Modern Quantum Chemistry, Szabo & Ostlund HW

wsr

July 7, 2020

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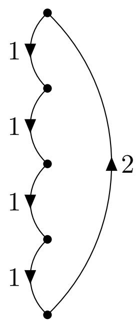
6 Many-body Perturbation Theory

6.1 RS Perturbation Theory

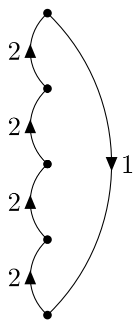
6.2 Diagrammatic Representation of RS Perturbation Theory

6.2.1 Diagrammatic Perturbation Theory for Two States

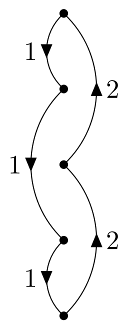
Ex 6.1



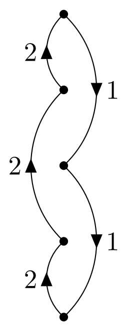
$$= (-1)^5 \frac{V_{12}V_{21}V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4} = -\frac{V_{12}V_{21}V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4}$$



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

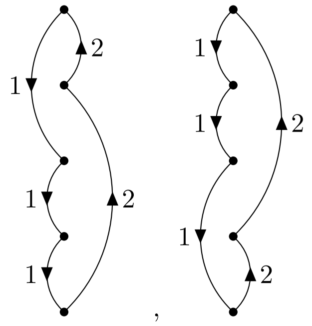


$$= (-1)^4 \frac{V_{12}V_{21}V_{11}^2V_{22}}{(E_1^{(0)} - E_2^{(0)})^4} = \frac{V_{12}V_{21}V_{11}^2V_{22}}{(E_1^{(0)} - E_2^{(0)})^4}$$

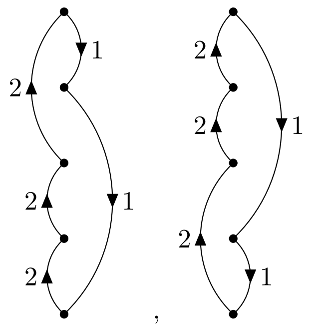


$$= (-1)^3 \frac{V_{12}V_{21}V_{11}V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4} = -\frac{V_{12}V_{21}V_{11}V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4}$$

Similarly,



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



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

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,

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

Ex 6.4 Eq 6.15 in textbook gives

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

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.

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

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

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:

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

Eigenvalues of $\mathbf{H}$ are

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

thus

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

b.

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

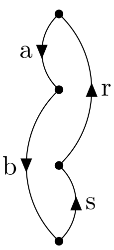
c.

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

6.4 Diagrammatic Representation of Orbital Perturbation Theory

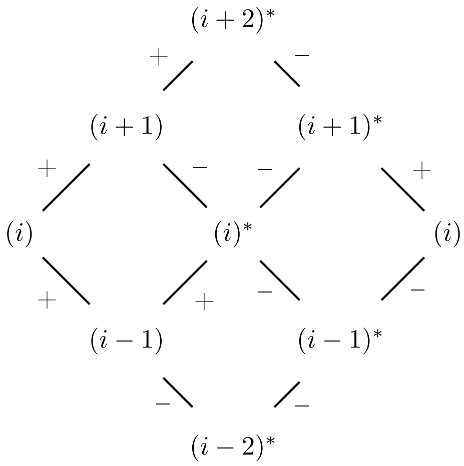
Ex 6.7

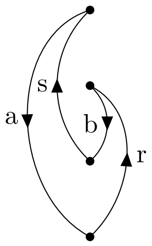
a.



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

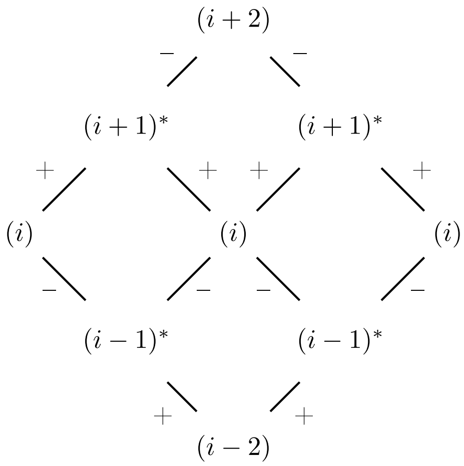
The pictorial representation of the summation are as follows thus





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

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

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

6.6 The N-dependence of the RS Perturbation Expansion

Ex 6.10 From Eq 6.68, we get

$$
\begin{aligned}
E_0^{(1)} = \langle\Psi_0\,|\,\mathscr{V}\,|\,\Psi_0\rangle &= -\frac{1}{2}\sum_{ab}\langle ab\,\|\,ab\rangle\\
&= -\frac{1}{2}\sum_{i=1}^{N}[\langle 1_i\bar{1}_i\,\|\,1_i\bar{1}_i\rangle+\langle\bar{1}_i1_i\,\|\,\bar{1}_i1_i\rangle]\\
&= -\frac{1}{2}\sum_{i=1}^{N}[\langle 1_i\bar{1}_i\,|\,1_i\bar{1}_i\rangle-\langle 1_i\bar{1}_i\,|\,\bar{1}_i1_i\rangle+\langle\bar{1}_i1_i\,|\,\bar{1}_i1_i\rangle-\langle\bar{1}_i1_i\,|\,1_i\bar{1}_i\rangle]
\end{aligned}
$$

