

Modern Quantum Chemistry, Szabo & Ostlund

HW

WSR

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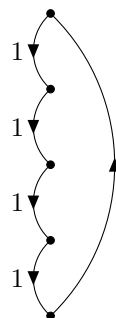
6 Many-body Perturbation Theory

6.1 RS Perturbation Theory

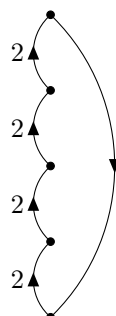
6.2 Diagrammatic Representation of RS Perturbation Theory

6.2.1 Diagrammatic Perturbation Theory for Two States

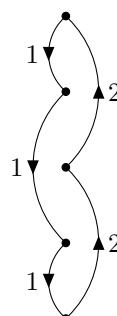
Ex 6.1



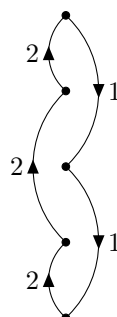
$$= (-1)^5 \frac{V_{12}V_{21}V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4} = -\frac{V_{12}V_{21}V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4}$$



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



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



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

Similarly,

$$\begin{aligned}
& \text{Top set of diagrams} = \frac{V_{12}V_{21}V_{11}^2V_{22}}{(E_1^{(0)} - E_2^{(0)})^4} \\
& \text{Bottom set of diagrams} = -\frac{V_{12}V_{21}V_{11}V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4}
\end{aligned}$$

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

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

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

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

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

Ex 6.4 Eq 6.15 in textbook gives

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

a.

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

b.

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

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

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

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

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

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

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

If $a = b, r = s$,

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

d.

$$\begin{aligned}
E_0^{(3)} &= A_0^{(3)} + B_0^{(3)} \\
&= \sum_{a,r,b,s} \frac{v_{ar}v_{sb} \langle \Psi_a^r | \mathcal{V} | \Psi_b^s \rangle}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_s^{(0)})} - \sum_{a,b,r} \frac{v_{aa}v_{br}v_{rb}}{(\varepsilon_b - \varepsilon_r)^2} \\
&= \sum_{a,r \neq s} \frac{v_{ar}v_{sa}v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} + \sum_{a \neq b,r} \frac{v_{ar}v_{rb}(-v_{ba})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})} \\
&\quad + \sum_{a,r} \frac{v_{ar}v_{ra}(\sum_c v_{cc} - v_{aa} + v_{rr})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2} - \sum_{a,b,r} \frac{v_{aa}v_{br}v_{rb}}{(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})^2} \\
&= \sum_{a,r \neq s} \frac{v_{ar}v_{sa}v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} + \sum_{a \neq b,r} \frac{v_{ar}v_{rb}(-v_{ba})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})} \\
&\quad + \sum_{a,r} \frac{v_{ar}v_{ra}(\sum_c v_{cc} - v_{aa} + v_{rr})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2} - \sum_{a,r} \frac{\sum_c v_{cc}v_{ar}v_{ra}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2} \\
&= \sum_{a,r \neq s} \frac{v_{ar}v_{sa}v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} + \sum_{a \neq b,r} \frac{v_{ar}v_{rb}(-v_{ba})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})} + \sum_{a,r} \frac{v_{ar}v_{ra}(-v_{aa} + v_{rr})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2} \\
&= \sum_{a,r,s} \frac{v_{ar}v_{sa}v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} - \sum_{a,b,r} \frac{v_{ar}v_{rb}v_{ba}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})} \tag{6.3.9}
\end{aligned}$$

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

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

Ex 6.6

a. Using the general expression, we get

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

Using Hückel matrix:

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

Eigenvalues of \mathbf{H} are

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

thus

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

b.

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

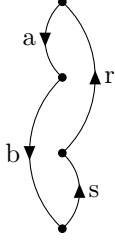
c.

