Modern Quantum Chemistry, Szabo & Ostlund HW

wsr

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Contents

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,

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

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

thus, the sum of above terms is

$$\frac{V_{12}V_{21}(V_{22}^3 - V_{11}^3)}{(E_1^{(0)} - E_2^{(0)})^4} + 3 \times \frac{V_{12}V_{21}(V_{11}^2 V_{22} - V_{11}V_{22}^2)}{(E_1^{(0)} - E_2^{(0)})^4} = \frac{V_{12}V_{21}(V_{22} - V_{11})^3}{(E_1^{(0)} - E_2^{(0)})^4} \tag{6.2.1}$$
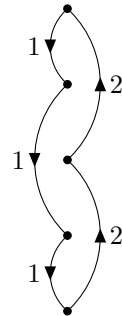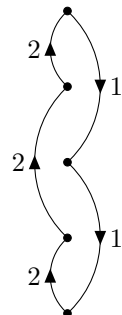
6.2.2 Diagrammatic Perturbation Theory for N States

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

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

$$- \sum_{m,n \neq i} \frac{V_{ii}V_{ni}V_{im}V_{mn}}{(E_i^{(0)} - E_m^{(0)})^2 (E_i^{(0)} - E_n^{(0)})} - \sum_{m,n \neq i} \frac{V_{mi}V_{im}V_{in}V_{ni}}{(E_i^{(0)} - E_m^{(0)})(E_i^{(0)} - E_n^{(0)})(2E_i^{(0)} - E_n^{(0)} - E_m^{(0)})}$$

$$- \sum_{m,n \neq i} \frac{V_{mi}V_{im}V_{in}V_{ni}}{(E_i^{(0)} - E_n^{(0)})^2 (2E_i^{(0)} - E_n^{(0)} - E_m^{(0)})}$$

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

$$- \sum_{m,n \neq i} \frac{V_{mi}V_{im}V_{in}V_{ni}}{(E_i^{(0)} - E_m^{(0)})(E_i^{(0)} - E_n^{(0)})^2} \tag{6.2.2}$$

while

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

$$(E_i^{(0)} - E_n^{(0)}) \left\langle n \left| \Psi_i^{(3)} \right\rangle = \left\langle n \left| \mathscr{V} \right| \Psi_i^{(2)} \right\rangle - E_i^{(1)} \left\langle n \left| \Psi_i^{(2)} \right\rangle - E_i^{(2)} \left\langle n \left| \Psi_i^{(1)} \right\rangle \right.$$

$$= \left\langle n \left| \mathscr{V} \right| \Psi_i^{(2)} \right\rangle - E_i^{(1)} \frac{\left\langle n \left| \mathscr{V} \right| \Psi_i^{(1)} \right\rangle - E_i^{(1)} \left\langle n \left| \Psi_i^{(1)} \right\rangle \right.}{E_i^{(0)} - E_n^{(0)}} - E_i^{(2)} \left\langle n \left| \Psi_i^{(1)} \right\rangle \right.$$

$$= \left\langle n \left| \mathscr{V} \right| \Psi_i^{(2)} \right\rangle - E_i^{(1)} \frac{\left\langle n \left| \mathscr{V} \right| \Psi_i^{(1)} \right\rangle}{E_i^{(0)} - E_n^{(0)}} + \left[E_i^{(1)} \right]^2 \frac{\left\langle n \left| \mathscr{V} \right| i \right\rangle}{\left[E_i^{(0)} - E_n^{(0)} \right]^2} - E_i^{(2)} \frac{\left\langle n \left| \mathscr{V} \right| i \right\rangle}{E_i^{(0)} - E_n^{(0)}}$$

$$\tag{6.2.4}$$

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$$E_i^{(4)} = \left\langle i \left| \mathscr{V} \right| \Psi_i^{(3)} \right\rangle$$

