Modern Quantum Chemistry, Szabo & Ostlund HW

王石嵘

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6 Many-body Perturbation Theory

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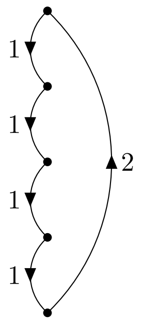
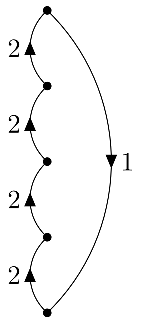
6.2.1 Diagrammatic Perturbation Theory for Two States

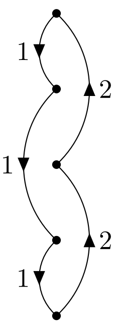
Ex 6.1



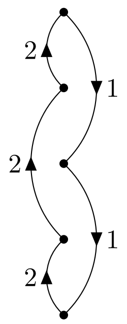
$$= (-1)^5 \frac{V_{12}V_{21}V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4} = -\frac{V_{12}V_{21}V_{11}^3}{(E_1^{(0)} - E_2^{(0)})^4}$$



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

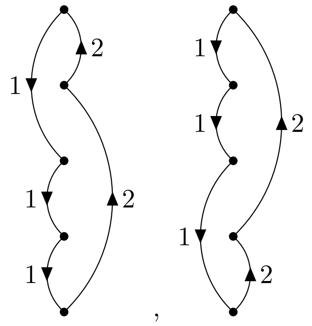


$$= (-1)^4 \frac{V_{12}V_{21}V_{11}^2V_{22}}{(E_1^{(0)} - E_2^{(0)})^4} = \frac{V_{12}V_{21}V_{11}^2V_{22}}{(E_1^{(0)} - E_2^{(0)})^4}$$

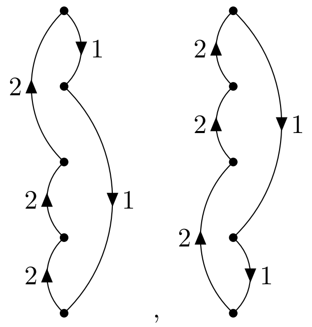


$$= (-1)^3 \frac{V_{12}V_{21}V_{11}V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4} = -\frac{V_{12}V_{21}V_{11}V_{22}^2}{(E_1^{(0)} - E_2^{(0)})^4}$$

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}
\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.

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

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

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

$$\begin{aligned}
-2\sum_{a,b,r}^{N/2} \frac{v_{ra}v_{ab}v_{br}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})} &= -\frac{2}{(2\beta)^2} \sum_i^n \sum_j^n \sum_k^n \langle i \,|\, v \,|\, j\rangle \langle j \,|\, v \,|\, k^*\rangle \langle k^* \,|\, v \,|\, i\rangle \\
&= -\frac{2}{(2\beta)^2} \sum_i^3 \begin{bmatrix} \langle i \,|\, v \,|\, i+1\rangle \langle i+1 \,|\, v \,|\, (i+2)^*\rangle \langle (i+2)^* \,|\, v \,|\, i\rangle \\ + \langle i \,|\, v \,|\, i+2\rangle \langle i+2 \,|\, v \,|\, (i+1)^*\rangle \langle (i+1)^* \,|\, v \,|\, i\rangle \end{bmatrix} \\
&= -\frac{2}{(2\beta)^2} \sum_i^3 [(\beta/2)(\beta/2)(-\beta/2) + (\beta/2)(-\beta/2)(\beta/2)] \\
&= -\frac{2}{(2\beta)^2} \times 3 \times (-\beta^3/4) \\
&= 3\beta/8
\end{aligned} \tag{6.3.10}$$