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

6.4 Diagrammatic Representation of Orbital Perturbation Theory

Ex 6.7

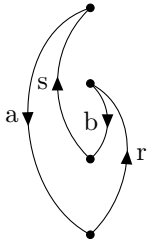
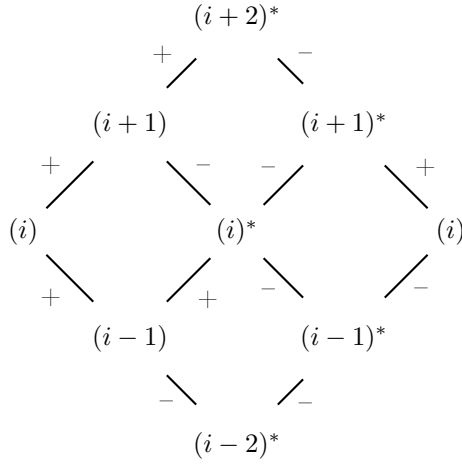
a.



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

(6.4.1)

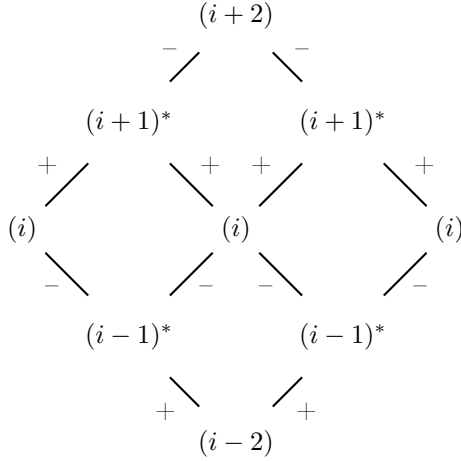
The pictorial representation of the summation are as follows



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

(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

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

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

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

Ex 6.9

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

6.6 The N -dependence of the RS Perturbation Expansion

Ex 6.10 From Eq 6.68, we get

$$\begin{aligned}
E_0^{(1)} &= \langle \Psi_0 | \mathcal{V} | \Psi_0 \rangle = -\frac{1}{2} \sum_{ab} \langle ab | ab \rangle \\
&= -\frac{1}{2} \sum_{i=1}^N [\langle 1_i \bar{1}_i | 1_i \bar{1}_i \rangle + \langle \bar{1}_i 1_i | \bar{1}_i 1_i \rangle] \\
&= -\frac{1}{2} \sum_{i=1}^N [\langle 1_i \bar{1}_i | 1_i \bar{1}_i \rangle - \langle 1_i \bar{1}_i | \bar{1}_i 1_i \rangle + \langle \bar{1}_i 1_i | \bar{1}_i 1_i \rangle - \langle \bar{1}_i 1_i | 1_i \bar{1}_i \rangle] \\
&= -\frac{1}{2} \times 2N [1_i 1_i | 1_i 1_i] \\
&= -NJ_{11}
\end{aligned} \tag{6.6.1}$$

