagrams	10
6.7.4	What Is the Linked-Cluster Theorem?	10
	Ex 6.13	10
6.8	Some Illustrative Calculations	10

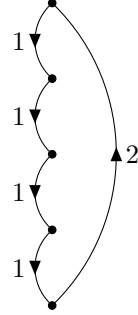
## 6 Many-body Perturbation Theory

### 6.1 RS Perturbation Theory

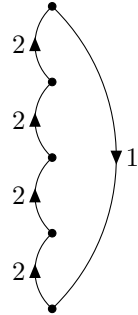
### 6.2 Diagrammatic Representation of RS Perturbation Theory

#### 6.2.1 Diagrammatic Perturbation Theory for Two States

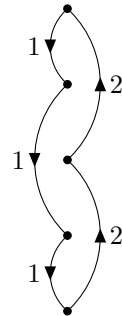
Ex 6.1



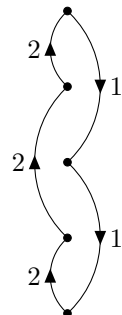
$$= (-1)^5 \frac{V_{12}V_{21}V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4} = -\frac{V_{12}V_{21}V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4}$$



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



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



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

Similarly,

$$\begin{aligned}
& \text{Diagram 1} + \text{Diagram 2} = \frac{V_{12}V_{21}V_{11}^2V_{22}}{(E_1^{(0)} - E_2^{(0)})^4} \\
& \text{Diagram 3} + \text{Diagram 4} = -\frac{V_{12}V_{21}V_{11}V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4}
\end{aligned}$$

thus, the sum of above terms is

$$\frac{V_{12}V_{21}(V_{22}^3 - V_{11}^3)}{(E_1^{(0)} - E_2^{(0)})^4} + 3 \times \frac{V_{12}V_{21}(V_{11}^2V_{22} - V_{11}V_{22}^2)}{(E_1^{(0)} - E_2^{(0)})^4} = \frac{V_{12}V_{21}(V_{22} - V_{11})^3}{(E_1^{(0)} - E_2^{(0)})^4} \quad (6.2.1)$$

### 6.2.2 Diagrammatic Perturbation Theory for $N$ States

**Ex 6.2** The 4th-order perturbation energy of state  $i$  can be expressed as

$$\begin{aligned}
& \sum_{k,n,m \neq i} \frac{V_{ki}V_{nk}V_{mn}V_{im}}{(E_i^{(0)} - E_k^{(0)})(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})} + \sum_{n \neq i} \frac{V_{ii}^2V_{ni}V_{in}}{(E_i^{(0)} - E_n^{(0)})^3} - \sum_{m,n \neq i} \frac{V_{ii}V_{mi}V_{in}V_{nm}}{(E_i^{(0)} - E_m^{(0)})^2(E_i^{(0)} - E_n^{(0)})} \\
& - \sum_{m,n \neq i} \frac{V_{ii}V_{ni}V_{im}V_{mn}}{(E_i^{(0)} - E_m^{(0)})^2(E_i^{(0)} - E_n^{(0)})} - \sum_{m,n \neq i} \frac{V_{mi}V_{im}V_{in}V_{ni}}{(E_i^{(0)} - E_m^{(0)})(E_i^{(0)} - E_n^{(0)})(2E_i^{(0)} - E_n^{(0)} - E_m^{(0)})} \\
& - \sum_{m,n \neq i} \frac{V_{mi}V_{im}V_{in}V_{ni}}{(E_i^{(0)} - E_n^{(0)})^2(2E_i^{(0)} - E_n^{(0)} - E_m^{(0)})} \\
& = \sum_{k,n,m \neq i} \frac{V_{ki}V_{nk}V_{mn}V_{im}}{(E_i^{(0)} - E_k^{(0)})(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})} + \sum_{n \neq i} \frac{V_{ii}^2V_{ni}V_{in}}{(E_i^{(0)} - E_n^{(0)})^3} - 2 \sum_{m,n \neq i} \frac{V_{ii}V_{mi}V_{in}V_{nm}}{(E_i^{(0)} - E_m^{(0)})^2(E_i^{(0)} - E_n^{(0)})} \\
& - \sum_{m,n \neq i} \frac{V_{mi}V_{im}V_{in}V_{ni}}{(E_i^{(0)} - E_m^{(0)})(E_i^{(0)} - E_n^{(0)})^2} \quad (6.2.2)
\end{aligned}$$