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

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

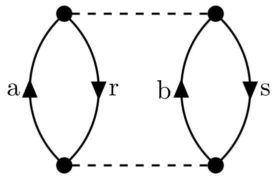
6.7 Diagrammatic Representation of the Perturbation Expansion of the Correlation Energy

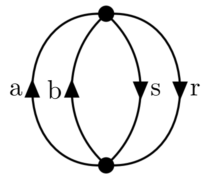
6.7.1 Hugenholtz Diagrams

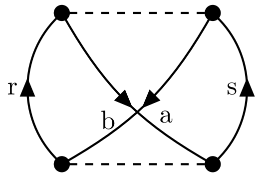
Ex 6.11 The numerator and denominator are obvious.
$h = 5$, and $l = 2$ since closed loops are $r \to a \to d \to t \to e \to r$; $s \to c \to b \to s$. The number of quivalent line pairs is one (r, s). Thus the pre-factor is $-\dfrac{1}{2}$.

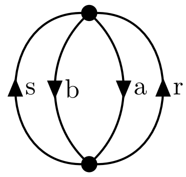
6.7.2 Goldstone Diagrams

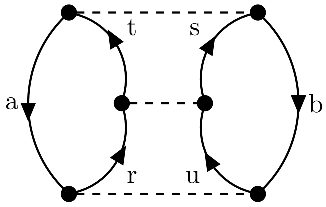
Ex 6.12

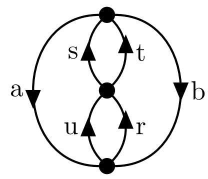
1 

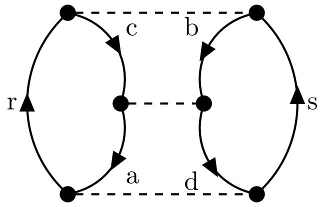
$\longrightarrow$ 

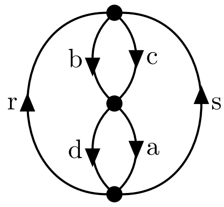
2 

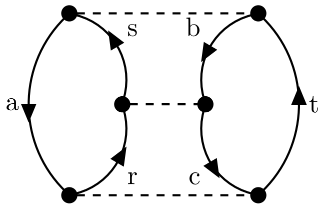
$\longrightarrow$ 

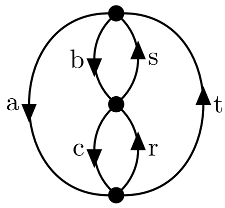
1 

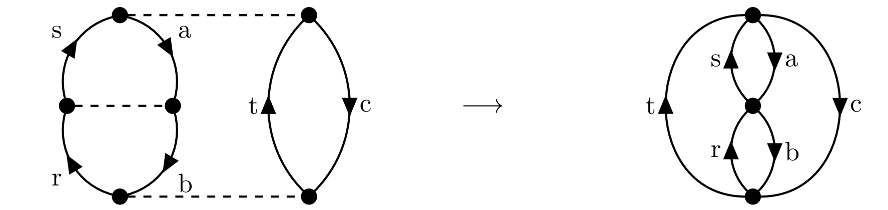
$\longrightarrow$ 