$$= \sum_{n \neq i} \frac{\langle i \, | \, \mathscr{V} \, | \, n \rangle}{E_i^{(0)} - E_n^{(0)}} \left\{ \left\langle n \left| \mathscr{V} \right| \Psi_i^{(2)} \right\rangle - E_i^{(1)} \frac{\left\langle n \left| \mathscr{V} \right| \Psi_i^{(1)} \right\rangle}{E_i^{(0)} - E_n^{(0)}} + \left[E_i^{(1)} \right]^2 \frac{\langle n \, | \, \mathscr{V} \, | \, i \rangle}{\left[E_i^{(0)} - E_n^{(0)} \right]^2} - E_i^{(2)} \frac{\langle n \, | \, \mathscr{V} \, | \, i \rangle}{E_i^{(0)} - E_n^{(0)}} \right\}$$

$$= \sum_{n \neq i} \frac{\langle i \, | \, \mathscr{V} \, | \, n \rangle}{E_i^{(0)} - E_n^{(0)}} \left\langle n \left| \mathscr{V} \right| \Psi_i^{(2)} \right\rangle - E_i^{(1)} \sum_{n \neq i} \frac{\langle i \, | \, \mathscr{V} \, | \, n \rangle}{\left[E_i^{(0)} - E_n^{(0)} \right]^2} \left\langle n \left| \mathscr{V} \right| \Psi_i^{(1)} \right\rangle$$

$$+ \left[E_i^{(1)} \right]^2 \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^3} - E_i^{(2)} \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^2}$$

$$= \sum_{n,m \neq i} \frac{\langle i \, | \, \mathscr{V} \, | \, n \rangle}{E_i^{(0)} - E_n^{(0)}} \langle n \, | \, \mathscr{V} \, | \, m \rangle \left\langle m \left| \Psi_i^{(2)} \right\rangle - E_i^{(1)} \sum_{n,m \neq i} \frac{\langle i \, | \, \mathscr{V} \, | \, n \rangle \langle n \, | \, \mathscr{V} \, | \, m \rangle \langle m \, | \, \mathscr{V} \, | \, i \rangle}{\left[E_i^{(0)} - E_n^{(0)} \right]^2 \left[E_i^{(0)} - E_m^{(0)} \right]} \right.$$

$$+ \left[E_i^{(1)} \right]^2 \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^3} - E_i^{(2)} \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^2}$$

$$= \sum_{n,m \neq i} \frac{V_{in} V_{nm}}{E_i^{(0)} - E_n^{(0)}} \frac{\left\langle m \left| \mathscr{V} \right| \Psi_i^{(1)} \right\rangle - E_i^{(1)} \left\langle m \left| \Psi_i^{(1)} \right\rangle}{E_i^{(0)} - E_m^{(0)}} - E_i^{(1)} \sum_{n,m \neq i} \frac{V_{in} V_{nm} V_{mi}}{\left[E_i^{(0)} - E_n^{(0)} \right]^2 \left[E_i^{(0)} - E_m^{(0)} \right]}$$

$$+ \left[E_i^{(1)} \right]^2 \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^3} - E_i^{(2)} \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^2}$$

$$= \sum_{n,m,k \neq i} \frac{V_{in} V_{nm}}{E_i^{(0)} - E_n^{(0)}} \frac{\langle m \, | \, \mathscr{V} \, | \, k \rangle \langle k \, | \, \mathscr{V} \, | \, i \rangle}{\left[E_i^{(0)} - E_m^{(0)} \right] \left[E_i^{(0)} - E_k^{(0)} \right]} - E_i^{(1)} \sum_{n,m \neq i} \frac{V_{in} V_{nm}}{E_i^{(0)} - E_n^{(0)}} \frac{\langle m \, | \, \mathscr{V} \, | \, i \rangle}{\left[E_i^{(0)} - E_m^{(0)} \right]^2}$$