while

$$\langle n | \mathcal{H} | \Psi_i^{(3)} \rangle + \langle n | \mathcal{V} | \Psi_i^{(2)} \rangle = E_i^{(0)} \langle n | \Psi_i^{(3)} \rangle + E_i^{(1)} \langle n | \Psi_i^{(2)} \rangle + E_i^{(2)} \langle n | \Psi_i^{(1)} \rangle \quad (6.2.3)$$

$$\begin{aligned}
(E_i^{(0)} - E_n^{(0)}) \langle n | \Psi_i^{(3)} \rangle &= \langle n | \mathcal{V} | \Psi_i^{(2)} \rangle - E_i^{(1)} \langle n | \Psi_i^{(2)} \rangle - E_i^{(2)} \langle n | \Psi_i^{(1)} \rangle \\
&= \langle n | \mathcal{V} | \Psi_i^{(2)} \rangle - E_i^{(1)} \frac{\langle n | \mathcal{V} | \Psi_i^{(1)} \rangle - E_i^{(1)} \langle n | \Psi_i^{(1)} \rangle}{E_i^{(0)} - E_n^{(0)}} - E_i^{(2)} \langle n | \Psi_i^{(1)} \rangle \\
&= \langle n | \mathcal{V} | \Psi_i^{(2)} \rangle - E_i^{(1)} \frac{\langle n | \mathcal{V} | \Psi_i^{(1)} \rangle}{E_i^{(0)} - E_n^{(0)}} + [E_i^{(1)}]^2 \frac{\langle n | \mathcal{V} | i \rangle}{[E_i^{(0)} - E_n^{(0)}]^2} - E_i^{(2)} \frac{\langle n | \mathcal{V} | i \rangle}{E_i^{(0)} - E_n^{(0)}} \quad (6.2.4)
\end{aligned}$$