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

6.7 Diagrammatic Representation of the Perturbation Expansion of the Correlation Energy

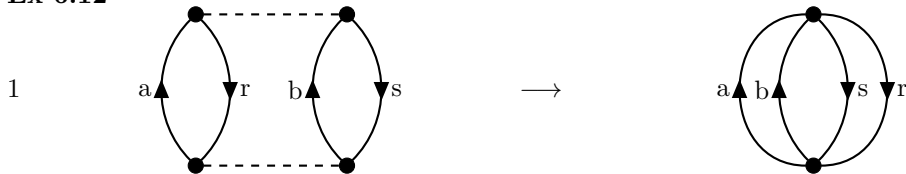
6.7.1 Hugenholtz Diagrams

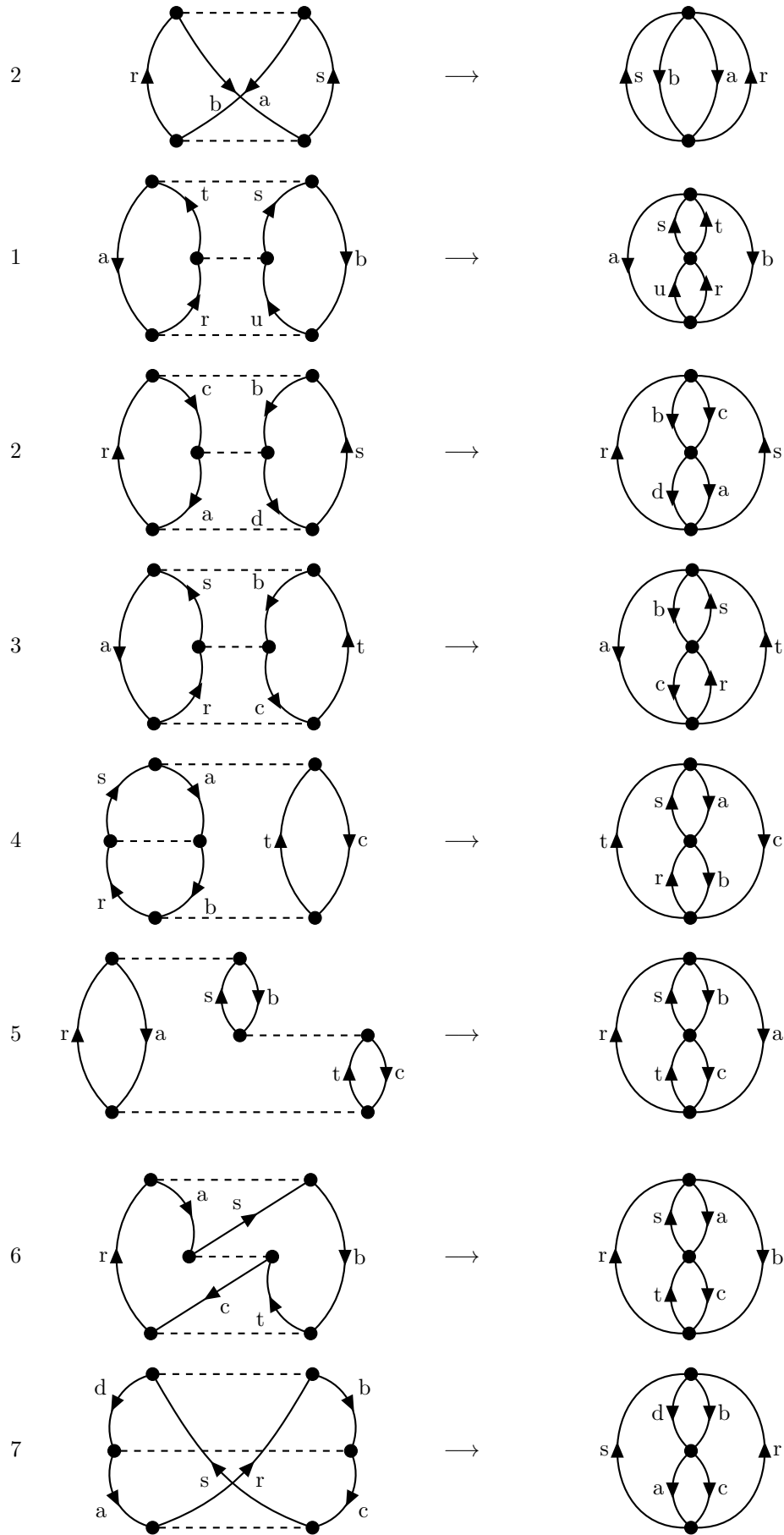
Ex 6.11 The numerator and denominator are obvious.