$$- E_i^{(1)} \sum_{n,m \neq i} \frac{V_{in} V_{nm} V_{mi}}{\left[E_i^{(0)} - E_n^{(0)} \right]^2 \left[E_i^{(0)} - E_m^{(0)} \right]} + \left[E_i^{(1)} \right]^2 \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^3} - E_i^{(2)} \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^2}$$

$$= \sum_{n,m,k \neq i} \frac{V_{in} V_{nm} V_{mk} V_{ki}}{\left[E_i^{(0)} - E_n^{(0)} \right] \left[E_i^{(0)} - E_m^{(0)} \right] \left[E_i^{(0)} - E_k^{(0)} \right]} - 2 V_{ii} \sum_{n,m \neq i} \frac{V_{in} V_{nm} V_{mi}}{\left[E_i^{(0)} - E_n^{(0)} \right] \left[E_i^{(0)} - E_m^{(0)} \right]^2}$$

$$+ V_{ii}^2 \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^3} - \sum_{m \neq i} \frac{V_{mi} V_{im}}{\left[E_i^{(0)} - E_m^{(0)} \right]} \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^2} \tag{6.2.5}$$

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,

$$E_0^{(2)} = \sum_{a,r} \frac{|\langle \Psi_0 \, | \, \sum_i v(i) \, | \, \Psi_a^r \rangle|^2}{\langle \Psi_0 \, | \, \mathscr{H} \, | \, \Psi_0 \rangle - \langle \Psi_a^r \, | \, \mathscr{H} \, | \, \Psi_a^r \rangle}$$

$$= \sum_{a,r} \frac{v_{ar} v_{ra}}{\sum_b \varepsilon_b^{(0)} - \left(\sum_{b \neq a} \varepsilon_b^{(0)} + \varepsilon_r^{(0)} \right)}$$

$$= \sum_{a,r} \frac{v_{ar} v_{ra}}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}} \tag{6.3.1}$$

Ex 6.4 Eq 6.15 in textbook gives

$$E_i^{(3)} = \sum_{n,m \neq i} \frac{\langle i \, | \, \mathscr{V} \, | \, n \rangle \langle n \, | \, \mathscr{V} \, | \, m \rangle \langle m \, | \, \mathscr{V} \, | \, i \rangle}{(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})} - E_i^{(1)} \sum_{n \neq i} \frac{|\langle i \, | \, \mathscr{V} \, | \, n \rangle|^2}{(E_i^{(0)} - E_n^{(0)})^2}$$

$$= A_i^{(3)} + B_i^{(3)} \tag{6.3.2}$$

a.

$$B_0^{(3)} = -E_0^{(1)} \sum_{n \neq 0} \frac{|\langle \Psi_0 \,|\, \mathscr{V} \,|\, n \rangle|^2}{(E_0^{(0)} - E_n^{(0)})^2}$$

$$= -\sum_b v_{bb} \sum_{a,r} \frac{v_{ar} v_{ra}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2}$$

$$= -\sum_{a,b,r} \frac{v_{aa} v_{br} v_{rb}}{(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})^2} \tag{6.3.3}$$

b.

$$A_0^{(3)} = \sum_{n,m \neq 0} \frac{\langle \Psi_0 \,|\, \mathscr{V} \,|\, n \rangle \langle n \,|\, \mathscr{V} \,|\, m \rangle \langle m \,|\, \mathscr{V} \,|\, \Psi_0 \rangle}{(E_0^{(0)} - E_n^{(0)})(E_0^{(0)} - E_m^{(0)})}$$

$$= \sum_{a,r,b,s} \frac{\langle \Psi_0 \,|\, \mathscr{V} \,|\, \Psi_a^r \rangle \langle \Psi_a^r \,|\, \mathscr{V} \,|\, \Psi_b^s \rangle \langle \Psi_b^s \,|\, \mathscr{V} \,|\, \Psi_0 \rangle}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_s^{(0)})}$$

$$= \sum_{a,r,b,s} \frac{v_{ar} v_{sb} \langle \Psi_a^r \,|\, \mathscr{V} \,|\, \Psi_b^s \rangle}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_s^{(0)})} \tag{6.3.4}$$

