

Modern Quantum Chemistry, Szabo & Ostlund

HW

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Contents

6	Many-body Perturbation Theory	2
6.1	RS Perturbation Theory	2
6.2	Diagrammatic Representation of RS Perturbation Theory	2
6.2.1	Diagrammatic Perturbation Theory for Two States	2
	Ex 6.1	2
6.2.2	Diagrammatic Perturbation Theory for N States	3
	Ex 6.2	3

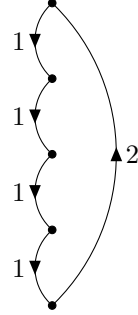
6 Many-body Perturbation Theory

6.1 RS Perturbation Theory

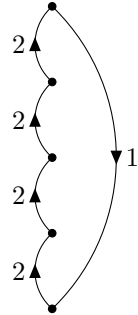
6.2 Diagrammatic Representation of RS Perturbation Theory

6.2.1 Diagrammatic Perturbation Theory for Two States

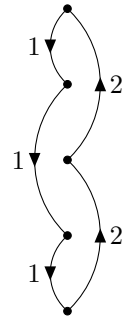
Ex 6.1



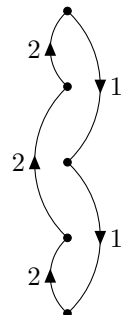
$$= (-1)^5 \frac{V_{12}V_{21}V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4} = -\frac{V_{12}V_{21}V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4}$$



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



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



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

Similarly,

$$\begin{aligned}
& \text{Diagram 1} + \text{Diagram 2} = \frac{V_{12}V_{21}V_{11}^2V_{22}}{(E_1^{(0)} - E_2^{(0)})^4} \\
& \text{Diagram 3} + \text{Diagram 4} = -\frac{V_{12}V_{21}V_{11}V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4}
\end{aligned}$$

thus, the sum of above terms is

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

6.2.2 Diagrammatic Perturbation Theory for N States

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

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

while

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

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

$$\begin{aligned}
E_i^{(4)} &= \langle i | \mathcal{V} | \Psi_i^{(3)} \rangle \\
&= \sum_{n \neq i} \frac{\langle i | \mathcal{V} | n \rangle}{E_i^{(0)} - E_n^{(0)}} \left\{ \langle n | \mathcal{V} | \Psi_i^{(2)} \rangle - E_i^{(1)} \frac{\langle n | \mathcal{V} | \Psi_i^{(1)} \rangle}{E_i^{(0)} - E_n^{(0)}} + \left[E_i^{(1)} \right]^2 \frac{\langle n | \mathcal{V} | i \rangle}{\left[E_i^{(0)} - E_n^{(0)} \right]^2} - E_i^{(2)} \frac{\langle n | \mathcal{V} | i \rangle}{E_i^{(0)} - E_n^{(0)}} \right\} \\
&= \sum_{n \neq i} \frac{\langle i | \mathcal{V} | n \rangle}{E_i^{(0)} - E_n^{(0)}} \langle n | \mathcal{V} | \Psi_i^{(2)} \rangle - E_i^{(1)} \sum_{n \neq i} \frac{\langle i | \mathcal{V} | n \rangle}{\left[E_i^{(0)} - E_n^{(0)} \right]^2} \langle n | \mathcal{V} | \Psi_i^{(1)} \rangle \\
&\quad + \left[E_i^{(1)} \right]^2 \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^3} - E_i^{(2)} \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^2} \\
&= \sum_{n, m \neq i} \frac{\langle i | \mathcal{V} | n \rangle}{E_i^{(0)} - E_n^{(0)}} \langle n | \mathcal{V} | m \rangle \langle m | \Psi_i^{(2)} \rangle - E_i^{(1)} \sum_{n, m \neq i} \frac{\langle i | \mathcal{V} | n \rangle \langle n | \mathcal{V} | m \rangle \langle m | \mathcal{V} | i \rangle}{\left[E_i^{(0)} - E_n^{(0)} \right]^2 \left[E_i^{(0)} - E_m^{(0)} \right]} \\
&\quad + \left[E_i^{(1)} \right]^2 \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^3} - E_i^{(2)} \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^2} \\
&= \sum_{n, m \neq i} \frac{V_{in} V_{nm}}{E_i^{(0)} - E_n^{(0)}} \frac{\langle m | \mathcal{V} | \Psi_i^{(1)} \rangle - E_i^{(1)} \langle m | \Psi_i^{(1)} \rangle}{E_i^{(0)} - E_m^{(0)}} - E_i^{(1)} \sum_{n, m \neq i} \frac{V_{in} V_{nm} V_{mi}}{\left[E_i^{(0)} - E_n^{(0)} \right]^2 \left[E_i^{(0)} - E_m^{(0)} \right]} \\
&\quad + \left[E_i^{(1)} \right]^2 \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^3} - E_i^{(2)} \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^2} \\
&= \sum_{n, m, k \neq i} \frac{V_{in} V_{nm}}{E_i^{(0)} - E_n^{(0)}} \frac{\langle m | \mathcal{V} | k \rangle \langle k | \mathcal{V} | i \rangle}{\left[E_i^{(0)} - E_m^{(0)} \right] \left[E_i^{(0)} - E_k^{(0)} \right]} - E_i^{(1)} \sum_{n, m \neq i} \frac{V_{in} V_{nm}}{E_i^{(0)} - E_n^{(0)}} \frac{\langle m | \mathcal{V} | i \rangle}{\left[E_i^{(0)} - E_m^{(0)} \right]^2} \\
&\quad - E_i^{(1)} \sum_{n, m \neq i} \frac{V_{in} V_{nm} V_{mi}}{\left[E_i^{(0)} - E_n^{(0)} \right]^2 \left[E_i^{(0)} - E_m^{(0)} \right]} + \left[E_i^{(1)} \right]^2 \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^3} - E_i^{(2)} \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^2} \\
&= \sum_{n, m, k \neq i} \frac{V_{in} V_{nm} V_{mk} V_{ki}}{\left[E_i^{(0)} - E_n^{(0)} \right] \left[E_i^{(0)} - E_m^{(0)} \right] \left[E_i^{(0)} - E_k^{(0)} \right]} - 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} \\
&\quad - V_{ii} \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]} + V_{ii}^2 \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^3} \\
&\quad - \sum_{m \neq i} \frac{V_{mi} V_{im}}{\left[E_i^{(0)} - E_m^{(0)} \right]} \sum_{n \neq i} \frac{V_{in} V_{ni}}{\left[E_i^{(0)} - E_n^{(0)} \right]^2} \tag{6.2.5}
\end{aligned}$$