Modern Quantum Chemistry, Szabo & Ostlund HW

wsr

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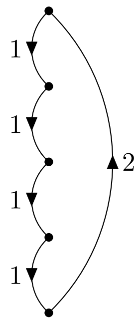
6 Many-body Perturbation Theory

6.1 RS Perturbation Theory

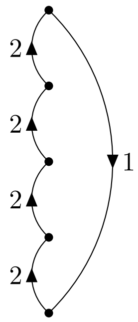
6.2 Diagrammatic Representation of RS Perturbation Theory

6.2.1 Diagrammatic Perturbation Theory for Two States

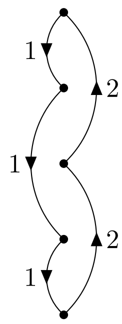
Ex 6.1



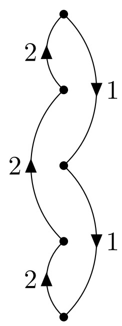
$$= (-1)^5 \frac{V_{12}V_{21}V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4} = -\frac{V_{12}V_{21}V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4}$$



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

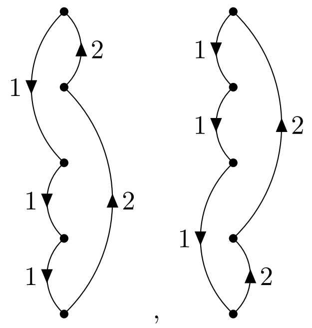


$$= (-1)^4 \frac{V_{12}V_{21}V_{11}^2 V_{22}}{(E_1^{(0)} - E_2^{(0)})^4} = \frac{V_{12}V_{21}V_{11}^2 V_{22}}{(E_1^{(0)} - E_2^{(0)})^4}$$

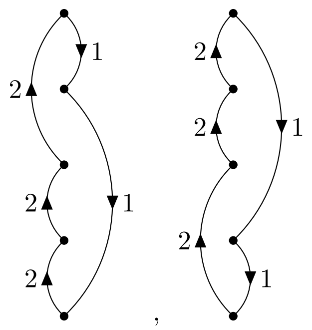


$$= (-1)^3 \frac{V_{12}V_{21}V_{11} V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4} = -\frac{V_{12}V_{21}V_{11} V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4}$$

Similarly,



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



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

thus, the sum of above terms is

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

6.2.2 Diagrammatic Perturbation Theory for N States

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

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

while

$$\left\langle n\middle|\mathscr{H}\middle|\Psi_i^{(3)}\right\rangle + \left\langle n\middle|\mathscr{V}\middle|\Psi_i^{(2)}\right\rangle = E_i^{(0)}\left\langle n\middle|\Psi_i^{(3)}\right\rangle + E_i^{(1)}\left\langle n\middle|\Psi_i^{(2)}\right\rangle + E_i^{(2)}\left\langle n\middle|\Psi_i^{(1)}\right\rangle \tag{6.2.3}$$

$$\begin{aligned}
(E_i^{(0)}-E_n^{(0)})\left\langle n\middle|\Psi_i^{(3)}\right\rangle &= \left\langle n\middle|\mathscr{V}\middle|\Psi_i^{(2)}\right\rangle - E_i^{(1)}\left\langle n\middle|\Psi_i^{(2)}\right\rangle - E_i^{(2)}\left\langle n\middle|\Psi_i^{(1)}\right\rangle\\
&= \left\langle n\middle|\mathscr{V}\middle|\Psi_i^{(2)}\right\rangle - E_i^{(1)}\frac{\left\langle n\middle|\mathscr{V}\middle|\Psi_i^{(1)}\right\rangle - E_i^{(1)}\left\langle n\middle|\Psi_i^{(1)}\right\rangle}{E_i^{(0)}-E_n^{(0)}} - E_i^{(2)}\left\langle n\middle|\Psi_i^{(1)}\right\rangle\\
&= \left\langle n\middle|\mathscr{V}\middle|\Psi_i^{(2)}\right\rangle - E_i^{(1)}\frac{\left\langle n\middle|\mathscr{V}\middle|\Psi_i^{(1)}\right\rangle}{E_i^{(0)}-E_n^{(0)}} + \left[E_i^{(1)}\right]^2\frac{\langle n\,|\,\mathscr{V}\,|\,i\rangle}{\left[E_i^{(0)}-E_n^{(0)}\right]^2} - E_i^{(2)}\frac{\langle n\,|\,\mathscr{V}\,|\,i\rangle}{E_i^{(0)}-E_n^{(0)}}
\end{aligned}\tag{6.2.4}$$