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 $a = b, r \neq s$,

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

$$= v_{rs} \tag{6.3.6}$$

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

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

$$= \langle \Psi_a^r \,|\, \mathscr{V} \,|\, -\Psi_{ab}^{ra} \rangle$$

$$= -\langle b \,|\, v \,|\, a \rangle$$

$$= -v_{ba} \tag{6.3.7}$$

If $a = b, r = s$,

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

$$= \sum_c v_{cc} - v_{aa} + v_{rr} \tag{6.3.8}$$

d.

$$E_0^{(3)} = A_0^{(3)} + B_0^{(3)}$$

$$= \sum_{a,r,b,s} \frac{v_{ar} v_{sb} \langle \Psi_a^r \,|\, \mathscr{V} \,|\, \Psi_b^s \rangle}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_s^{(0)})} - \sum_{a,b,r} \frac{v_{aa} v_{br} v_{rb}}{(\varepsilon_b - \varepsilon_r)^2}$$

$$= \sum_{a,r \neq s} \frac{v_{ar} v_{sa} v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} + \sum_{a \neq b,r} \frac{v_{ar} v_{rb}(-v_{ba})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})}$$

$$+ \sum_{a,r} \frac{v_{ar} v_{ra}(\sum_c v_{cc} - v_{aa} + v_{rr})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2} - \sum_{a,b,r} \frac{v_{aa} v_{br} v_{rb}}{(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})^2}$$

$$= \sum_{a,r \neq s} \frac{v_{ar} v_{sa} v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} + \sum_{a \neq b,r} \frac{v_{ar} v_{rb}(-v_{ba})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})}$$

$$+ \sum_{a,r} \frac{v_{ar} v_{ra}(\sum_c v_{cc} - v_{aa} + v_{rr})}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2} - \sum_{a,r} \frac{\sum_c v_{cc} v_{ar} v_{ra}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})^2}$$

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

$$= \sum_{a,r,s} \frac{v_{ar}v_{sa}v_{rs}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} - \sum_{a,b,r} \frac{v_{ar}v_{rb}v_{ba}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})} \qquad (6.3.9)$$

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

$$-2 \sum_{a,b,r}^{N/2} \frac{v_{ra}v_{ab}v_{br}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})} = -\frac{2}{(2\beta)^2} \sum_i^n \sum_j^n \sum_k^n \langle i \,|\, v \,|\, j \rangle \langle j \,|\, v \,|\, k^* \rangle \langle k^* \,|\, v \,|\, i \rangle$$

$$= -\frac{2}{(2\beta)^2} \sum_i^3 \left[\begin{array}{l} \langle i \,|\, v \,|\, i+1 \rangle \langle i+1 \,|\, v \,|\, (i+2)^* \rangle \langle (i+2)^* \,|\, v \,|\, i \rangle \\ + \langle i \,|\, v \,|\, i+2 \rangle \langle i+2 \,|\, v \,|\, (i+1)^* \rangle \langle (i+1)^* \,|\, v \,|\, i \rangle \end{array} \right]$$

$$= -\frac{2}{(2\beta)^2} \sum_i^3 [(\beta/2)(\beta/2)(-\beta/2) + (\beta/2)(-\beta/2)(\beta/2)]$$

$$= -\frac{2}{(2\beta)^2} \times 3 \times (-\beta^3/4)$$

$$= 3\beta/8 \qquad (6.3.10)$$

Ex 6.6

a. Using the general expression, we get

$$\mathscr{E}_0 = 6\alpha - 2 \sum_{j=-1}^{1} (\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos \frac{2j\pi}{3})^{1/2}$$

$$= 6\alpha - 2(\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos \frac{-2\pi}{3})^{1/2} - 2(\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos 0)^{1/2} - 2(\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos \frac{2\pi}{3})^{1/2}$$