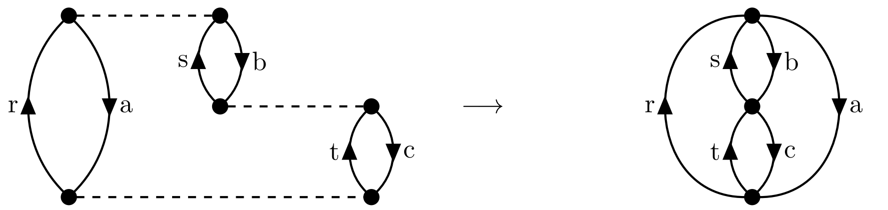
2 

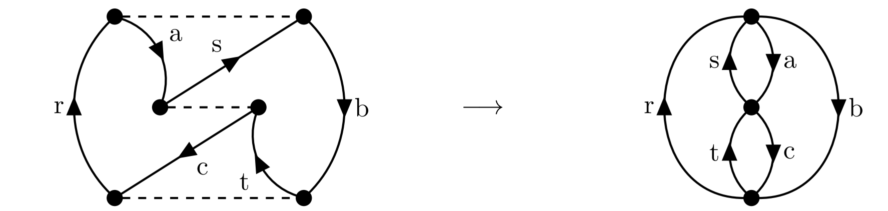
$\longrightarrow$ 

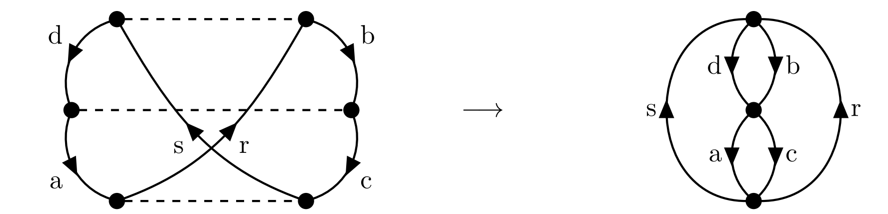
3 

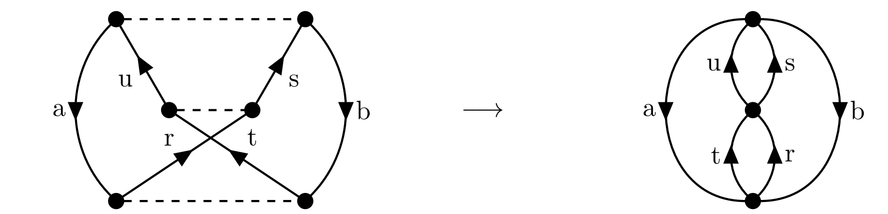
$\longrightarrow$ 

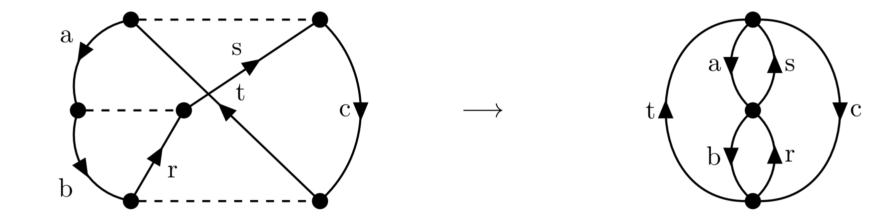
4 
s a r b t c ⟶ t s a r b c

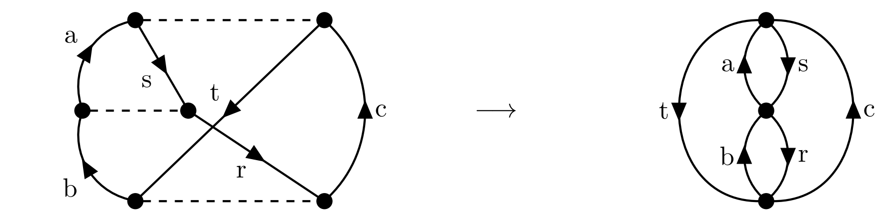
5 
r a s b t c ⟶ r s b t c a

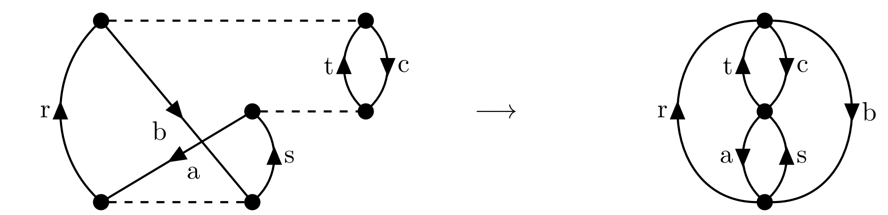
6 
a s r b c t ⟶ r s a t c b

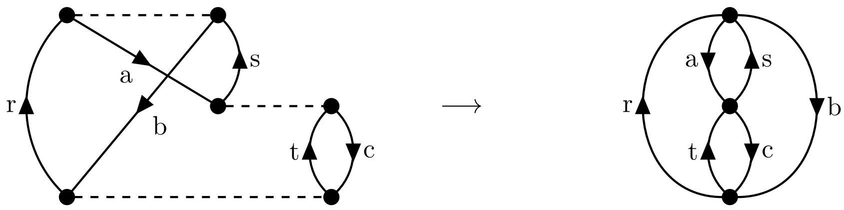
7 
d b s r a c ⟶ s d b a c r

8 
u s a b r t ⟶ a u s t r b

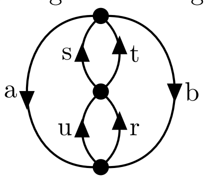
9 
a s t c r b ⟶ t a s b r c

10 
a s t c r b ⟶ t a s b r c

11 
t c r b a s ⟶ r t c a s b

12 

For the Hugenholtz diagram provided, its value is



$$= \left(\frac{1}{2}\right)^3 (-1)^{2+l} \sum \frac{\langle ab \parallel ru \rangle \langle ru \parallel ts \rangle \langle ts \parallel ab \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)}$$

6.7.3 Summation of Diagrams

6.7.4 What Is the Linked-Cluster Theorem?

Ex 6.13

6.8 Some Illustrative Calculations