$$
\begin{aligned}
E_i^{(4)} &= \left\langle i \,\middle|\, \mathscr{V} \,\middle|\, \Psi_i^{(3)} \right\rangle \\
&= \sum_{n\neq i} \frac{\langle i \,|\, \mathscr{V} \,|\, n\rangle}{E_i^{(0)}-E_n^{(0)}} \left\{ \left\langle n \,\middle|\, \mathscr{V} \,\middle|\, \Psi_i^{(2)} \right\rangle - E_i^{(1)} \frac{\left\langle n \,\middle|\, \mathscr{V} \,\middle|\, \Psi_i^{(1)} \right\rangle}{E_i^{(0)}-E_n^{(0)}} + \left[E_i^{(1)}\right]^2 \frac{\langle n \,|\, \mathscr{V} \,|\, i\rangle}{\left[E_i^{(0)}-E_n^{(0)}\right]^2} - E_i^{(2)} \frac{\langle n \,|\, \mathscr{V} \,|\, i\rangle}{E_i^{(0)}-E_n^{(0)}} \right\} \\
&= \sum_{n\neq i} \frac{\langle i \,|\, \mathscr{V} \,|\, n\rangle}{E_i^{(0)}-E_n^{(0)}} \left\langle n \,\middle|\, \mathscr{V} \,\middle|\, \Psi_i^{(2)} \right\rangle - E_i^{(1)} \sum_{n\neq i} \frac{\langle i \,|\, \mathscr{V} \,|\, n\rangle}{\left[E_i^{(0)}-E_n^{(0)}\right]^2} \left\langle n \,\middle|\, \mathscr{V} \,\middle|\, \Psi_i^{(1)} \right\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 \,|\, \mathscr{V} \,|\, n\rangle}{E_i^{(0)}-E_n^{(0)}} \langle n \,|\, \mathscr{V} \,|\, m\rangle \left\langle m \,\middle|\, \Psi_i^{(2)} \right\rangle - E_i^{(1)} \sum_{n,m\neq i} \frac{\langle i \,|\, \mathscr{V} \,|\, n\rangle \langle n \,|\, \mathscr{V} \,|\, m\rangle \langle m \,|\, \mathscr{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{\left\langle m \,\middle|\, \mathscr{V} \,\middle|\, \Psi_i^{(1)} \right\rangle - E_i^{(1)} \left\langle m \,\middle|\, \Psi_i^{(1)} \right\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 \,|\, \mathscr{V} \,|\, k\rangle \langle k \,|\, \mathscr{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 \,|\, \mathscr{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}
\end{aligned} \tag{6.2.5}
$$

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,

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

Ex 6.4 Eq 6.15 in textbook gives

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

a.

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

b.

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

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

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

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

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

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

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

If $a = b, r = s$,

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

d.

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

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

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

Ex 6.6

a. Using the general expression, we get

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

Using Hückel matrix:

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

Eigenvalues of $\mathbf{H}$ are

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

thus

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

b.

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

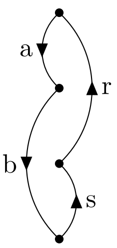
c.

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

6.4 Diagrammatic Representation of Orbital Perturbation Theory

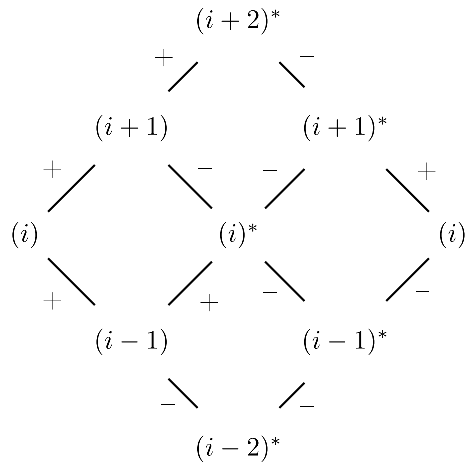
Ex 6.7

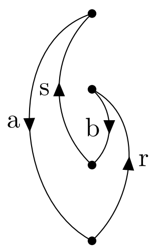
a.



$$
\begin{aligned}
&= -\sum_{a,b,r,s} \frac{v_{ab}v_{bs}v_{sr}v_{ra}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_b^{(0)})} \\
&= -\frac{1}{(2\beta)^3} \sum_{i,j,k,l} \langle i \,|\, v \,|\, j \rangle \, \langle j \,|\, v \,|\, k^* \rangle \, \langle k^* \,|\, v \,|\, l^* \rangle \, \langle l^* \,|\, v \,|\, i \rangle \\
&= -\frac{2}{(2\beta)^3} \sum_{i}^{N/2} [-1 + 1 - 1 - 1 + 1 - 1] \times (\beta/2)^4 \\
&= \frac{N\beta}{64}
\end{aligned}
\tag{6.4.1}
$$