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

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

$$= 6\alpha + 2(\beta_1 + \beta_2) - 4(\beta_1^2 + \beta_2^2 - \beta_1\beta_2)^{1/2} \qquad (6.3.11)$$

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

$$\alpha + (\beta_1 + \beta_2),$$
$$\alpha - \sqrt{\beta_1^2 + \beta_2^2 - \beta_1\beta_2} \quad \text{(2-fold)},$$
$$\alpha + \sqrt{\beta_1^2 + \beta_2^2 - \beta_1\beta_2} \quad \text{(2-fold)},$$
$$\alpha - (\beta_1 + \beta_2), \qquad (6.3.13)$$

thus

$$\mathscr{E}_0 = 2[\alpha + (\beta_1 + \beta_2)] + 4\left[\alpha - \sqrt{\beta_1^2 + \beta_2^2 - \beta_1\beta_2}\right]$$

$$= 6\alpha + 2(\beta_1 + \beta_2) - 4\sqrt{\beta_1^2 + \beta_2^2 - \beta_1\beta_2} \qquad (6.3.14)$$

b.

$$E_R = \mathscr{E}_0 - (N\alpha + N\beta)$$

$$= 6\alpha + 2(\beta_1 + \beta_2) - 4\sqrt{\beta_1^2 + \beta_2^2 - \beta_1\beta_2} - (6\alpha + 6\beta)$$

$$= -4\beta_1 + 2\beta_2 - 4\sqrt{\beta_1^2 + \beta_2^2 - \beta_1\beta_2}$$

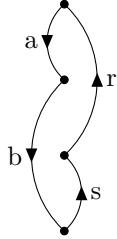$$= 4\beta\left(-1 + \frac{1}{2}x + \sqrt{1 + x^2 - x}\right) \tag{6.3.15}$$

c.

$$E_R = 4\beta\left(-1 + \frac{1}{2}x + \sqrt{1 + x^2 - x}\right)$$

$$= 4\beta\left[-1 + \frac{1}{2}x + 1 + \frac{1}{2}(x^2 - x) - \frac{1}{8}(x^2 - x)^2 + \frac{1}{16}(x^2 - x)^3 - \frac{5}{128}(x^2 - x)^4\right]$$

$$= 4\beta\left[\frac{1}{2}x^2 - \frac{1}{8}(x^4 + x^2 - 2x^3) + \frac{1}{16}(-x^3 + 3x^4) - \frac{5}{128}x^4 + \cdots\right]$$

$$= 4\beta\left[\frac{3}{8}x^2 + \frac{3}{16}x^3 + \frac{3}{128}x^4 + \cdots\right]$$

$$= \beta\left[\frac{3}{2}x^2 + \frac{3}{4}x^3 + \frac{3}{32}x^4 + \cdots\right] \tag{6.3.16}$$

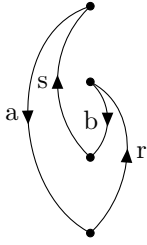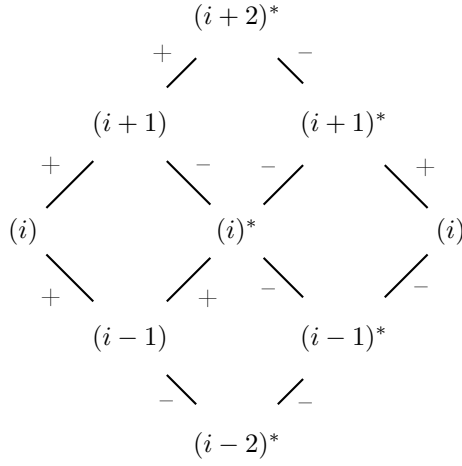## 6.4 Diagrammatic Representation of Orbital Perturbation Theory

Ex 6.7

a.