$$\begin{aligned}
E_i^{(4)} &= \langle i | \mathcal{V} | \Psi_i^{(3)} \rangle \\
&= \sum_{n \neq i} \frac{\langle i | \mathcal{V} | n \rangle}{E_i^{(0)} - E_n^{(0)}} \left\{ \langle n | \mathcal{V} | \Psi_i^{(2)} \rangle - E_i^{(1)} \frac{\langle n | \mathcal{V} | \Psi_i^{(1)} \rangle}{E_i^{(0)} - E_n^{(0)}} + [E_i^{(1)}]^2 \frac{\langle n | \mathcal{V} | i \rangle}{[E_i^{(0)} - E_n^{(0)}]^2} - E_i^{(2)} \frac{\langle n | \mathcal{V} | i \rangle}{E_i^{(0)} - E_n^{(0)}} \right\} \\
&= \sum_{n \neq i} \frac{\langle i | \mathcal{V} | n \rangle}{E_i^{(0)} - E_n^{(0)}} \langle n | \mathcal{V} | \Psi_i^{(2)} \rangle - E_i^{(1)} \sum_{n \neq i} \frac{\langle i | \mathcal{V} | n \rangle}{[E_i^{(0)} - E_n^{(0)}]^2} \langle n | \mathcal{V} | \Psi_i^{(1)} \rangle \\
&\quad + [E_i^{(1)}]^2 \sum_{n \neq i} \frac{V_{in} V_{ni}}{[E_i^{(0)} - E_n^{(0)}]^3} - E_i^{(2)} \sum_{n \neq i} \frac{V_{in} V_{ni}}{[E_i^{(0)} - E_n^{(0)}]^2} \\
&= \sum_{n, m \neq i} \frac{\langle i | \mathcal{V} | n \rangle}{E_i^{(0)} - E_n^{(0)}} \langle n | \mathcal{V} | m \rangle \langle m | \Psi_i^{(2)} \rangle - E_i^{(1)} \sum_{n, m \neq i} \frac{\langle i | \mathcal{V} | n \rangle \langle n | \mathcal{V} | m \rangle \langle m | \mathcal{V} | i \rangle}{[E_i^{(0)} - E_n^{(0)}]^2 [E_i^{(0)} - E_m^{(0)}]} \\
&\quad + [E_i^{(1)}]^2 \sum_{n \neq i} \frac{V_{in} V_{ni}}{[E_i^{(0)} - E_n^{(0)}]^3} - E_i^{(2)} \sum_{n \neq i} \frac{V_{in} V_{ni}}{[E_i^{(0)} - E_n^{(0)}]^2} \\
&= \sum_{n, m \neq i} \frac{V_{in} V_{nm}}{E_i^{(0)} - E_n^{(0)}} \frac{\langle m | \mathcal{V} | \Psi_i^{(1)} \rangle - E_i^{(1)} \langle m | \Psi_i^{(1)} \rangle}{E_i^{(0)} - E_m^{(0)}} - E_i^{(1)} \sum_{n, m \neq i} \frac{V_{in} V_{nm} V_{mi}}{[E_i^{(0)} - E_n^{(0)}]^2 [E_i^{(0)} - E_m^{(0)}]} \\
&\quad + [E_i^{(1)}]^2 \sum_{n \neq i} \frac{V_{in} V_{ni}}{[E_i^{(0)} - E_n^{(0)}]^3} - E_i^{(2)} \sum_{n \neq i} \frac{V_{in} V_{ni}}{[E_i^{(0)} - E_n^{(0)}]^2} \\
&= \sum_{n, m, k \neq i} \frac{V_{in} V_{nm}}{E_i^{(0)} - E_n^{(0)}} \frac{\langle m | \mathcal{V} | k \rangle \langle k | \mathcal{V} | i \rangle}{[E_i^{(0)} - E_m^{(0)}] [E_i^{(0)} - E_k^{(0)}]} - E_i^{(1)} \sum_{n, m \neq i} \frac{V_{in} V_{nm}}{E_i^{(0)} - E_n^{(0)}} \frac{\langle m | \mathcal{V} | i \rangle}{[E_i^{(0)} - E_m^{(0)}]^2} \\
&\quad - E_i^{(1)} \sum_{n, m \neq i} \frac{V_{in} V_{nm} V_{mi}}{[E_i^{(0)} - E_n^{(0)}]^2 [E_i^{(0)} - E_m^{(0)}]} + [E_i^{(1)}]^2 \sum_{n \neq i} \frac{V_{in} V_{ni}}{[E_i^{(0)} - E_n^{(0)}]^3} - E_i^{(2)} \sum_{n \neq i} \frac{V_{in} V_{ni}}{[E_i^{(0)} - E_n^{(0)}]^2} \\
&= \sum_{n, m, k \neq i} \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)}]} - 2V_{ii} \sum_{n, m \neq i} \frac{V_{in} V_{nm} V_{mi}}{[E_i^{(0)} - E_n^{(0)}] [E_i^{(0)} - E_m^{(0)}]^2} \\
&\quad + V_{ii}^2 \sum_{n \neq i} \frac{V_{in} V_{ni}}{[E_i^{(0)} - E_n^{(0)}]^3} - \sum_{m \neq i} \frac{V_{mi} V_{im}}{[E_i^{(0)} - E_m^{(0)}]} \sum_{n \neq i} \frac{V_{in} V_{ni}}{[E_i^{(0)} - E_n^{(0)}]^2} \tag{6.2.5}
\end{aligned}$$

which agrees with diagrammatic results above.

### 6.2.3 Summation of Diagrams

## 6.3 Orbital Perturbation Theory: One-Particle Perturbations

**Ex 6.3** Since  $n \neq 0$  and  $v(i)$  is one-particle operator,  $n$  must be single-excited, i.e.  $|\Psi_a^r\rangle$ . Thus,

$$\begin{aligned}
E_0^{(2)} &= \sum_{a,r} \frac{|\langle \Psi_0 | \sum_i v(i) | \Psi_a^r \rangle|^2}{\langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle - \langle \Psi_a^r | \mathcal{H} | \Psi_a^r \rangle} \\
&= \sum_{a,r} \frac{v_{ar} v_{ra}}{\sum_b \varepsilon_b^{(0)} - (\sum_{b \neq a} \varepsilon_b^{(0)} + \varepsilon_r^{(0)})} \\
&= \sum_{a,r} \frac{v_{ar} v_{ra}}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}} \tag{6.3.1}
\end{aligned}$$

**Ex 6.4** Eq 6.15 in textbook gives

$$\begin{aligned}
E_i^{(3)} &= \sum_{n, m \neq i} \frac{\langle i | \mathcal{V} | n \rangle \langle n | \mathcal{V} | m \rangle \langle m | \mathcal{V} | i \rangle}{(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})} - E_i^{(1)} \sum_{n \neq i} \frac{|\langle i | \mathcal{V} | n \rangle|^2}{(E_i^{(0)} - E_n^{(0)})^2} \\
&= A_i^{(3)} + B_i^{(3)} \tag{6.3.2}
\end{aligned}$$

a.