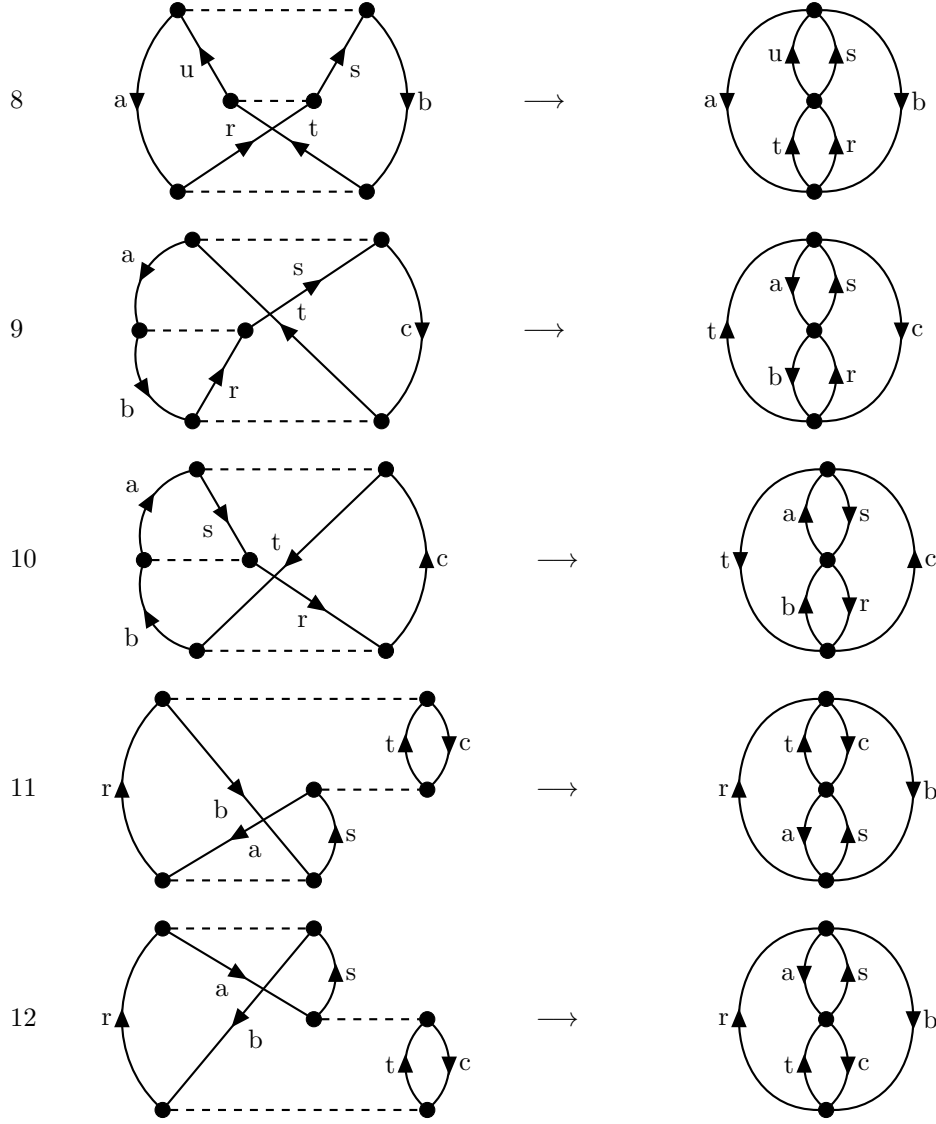
$h = 5$, and $l = 2$ since closed loops are $r \rightarrow a \rightarrow d \rightarrow t \rightarrow e \rightarrow r$; $s \rightarrow c \rightarrow b \rightarrow s$. The number of equivalent line pairs is one (r, s) . Thus the pre-factor is $-\frac{1}{2}$.