$$= -\sum_{a,b,r,s} \frac{v_{ab}v_{bs}v_{sr}v_{ra}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_b^{(0)})}$$

$$= -\frac{1}{(2\beta)^3}\sum_{i,j,k,l} \langle i\,|\,v\,|\,j\rangle\,\langle j\,|\,v\,|\,k^*\rangle\,\langle k^*\,|\,v\,|\,l^*\rangle\,\langle l^*\,|\,v\,|\,i\rangle$$

$$= -\frac{2}{(2\beta)^3}\sum_i^{N/2}[-1 + 1 - 1 - 1 + 1 - 1] \times (\beta/2)^4$$

$$= \frac{N\beta}{64}$$

$$\tag{6.4.1}$$
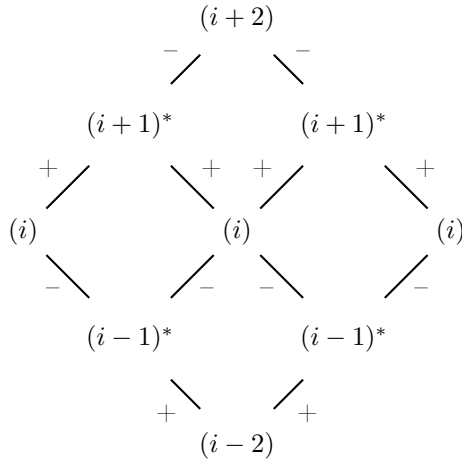
The pictorial representation of the summation are as follows

$$= -\sum_{a,r,b,s} \frac{v_{ar}v_{rb}v_{bs}v_{sa}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})(\varepsilon_a^{(0)} + \varepsilon_b^{(0)} - \varepsilon_r^{(0)} - \varepsilon_s^{(0)})}$$

$$= -\frac{1}{(2\beta)^2 \times 4\beta} \sum_{i,j,k,l} \langle i \,|\, v \,|\, j^* \rangle \langle j^* \,|\, v \,|\, k \rangle \langle k \,|\, v \,|\, l^* \rangle \langle l^* \,|\, v \,|\, i \rangle$$

$$= -\frac{2}{(2\beta)^2 \times 4\beta} \sum_i^{N/2} 6 \times (\beta/2)^4$$

$$= -\frac{3N\beta}{128}$$

(6.4.2)

The pictorial representation of the summation are as follows

thus

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

(6.4.3)

b. Let $N = 6$, we get

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

(6.4.4)

which agrees with the result in Ex 6.6.

6.5   Perturbation Expansion of the Correlation Energy

Ex 6.8

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

For a closed-shell system, the possible spin part of a, b, r, s of the non-zero terms are
first term: $\alpha, \alpha, \alpha, \alpha$; $\quad \alpha, \beta, \alpha, \beta$; $\quad \beta, \alpha, \beta, \alpha$; $\quad \beta, \beta, \beta, \beta$
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

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

6.6   The N-dependence of the RS Perturbation Expansion

Ex 6.10   From Eq 6.68, we get

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

$$= -\frac{1}{2} \times 2N[1_i 1_i | 1_i 1_i]$$
$$= -N J_{11} \tag{6.6.1}$$

$$\left\langle \Psi^{2_i \bar{2}_i}_{1_i \bar{1}_i} \middle| \mathscr{V} \middle| \Psi^{2_i \bar{2}_i}_{1_i \bar{1}_i} \right\rangle = \left\langle \Psi^{2_i \bar{2}_i}_{1_i \bar{1}_i} \middle| \mathscr{H} \middle| \Psi^{2_i \bar{2}_i}_{1_i \bar{1}_i} \right\rangle - \left\langle \Psi^{2_i \bar{2}_i}_{1_i \bar{1}_i} \middle| \mathscr{H}_0 \middle| \Psi^{2_i \bar{2}_i}_{1_i \bar{1}_i} \right\rangle$$

$$= (2N-2)h_{11} + 2h_{22} + (N-1)J_{11} + J_{22} - (2N-2)\varepsilon_1 - 2\varepsilon_2$$
$$= (2N-2)h_{11} + 2h_{22} + (N-1)J_{11} + J_{22} - (2N-2)(h_{11} + J_{11}) - 2(h_{22} + 2J_{12} - K_{12})$$
$$= -(N-1)J_{11} + J_{22} - 4J_{12} + 2K_{12} \tag{6.6.2}$$