$$\begin{aligned}
B_0^{(3)} &= -E_0^{(1)} \sum_{n \neq 0} \frac{|\langle \Psi_0 | \mathcal{V} | n \rangle|^2}{(E_0^{(0)} - E_n^{(0)})^2} \\
&= -\sum_b v_{bb} \sum_{a,r} \frac{v_{ar} v_{ra}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2} \\
&= -\sum_{a,b,r} \frac{v_{aa} v_{br} v_{rb}}{(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})^2}
\end{aligned} \tag{6.3.3}$$

b.

$$\begin{aligned}
A_0^{(3)} &= \sum_{n,m \neq 0} \frac{\langle \Psi_0 | \mathcal{V} | n \rangle \langle n | \mathcal{V} | m \rangle \langle m | \mathcal{V} | \Psi_0 \rangle}{(E_0^{(0)} - E_n^{(0)})(E_0^{(0)} - E_m^{(0)})} \\
&= \sum_{a,r,b,s} \frac{\langle \Psi_0 | \mathcal{V} | \Psi_a^r \rangle \langle \Psi_a^r | \mathcal{V} | \Psi_b^s \rangle \langle \Psi_b^s | \mathcal{V} | \Psi_0 \rangle}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_s^{(0)})} \\
&= \sum_{a,r,b,s} \frac{v_{ar} v_{sb} \langle \Psi_a^r | \mathcal{V} | \Psi_b^s \rangle}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_s^{(0)})}
\end{aligned} \tag{6.3.4}$$

c. Clearly, if  $a \neq b, r \neq s$

$$\langle \Psi_a^r | \mathcal{V} | \Psi_b^s \rangle = 0 \tag{6.3.5}$$

If  $a = b, r \neq s$ ,

$$\begin{aligned}
\langle \Psi_a^r | \mathcal{V} | \Psi_b^s \rangle &= \langle r | v | s \rangle \\
&= v_{rs}
\end{aligned} \tag{6.3.6}$$

If  $a \neq b, r = s$ ,

$$\begin{aligned}
\langle \Psi_a^r | \mathcal{V} | \Psi_b^s \rangle &= \langle \Psi_a^r | \mathcal{V} | \Psi_b^r \rangle \\
&= \langle \Psi_a^r | \mathcal{V} | -\Psi_{ab}^r \rangle \\
&= -\langle b | v | a \rangle \\
&= -v_{ba}
\end{aligned} \tag{6.3.7}$$

If  $a = b, r = s$ ,

$$\begin{aligned}
\langle \Psi_a^r | \mathcal{V} | \Psi_b^s \rangle &= \langle \Psi_a^r | \mathcal{V} | \Psi_a^r \rangle \\
&= \sum_c v_{cc} - v_{aa} + v_{rr}
\end{aligned} \tag{6.3.8}$$

d.

$$\begin{aligned}
E_0^{(3)} &= A_0^{(3)} + B_0^{(3)} \\
&= \sum_{a,r,b,s} \frac{v_{ar} v_{sb} \langle \Psi_a^r | \mathcal{V} | \Psi_b^s \rangle}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_s^{(0)})} - \sum_{a,b,r} \frac{v_{aa} v_{br} v_{rb}}{(\varepsilon_b - \varepsilon_r)^2} \\
&= \sum_{a,r \neq s} \frac{v_{ar} v_{sa} v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} + \sum_{a \neq b, r} \frac{v_{ar} v_{rb} (-v_{ba})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})} \\
&\quad + \sum_{a,r} \frac{v_{ar} v_{ra} (\sum_c v_{cc} - v_{aa} + v_{rr})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2} - \sum_{a,b,r} \frac{v_{aa} v_{br} v_{rb}}{(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})^2} \\
&= \sum_{a,r \neq s} \frac{v_{ar} v_{sa} v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} + \sum_{a \neq b, r} \frac{v_{ar} v_{rb} (-v_{ba})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})} \\
&\quad + \sum_{a,r} \frac{v_{ar} v_{ra} (\sum_c v_{cc} - v_{aa} + v_{rr})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2} - \sum_{a,r} \frac{\sum_c v_{cc} v_{ar} v_{ra}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2}
\end{aligned}$$