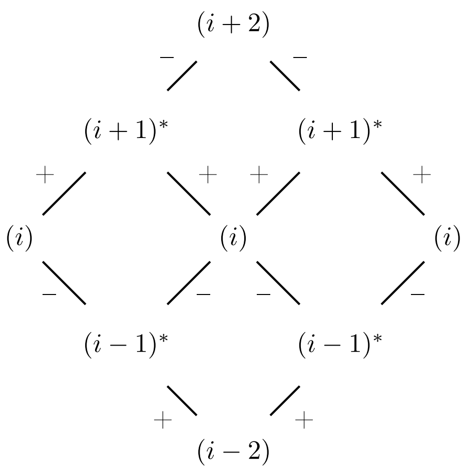
The pictorial representation of the summation are as follows





$$
\begin{aligned}
&= -\sum_{a,r,b,s} \frac{v_{ar}v_{rb}v_{bs}v_{sa}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})(\varepsilon_a^{(0)} + \varepsilon_b^{(0)} - \varepsilon_r^{(0)} - \varepsilon_s^{(0)})} \\
&= -\frac{1}{(2\beta)^2 \times 4\beta} \sum_{i,j,k,l} \langle i \,|\, v \,|\, j^* \rangle \, \langle j^* \,|\, v \,|\, k \rangle \, \langle k \,|\, v \,|\, l^* \rangle \, \langle l^* \,|\, v \,|\, i \rangle \\
&= -\frac{2}{(2\beta)^2 \times 4\beta} \sum_{i}^{N/2} 6 \times (\beta/2)^4 \\
&= -\frac{3N\beta}{128}
\end{aligned}
\tag{6.4.2}
$$

The pictorial representation of the summation are as follows



thus

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

b. Let $N = 6$, we get

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

which agrees with the result in Ex 6.6.

6.5 Perturbation Expansion of the Correlation Energy

Ex 6.8

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

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

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

Ex 6.9

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

6.6 The N-dependence of the RS Perturbation Expansion

Ex 6.10 From Eq 6.68, we get

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

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

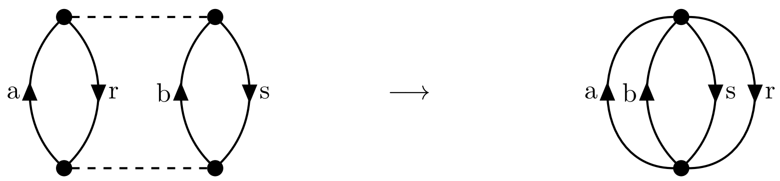
6.7 Diagrammatic Representation of the Perturbation Expansion of the Correlation Energy

6.7.1 Hugenholtz Diagrams

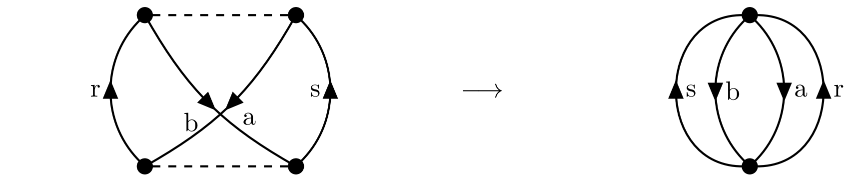
Ex 6.11 The numerator and denominator are obvious.
$h = 5$, and $l = 2$ since closed loops are $r \to a \to d \to t \to e \to r$; $s \to c \to b \to s$. The number of quivalent line pairs is one (r, s). Thus the pre-factor is $-\dfrac{1}{2}$.