6.7 Diagrammatic Representation of the Perturbation Expansion of the Correlation Energy
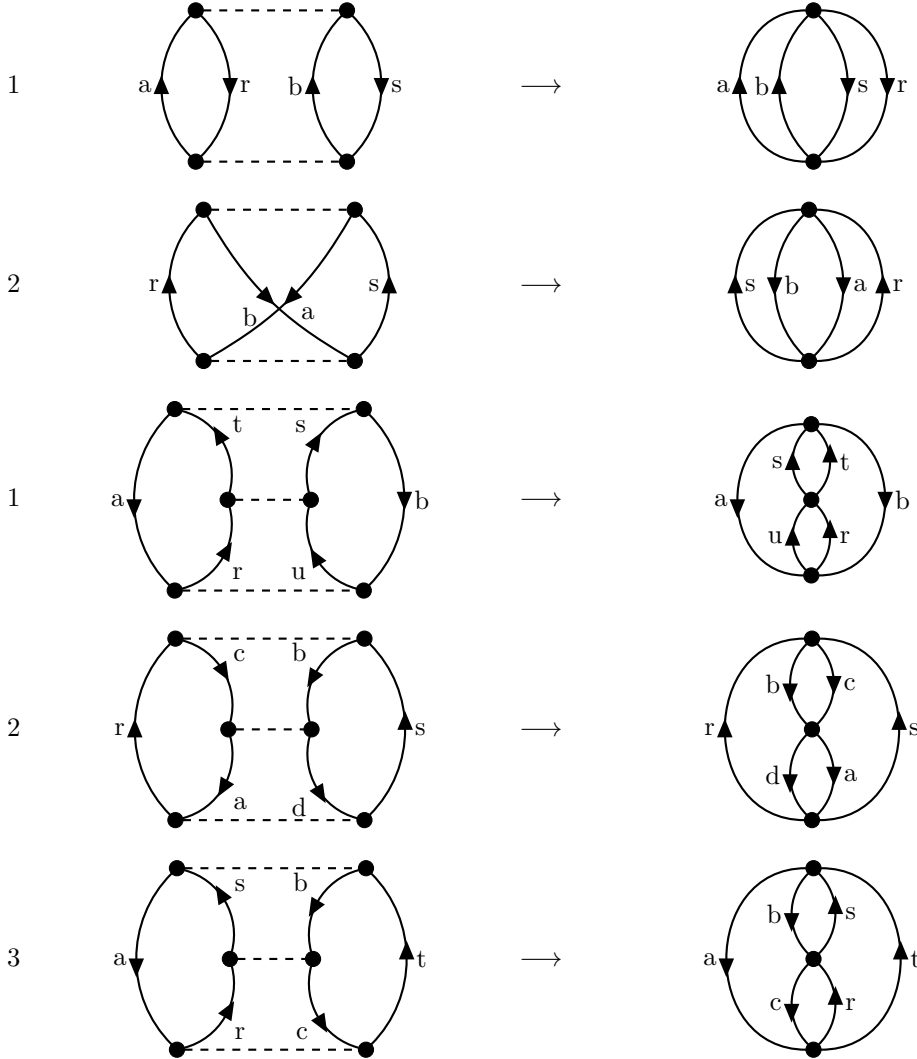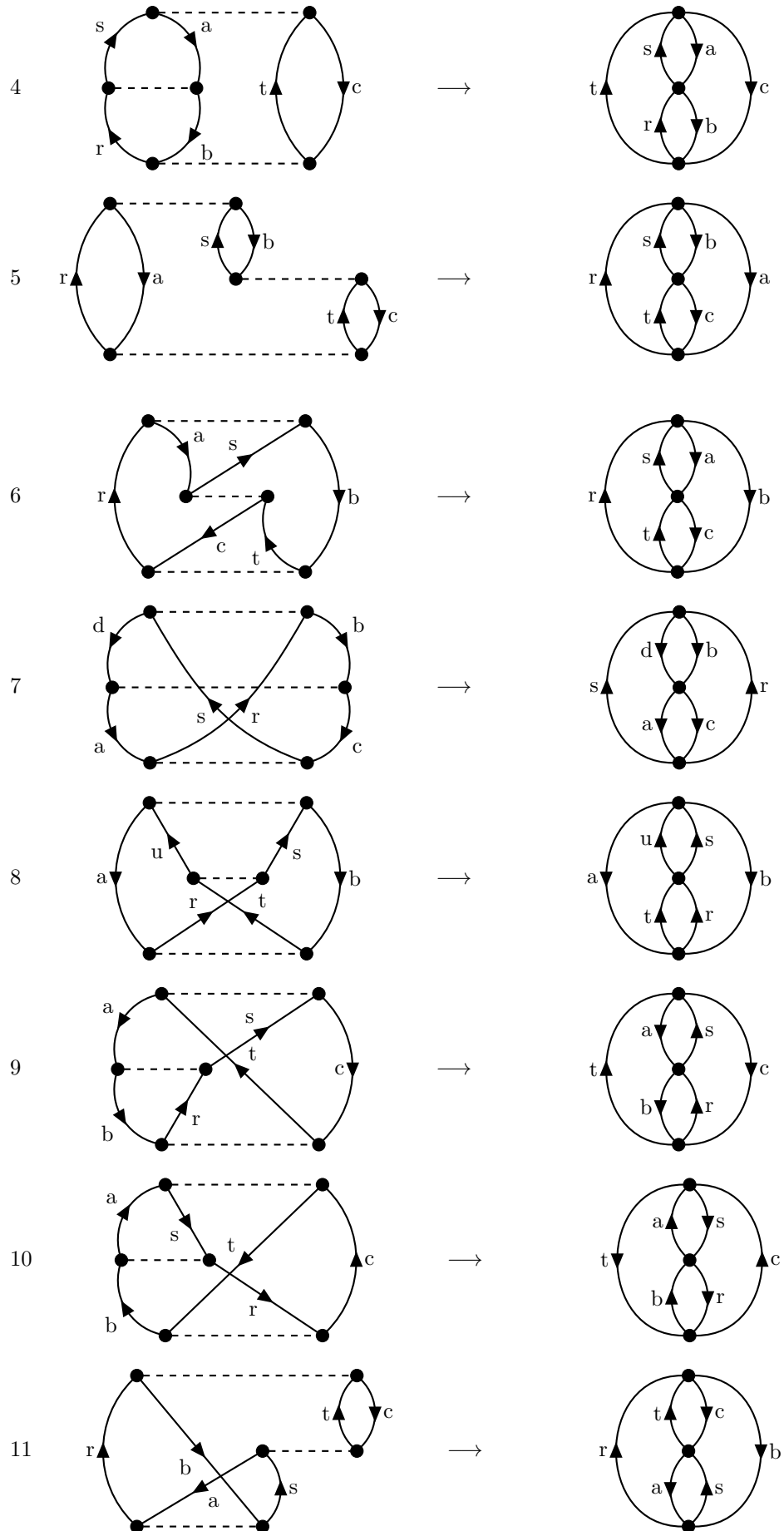
6.7.1 Hugenholtz Diagrams

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 $-\frac{1}{2}$.

6.7.2 Goldstone Diagrams

Ex 6.12

6.8   Some Illustrative Calculations