$$\begin{aligned}
&= \sum_{a,r \neq s} \frac{v_{ar}v_{sa}v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} + \sum_{a \neq b,r} \frac{v_{ar}v_{rb}(-v_{ba})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})} + \sum_{a,r} \frac{v_{ar}v_{ra}(-v_{aa} + v_{rr})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2} \\
&= \sum_{a,r,s} \frac{v_{ar}v_{sa}v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} - \sum_{a,b,r} \frac{v_{ar}v_{rb}v_{ba}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})}
\end{aligned} \tag{6.3.9}$$

e. That's obvious.

**Ex 6.5** Since  $a, b$  run over all  $n$  occupied orbitals  $i, j$  and  $r$  runs over all  $n$  unoccupied orbitals  $k^*$ , we have

$$\begin{aligned}
-2 \sum_{a,b,r}^{N/2} \frac{v_{ra}v_{ab}v_{br}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})} &= -\frac{2}{(2\beta)^2} \sum_i^n \sum_j^n \sum_k^n \langle i | v | j \rangle \langle j | v | k^* \rangle \langle k^* | v | i \rangle \\
&= -\frac{2}{(2\beta)^2} \sum_i^3 \left[ \langle i | v | i+1 \rangle \langle i+1 | v | (i+2)^* \rangle \langle (i+2)^* | v | i \rangle \right. \\
&\quad \left. + \langle i | v | i+2 \rangle \langle i+2 | v | (i+1)^* \rangle \langle (i+1)^* | v | i \rangle \right] \\
&= -\frac{2}{(2\beta)^2} \sum_i^3 [(\beta/2)(\beta/2)(-\beta/2) + (\beta/2)(-\beta/2)(\beta/2)] \\
&= -\frac{2}{(2\beta)^2} \times 3 \times (-\beta^3/4) \\
&= 3\beta/8
\end{aligned} \tag{6.3.10}$$

**Ex 6.6**

a. Using the general expression, we get

$$\begin{aligned}
\mathcal{E}_0 &= 6\alpha - 2 \sum_{j=-1}^1 (\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos \frac{2j\pi}{3})^{1/2} \\
&= 6\alpha - 2(\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos \frac{-2\pi}{3})^{1/2} - 2(\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos 0)^{1/2} - 2(\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos \frac{2\pi}{3})^{1/2} \\
&= 6\alpha - 2(\beta_1^2 + \beta_2^2 - \beta_1\beta_2)^{1/2} - 2(\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2)^{1/2} - 2(\beta_1^2 + \beta_2^2 - \beta_1\beta_2)^{1/2} \\
&= 6\alpha - 2|\beta_1 + \beta_2| - 4(\beta_1^2 + \beta_2^2 - \beta_1\beta_2)^{1/2} \\
&= 6\alpha + 2(\beta_1 + \beta_2) - 4(\beta_1^2 + \beta_2^2 - \beta_1\beta_2)^{1/2}
\end{aligned} \tag{6.3.11}$$

Using Hückel matrix:

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta_1 & 0 & 0 & 0 & \beta_2 \\ \beta_1 & \alpha & \beta_2 & 0 & 0 & 0 \\ 0 & \beta_2 & \alpha & \beta_1 & 0 & 0 \\ 0 & 0 & \beta_1 & \alpha & \beta_2 & 0 \\ 0 & 0 & 0 & \beta_2 & \alpha & \beta_1 \\ \beta_2 & 0 & 0 & 0 & \beta_1 & \alpha \end{pmatrix} \tag{6.3.12}$$

Eigenvalues of  $\mathbf{H}$  are

$$\begin{aligned}
&\alpha + (\beta_1 + \beta_2), \\
&\alpha - \sqrt{\beta_1^2 + \beta_2^2 - \beta_1\beta_2} \quad (2\text{-fold}), \\
&\alpha + \sqrt{\beta_1^2 + \beta_2^2 - \beta_1\beta_2} \quad (2\text{-fold}), \\
&\alpha - (\beta_1 + \beta_2),
\end{aligned} \tag{6.3.13}$$

thus

$$\begin{aligned}
\mathcal{E}_0 &= 2[\alpha + (\beta_1 + \beta_2)] + 4 \left[ \alpha - \sqrt{\beta_1^2 + \beta_2^2 - \beta_1\beta_2} \right] \\
&= 6\alpha + 2(\beta_1 + \beta_2) - 4\sqrt{\beta_1^2 + \beta_2^2 - \beta_1\beta_2}
\end{aligned} \tag{6.3.14}$$

b.