6.7.2 Goldstone Diagrams

Ex 6.12

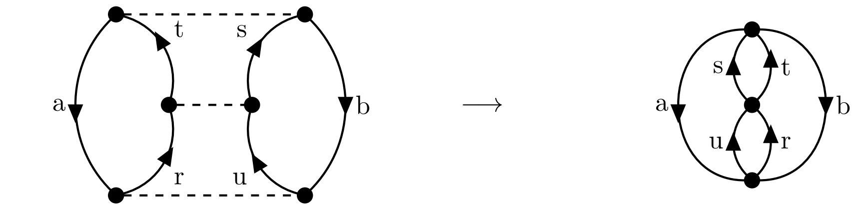
1 

2



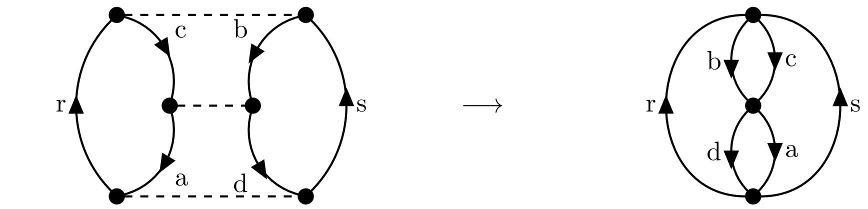
r
b
a
s
s
b
a
r

1



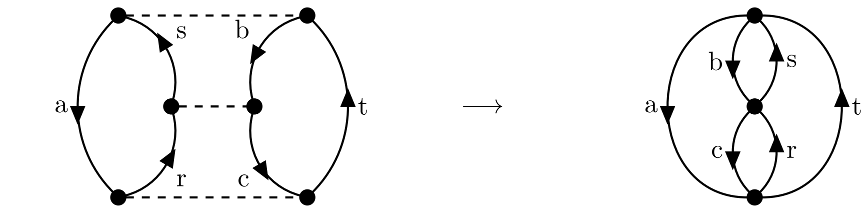
t
s
a
b
r
u
s
t
a
b
u
r

2



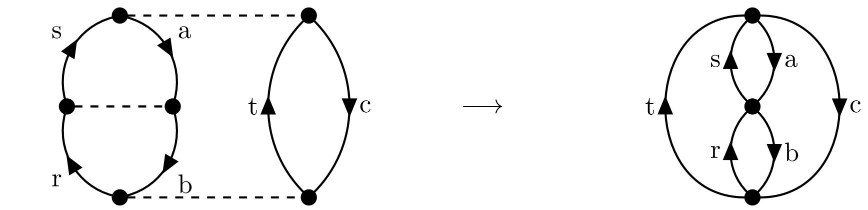
c
b
r
s
a
d
b
c
r
s
d
a

3



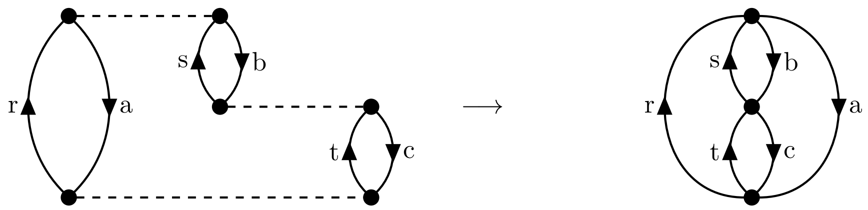
s
b
a
t
r
c
b
s
a
t
c
r

4



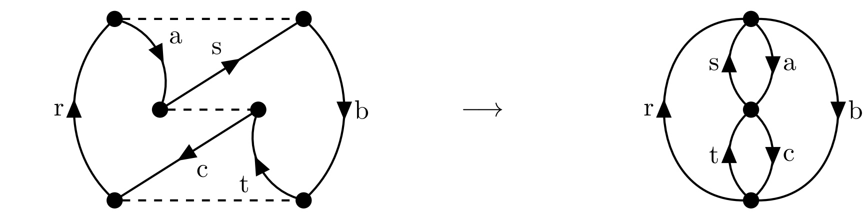
s
a
t
c
r
b
s
a
t
c
r
b

5



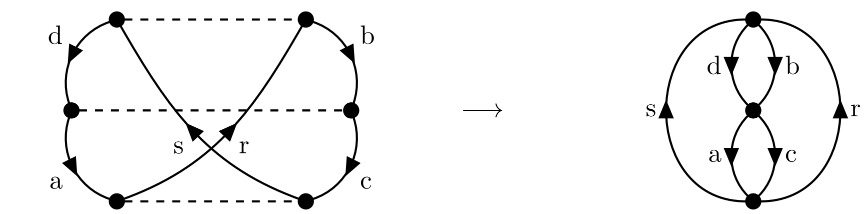
s
b
r
a
t
c
s
b
r
a
t
c

6

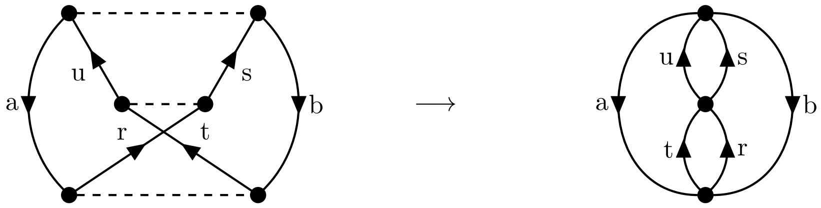


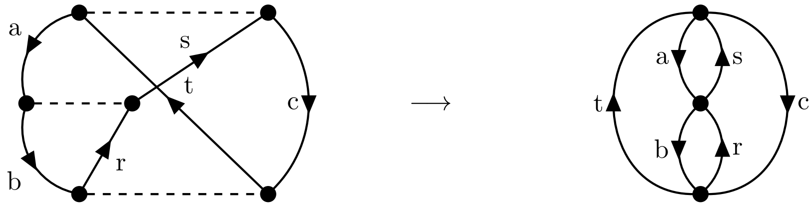
a
s
r
b
c
t
s
a
r
b
t
c

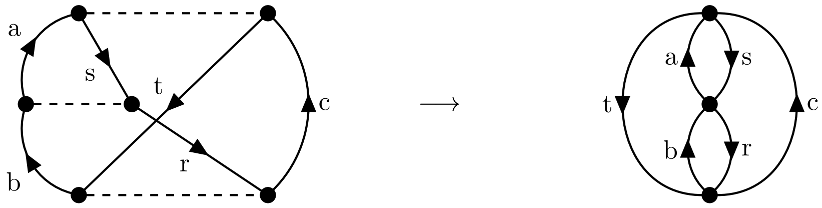
7

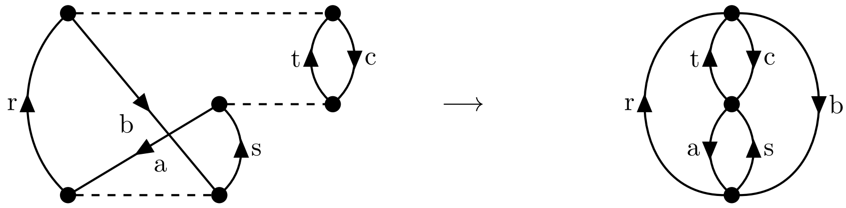


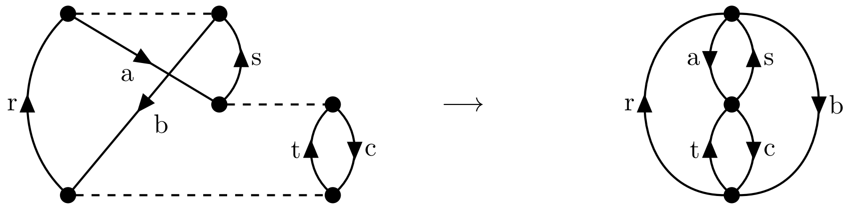
d
b
s
r
a
c
d
b
s
r
a
c

8 

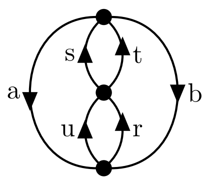
9 

10 

11 

12 

For the Hugenholtz diagram provided, its value is



$$= \left(\frac{1}{2}\right)^3 (-1)^{2+2} \sum_{a,b,r,s,u,t} \frac{\langle ab \,\|\, ru\rangle \langle ru \,\|\, ts\rangle \langle ts \,\|\, ab\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)}$$

