Modern Quantum Chemistry, Szabo & Ostlund HW

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6 Many-body Perturbation Theory

6.1 RS Perturbation Theory

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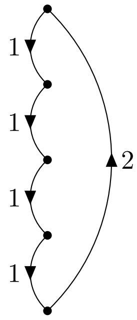
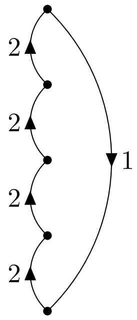
6.2.1 Diagrammatic Perturbation Theory for Two States

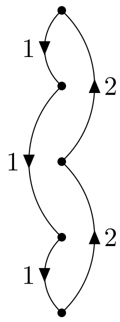
Ex 6.1



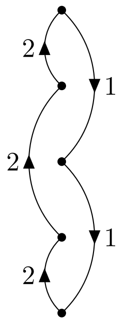
$$= (-1)^5 \frac{V_{12}V_{21}V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4} = -\frac{V_{12}V_{21}V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4}$$



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

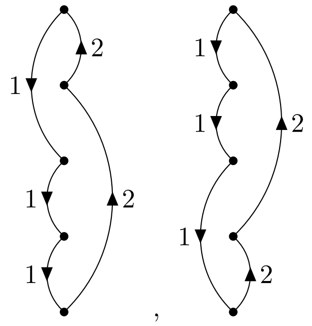


$$= (-1)^4 \frac{V_{12}V_{21}V_{11}^2V_{22}}{(E_1^{(0)} - E_2^{(0)})^4} = \frac{V_{12}V_{21}V_{11}^2V_{22}}{(E_1^{(0)} - E_2^{(0)})^4}$$

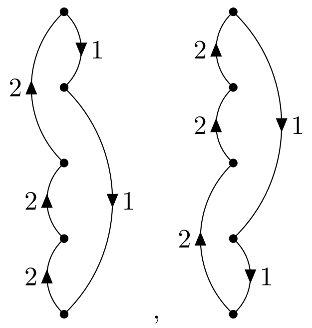


$$= (-1)^3 \frac{V_{12}V_{21}V_{11}V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4} = -\frac{V_{12}V_{21}V_{11}V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4}$$

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} \qquad (6.2.5)
\end{aligned}
$$

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,

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

Ex 6.4 Eq 6.15 in textbook gives

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

a.

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

b.

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