$$\begin{aligned}
E_R &= \mathcal{E}_0 - (N\alpha + N\beta) \\
&= 6\alpha + 2(\beta_1 + \beta_2) - 4\sqrt{\beta_1^2 + \beta_2^2 - \beta_1\beta_2} - (6\alpha + 6\beta) \\
&= -4\beta_1 + 2\beta_2 - 4\sqrt{\beta_1^2 + \beta_2^2 - \beta_1\beta_2} \\
&= 4\beta \left( -1 + \frac{1}{2}x + \sqrt{1 + x^2 - x} \right)
\end{aligned} \tag{6.3.15}$$

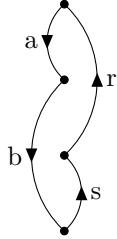
c.

$$\begin{aligned}
E_R &= 4\beta \left( -1 + \frac{1}{2}x + \sqrt{1 + x^2 - x} \right) \\
&= 4\beta \left[ -1 + \frac{1}{2}x + 1 + \frac{1}{2}(x^2 - x) - \frac{1}{8}(x^2 - x)^2 + \frac{1}{16}(x^2 - x)^3 - \frac{5}{128}(x^2 - x)^4 \right] \\
&= 4\beta \left[ \frac{1}{2}x^2 - \frac{1}{8}(x^4 + x^2 - 2x^3) + \frac{1}{16}(-x^3 + 3x^4) - \frac{5}{128}x^4 + \dots \right] \\
&= 4\beta \left[ \frac{3}{8}x^2 + \frac{3}{16}x^3 + \frac{3}{128}x^4 + \dots \right] \\
&= \beta \left[ \frac{3}{2}x^2 + \frac{3}{4}x^3 + \frac{3}{32}x^4 + \dots \right]
\end{aligned} \tag{6.3.16}$$

## 6.4 Diagrammatic Representation of Orbital Perturbation Theory

Ex 6.7

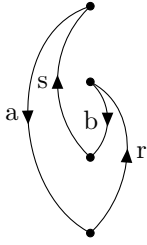
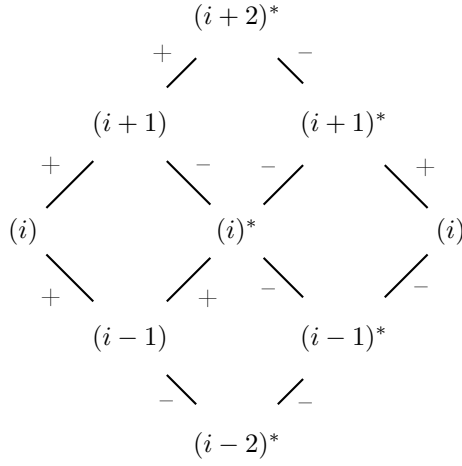
a.



$$\begin{aligned}
&= - \sum_{a,b,r,s} \frac{v_{ab}v_{bs}v_{sr}v_{ra}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_b^{(0)})} \\
&= - \frac{1}{(2\beta)^3} \sum_{i,j,k,l} \langle i | v | j \rangle \langle j | v | k^* \rangle \langle k^* | v | l^* \rangle \langle l^* | v | i \rangle \\
&= - \frac{2}{(2\beta)^3} \sum_i^{N/2} [-1 + 1 - 1 - 1 + 1 - 1] \times (\beta/2)^4 \\
&= \frac{N\beta}{64}
\end{aligned}$$

(6.4.1)

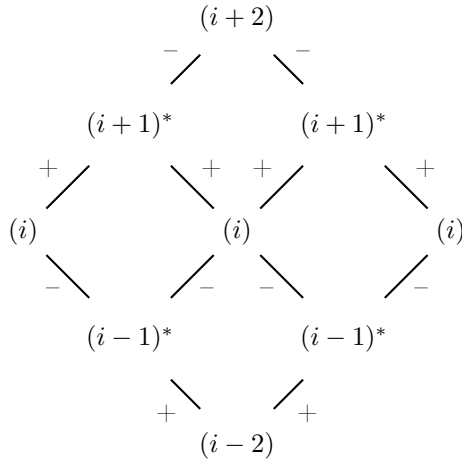
The pictorial representation of the summation are as follows



