Modern Quantum Chemistry, Szabo & Ostlund HW

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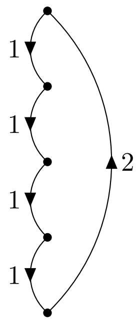
6 Many-body Perturbation Theory

6.1 RS Perturbation Theory

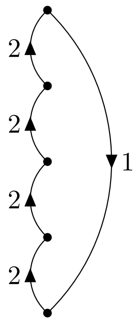
6.2 Diagrammatic Representation of RS Perturbation Theory

6.2.1 Diagrammatic Perturbation Theory for Two States

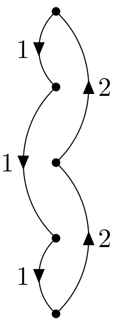
Ex 6.1



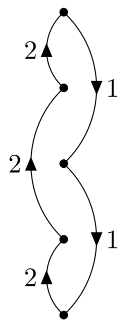
$$= (-1)^5 \frac{V_{12}V_{21}V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4} = -\frac{V_{12}V_{21}V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4}$$



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

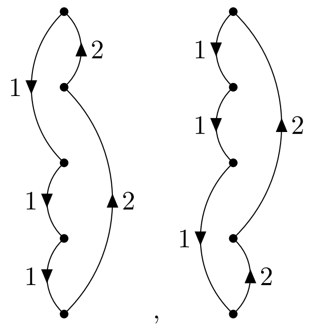


$$= (-1)^4 \frac{V_{12}V_{21}V_{11}^2V_{22}}{(E_1^{(0)} - E_2^{(0)})^4} = \frac{V_{12}V_{21}V_{11}^2V_{22}}{(E_1^{(0)} - E_2^{(0)})^4}$$

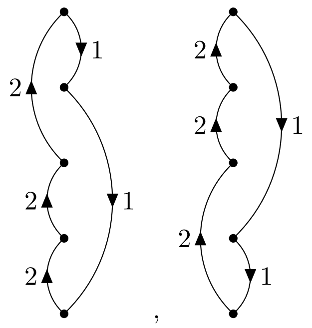


$$= (-1)^3 \frac{V_{12}V_{21}V_{11}V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4} = -\frac{V_{12}V_{21}V_{11}V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4}$$

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

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

while

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

$$\begin{aligned}
E_i^{(4)} &= \left\langle i \,\middle|\, \mathscr{V} \,\middle|\, \Psi_i^{(3)} \right\rangle \\
&= \sum_{n\neq i} \langle i \,|\, \mathscr{V} \,|\, n\rangle \left\langle n \,\middle|\, \Psi_i^{(3)} \right\rangle
\end{aligned} \tag{6.2.4}$$