6.7.2 Goldstone Diagrams

Ex 6.12



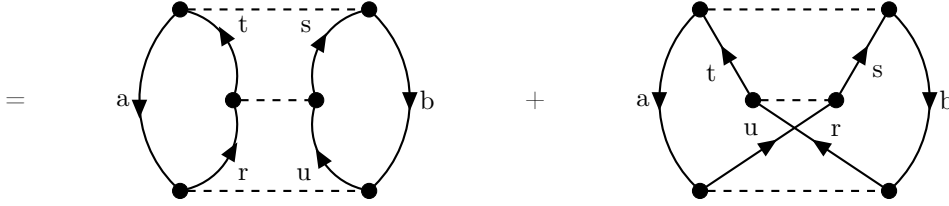




For the Hugenholtz diagram provided, its value is

$$\begin{aligned}
& \text{Diagram 8 (simplified)} = \left(\frac{1}{2}\right)^3 (-1)^{2+2} \sum_{a,b,r,s,u,t} \frac{\langle ab || ru \rangle \langle ru || ts \rangle \langle ts || ab \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} \\
& = \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab || ru \rangle \langle ru || ts \rangle \langle ts || ab \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} \\
& = \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{(\langle ab || ru \rangle - \langle ab || ur \rangle)(\langle ru || ts \rangle - \langle ru || st \rangle)(\langle ts || ab \rangle - \langle ts || ba \rangle)}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} \\
& = \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab || ru \rangle \langle ru || ts \rangle \langle ts || ab \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} - \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab || ur \rangle \langle ru || ts \rangle \langle ts || ab \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} \\
& \quad - \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab || ru \rangle \langle ru || st \rangle \langle ts || ab \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} + \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab || ur \rangle \langle ru || st \rangle \langle ts || ab \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} \\
& \quad - \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab || ru \rangle \langle ru || ts \rangle \langle ts || ba \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} + \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab || ur \rangle \langle ru || ts \rangle \langle ts || ba \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} \\
& \quad + \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab || ru \rangle \langle ru || st \rangle \langle ts || ba \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} - \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab || ur \rangle \langle ru || st \rangle \langle ts || ba \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)}
\end{aligned}$$

$$\begin{aligned}
&= \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab|ru\rangle \langle ru|ts\rangle \langle ts|ab\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} - \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab|ur\rangle \langle ru|ts\rangle \langle ts|ab\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} \\
&\quad - \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab|ur\rangle \langle ur|st\rangle \langle ts|ab\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_u)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} + \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab|ru\rangle \langle ur|st\rangle \langle ts|ab\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_u)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} \\
&\quad - \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab|ru\rangle \langle ru|ts\rangle \langle ts|ba\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} + \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab|ur\rangle \langle ru|ts\rangle \langle ts|ba\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} \\
&\quad + \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab|ur\rangle \langle ur|st\rangle \langle ts|ba\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_u)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} - \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab|ru\rangle \langle ur|st\rangle \langle ts|ba\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_u)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} \\
&= \frac{1}{4} \sum_{a,b,r,s,u,t} \frac{\langle ab|ru\rangle \langle ru|ts\rangle \langle ts|ab\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} - \frac{1}{4} \sum_{a,b,r,s,u,t} \frac{\langle ab|ur\rangle \langle ru|ts\rangle \langle ts|ab\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} \\
&\quad - \frac{1}{4} \sum_{a,b,r,s,u,t} \frac{\langle ab|ru\rangle \langle ru|ts\rangle \langle ts|ba\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} + \frac{1}{4} \sum_{a,b,r,s,u,t} \frac{\langle ab|ur\rangle \langle ru|ts\rangle \langle ts|ba\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} \\
&= \frac{1}{4} \sum_{a,b,r,s,u,t} \frac{\langle ab|ru\rangle \langle ru|ts\rangle \langle ts|ab\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} - \frac{1}{4} \sum_{a,b,r,s,u,t} \frac{\langle ab|ur\rangle \langle ru|ts\rangle \langle ts|ab\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} \\
&\quad - \frac{1}{4} \sum_{a,b,r,s,u,t} \frac{\langle ba|ru\rangle \langle ru|ts\rangle \langle ts|ab\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} + \frac{1}{4} \sum_{a,b,r,s,u,t} \frac{\langle ba|ur\rangle \langle ru|ts\rangle \langle ts|ab\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} \\
&= \frac{1}{2} \sum_{a,b,r,s,u,t} \frac{\langle ab|ru\rangle \langle ru|ts\rangle \langle ts|ab\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} - \frac{1}{2} \sum_{a,b,r,s,u,t} \frac{\langle ab|ur\rangle \langle ru|ts\rangle \langle ts|ab\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)} \tag{6.7.1}
\end{aligned}$$



6.7.3 Summation of Diagrams

6.7.4 What Is the Linked-Cluster Theorem?

Ex 6.13 For the 3rd-order Goldstone diagrams in Table 6.2,

$$\text{diagram1} = (-1)^4 \left(\frac{1}{2} \right) \sum_{ab} \sum_{rsut} \frac{\langle ab|ru\rangle \langle ru|ts\rangle \langle ts|ab\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_u)(\varepsilon_a + \varepsilon_b - \varepsilon_t - \varepsilon_s)} \tag{6.7.2}$$

a, b, r, s, u, t must come from 1 or 2 molecules. If they come from 2 molecules, $\langle ru|ts\rangle$ must be zero. Thus they only come from 1 molecule, i.e. the value of each Goldstone diagram is N times the result for a single molecule.

6.8 Some Illustrative Calculations