$$\begin{aligned}
&= - \sum_{a,r,b,s} \frac{v_{ar}v_{rb}v_{bs}v_{sa}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})(\varepsilon_a^{(0)} + \varepsilon_b^{(0)} - \varepsilon_r^{(0)} - \varepsilon_s^{(0)})} \\
&= - \frac{1}{(2\beta)^2 \times 4\beta} \sum_{i,j,k,l} \langle i | v | j^* \rangle \langle j^* | v | k \rangle \langle k | v | l^* \rangle \langle l^* | v | i \rangle \\
&= - \frac{2}{(2\beta)^2 \times 4\beta} \sum_i^{N/2} 6 \times (\beta/2)^4 \\
&= - \frac{3N\beta}{128}
\end{aligned}$$

(6.4.2)

The pictorial representation of the summation are as follows



thus

$$E_0^{(4)} = 4 \times \frac{N\beta}{64} + 3 \times \left( -\frac{3N\beta}{128} \right) = \frac{N\beta}{64} \quad (6.4.3)$$

**b.** Let  $N = 6$ , we get

$$E_0^{(4)} = \frac{3\beta}{32} \quad (6.4.4)$$



which agrees with the result in Ex 6.6.

## 6.5 Perturbation Expansion of the Correlation Energy

### Ex 6.8

$$\begin{aligned}
E_0^{(2)} &= \frac{1}{4} \sum_{a,b,r,s} \frac{|\langle ab || rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= \frac{1}{4} \sum_{a,b,r,s} \frac{(\langle ab | rs \rangle - \langle ab | sr \rangle)(\langle rs | ab \rangle - \langle sr | ab \rangle)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= \frac{1}{4} \sum_{a,b,r,s} \frac{\langle ab | rs \rangle \langle rs | ab \rangle - \langle ab | sr \rangle \langle rs | ab \rangle - \langle ab | rs \rangle \langle sr | ab \rangle + \langle ab | sr \rangle \langle sr | ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= \frac{1}{4} \left[ \sum_{a,b,r,s} \frac{\langle ab | rs \rangle \langle rs | ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \sum_{a,b,r,s} \frac{\langle ab | sr \rangle \langle rs | ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \sum_{a,b,r,s} \frac{\langle ab | rs \rangle \langle sr | ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} + \sum_{a,b,r,s} \frac{\langle ab | sr \rangle \langle sr | ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \right] \\
&= \frac{1}{4} \left[ 2 \sum_{a,b,r,s} \frac{\langle ab | rs \rangle \langle rs | ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - 2 \sum_{a,b,r,s} \frac{\langle ab | rs \rangle \langle sr | ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \right] \\
&= \frac{1}{2} \sum_{a,b,r,s} \frac{\langle ab | rs \rangle \langle rs | ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \frac{1}{2} \sum_{a,b,r,s} \frac{\langle ab | rs \rangle \langle rs | ba \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \tag{6.5.1}
\end{aligned}$$

For a closed-shell system, the possible spin part of  $a, b, r, s$  of the non-zero terms are

first term:  $\alpha, \alpha, \alpha, \alpha$ ;  $\alpha, \beta, \alpha, \beta$ ;  $\beta, \alpha, \beta, \alpha$ ;  $\beta, \beta, \beta, \beta$

second term:  $\alpha, \alpha, \alpha, \alpha$ ;  $\beta, \beta, \beta, \beta$

thus

$$E_0^{(2)} = 2 \sum_{a,b,r,s} \frac{\langle ab | rs \rangle \langle rs | ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \sum_{a,b,r,s} \frac{\langle ab | rs \rangle \langle rs | ba \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \tag{6.5.2}$$

### Ex 6.9

$$\begin{aligned}
E_{\text{corr}} &= \Delta - (\Delta^2 + K_{12}^2)^{1/2} \\
&= \Delta - \left[ \Delta + \frac{K_{12}^2}{2\Delta} \right] \\
&= -\frac{K_{12}^2}{2\Delta} \\
&= -\frac{K_{12}^2}{2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12}} \\
&= -K_{12}^2 \left( \frac{1}{2(\varepsilon_2 - \varepsilon_1)} - \frac{J_{11} + J_{22} - 4J_{12} + 2K_{12}}{4(\varepsilon_2 - \varepsilon_1)^2} \right) \\
&= \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)} + \frac{K_{12}^2(J_{11} + J_{22} - 4J_{12} + 2K_{12})}{4(\varepsilon_1 - \varepsilon_2)^2} \tag{6.5.3}
\end{aligned}$$