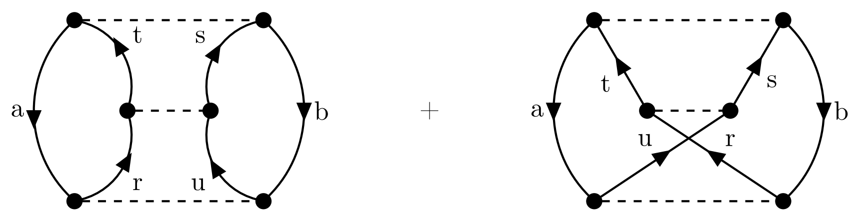
$$= \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{\langle ab \,\|\, ru\rangle \langle ru \,\|\, ts\rangle \langle ts \,\|\, ab\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)}$$

$$= \frac{1}{8} \sum_{a,b,r,s,u,t} \frac{(\langle ab \,|\, ru\rangle - \langle ab \,|\, ur\rangle)(\langle ru \,|\, ts\rangle - \langle ru \,|\, st\rangle)(\langle ts \,|\, ab\rangle - \langle ts \,|\, ba\rangle)}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)}$$

$$\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)} \\
&- \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)} \\
&- \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)} \\
&+ \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)}
\end{aligned}
\tag{6.7.1}
$$

$=$



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,

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

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