## 6.6 The $N$ -dependence of the RS Perturbation Expansion

**Ex 6.10** From Eq 6.68, we get

$$\begin{aligned}
E_0^{(1)} &= \langle \Psi_0 | \mathcal{V} | \Psi_0 \rangle = -\frac{1}{2} \sum_{ab} \langle ab || ab \rangle \\
&= -\frac{1}{2} \sum_{i=1}^N [\langle 1_i \bar{1}_i || 1_i \bar{1}_i \rangle + \langle \bar{1}_i 1_i || \bar{1}_i 1_i \rangle] \\
&= -\frac{1}{2} \sum_{i=1}^N [\langle 1_i \bar{1}_i | 1_i \bar{1}_i \rangle - \langle 1_i \bar{1}_i | \bar{1}_i 1_i \rangle + \langle \bar{1}_i 1_i | \bar{1}_i 1_i \rangle - \langle \bar{1}_i 1_i | 1_i \bar{1}_i \rangle]
\end{aligned}$$

$$\begin{aligned}
&= -\frac{1}{2} \times 2N[1_i 1_i | 1_i 1_i] \\
&= -NJ_{11}
\end{aligned} \tag{6.6.1}$$

$$\begin{aligned}
\langle \Psi_{1_i 1_i}^{2_i \bar{2}_i} | \mathcal{V} | \Psi_{1_i 1_i}^{2_i \bar{2}_i} \rangle &= \langle \Psi_{1_i 1_i}^{2_i \bar{2}_i} | \mathcal{H} | \Psi_{1_i 1_i}^{2_i \bar{2}_i} \rangle - \langle \Psi_{1_i 1_i}^{2_i \bar{2}_i} | \mathcal{H}_0 | \Psi_{1_i 1_i}^{2_i \bar{2}_i} \rangle \\
&= (2N-2)h_{11} + 2h_{22} + (N-1)J_{11} + J_{22} - (2N-2)\varepsilon_1 - 2\varepsilon_2 \\
&= (2N-2)h_{11} + 2h_{22} + (N-1)J_{11} + J_{22} - (2N-2)(h_{11} + J_{11}) - 2(h_{22} + 2J_{12} - K_{12}) \\
&= -(N-1)J_{11} + J_{22} - 4J_{12} + 2K_{12}
\end{aligned} \tag{6.6.2}$$

## 6.7 Diagrammatic Representation of the Perturbation Expansion of the Correlation Energy

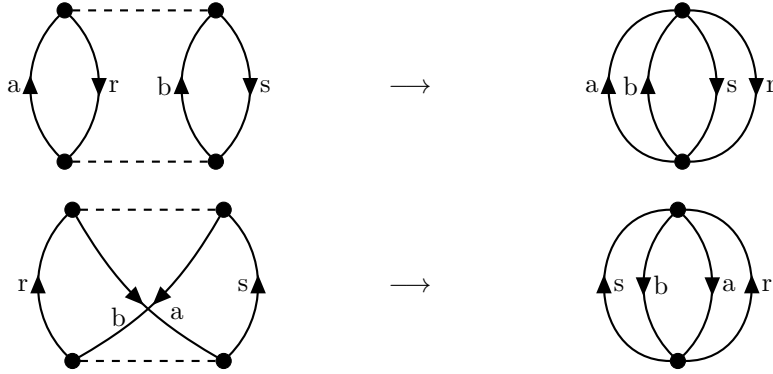
### 6.7.1 Hugenholtz Diagrams

**Ex 6.11** The numerator and denominator are obvious.

$h = 5$ , and  $l = 2$  since closed loops are  $r \rightarrow a \rightarrow d \rightarrow t \rightarrow e \rightarrow r$ ;  $s \rightarrow c \rightarrow b \rightarrow s$ . The number of equivalent line pairs is one  $(r, s)$ . Thus the pre-factor is  $-\frac{1}{2}$ .

### 6.7.2 Goldstone Diagrams

**Ex 6.12**



### 6.7.3 Summation of Diagrams

### 6.7.4 What Is the Linked-Cluster Theorem?

**Ex 6.13**

## 6.8 Some Illustrative Calculations