从而本征多项式为 $c^2+\beta c-3\beta^2=0$。从而 $E_R(SCI)=\frac{1}{2}(\sqrt{13}-1)\beta=1.3028\beta$.

练习5.21 $\langle\Psi_0|\mathcal{H}|{}^{*}_{i}\rangle=\frac{1}{\sqrt{2}}\langle\Psi_0|\mathcal{H}|\Psi_i^{(i+1)^*}\rangle-\frac{1}{\sqrt{2}}\langle\Psi_0|\mathcal{H}|\Psi_i^{(i-1)^*}\rangle=\frac{1}{\sqrt{2}}\frac{1}{2}\beta-\frac{1}{\sqrt{2}}\left(-\frac{1}{2}\beta\right)=\frac{1}{\sqrt{2}}\beta$.

$\langle{}^{*}_{i}|\mathcal{H}-E_0|{}^{*}_{i}\rangle=\frac{1}{2}[\langle\Psi_i^{(i+1)^*}|\mathcal{H}-E_0|\Psi_i^{(i+1)^*}\rangle-\langle\Psi_i^{(i+1)^*}|\mathcal{H}-E_0|\Psi_i^{(i-1)^*}\rangle-\langle\Psi_i^{(i-1)^*}|\mathcal{H}-E_0|\Psi_i^{(i+1)^*}\rangle+\langle\Psi_i^{(i-1)^*}|\mathcal{H}-E_0|\Psi$

$=\frac{1}{2}[-2\beta+0+0-2\beta]=-2\beta$.

当 $N>6$ 时，$i\neq j$ 时，$i\pm1\neq j\pm1$ 通 $i\pm1=j\mp1$ 是可能的，但 ~~使 $\langle{}^{*}_{i}|\mathcal{H}-E_0|{}^{*}_{j}\rangle=0$~~ 此时 $i=j+2$ 或 $j=i+2$.

从而势能积分为0. 从而 $\langle{}^{*}_{i}|\mathcal{H}-E_0|{}^{*}_{i}\rangle=0$. 从而综上，$\langle{}^{*}_{i}|\mathcal{H}-E_0|{}^{*}_{j}\rangle=\delta_{ij}(-2\beta)$.

不同的原因是 $N>6$ 时 $\langle{}^{*}_{i}|\mathcal{H}-E_0|{}^{*}_{j}\rangle=-2\beta\delta_{ij}$. 从而同练习5.20.

$$Nc\cdot\frac{1}{\sqrt{2}}\beta=E_R(SCI)$$

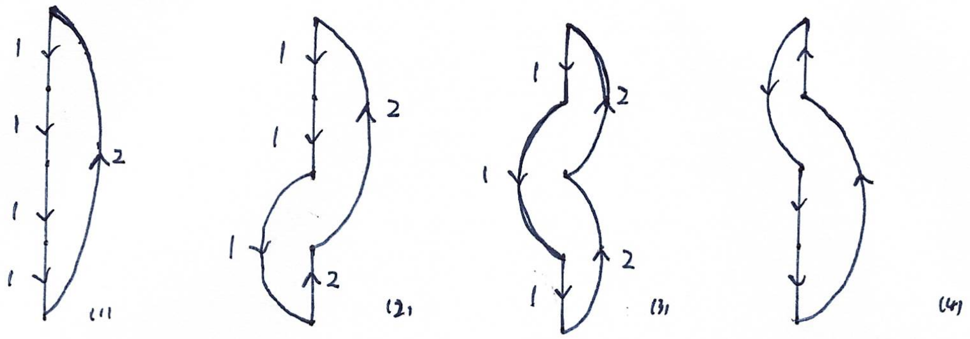
$$\frac{1}{\sqrt{2}}\beta-2\beta\cdot c=E_R(SCI)c.$$

同理，得本征多项式为 $\varepsilon^2+2\beta\varepsilon-\frac{1}{2}N\beta^2=0$. $\therefore E_R(SCI)=(\sqrt{\beta^2+N\beta^2/2}-\beta)=(\sqrt{1+N/2}-1)\beta$.

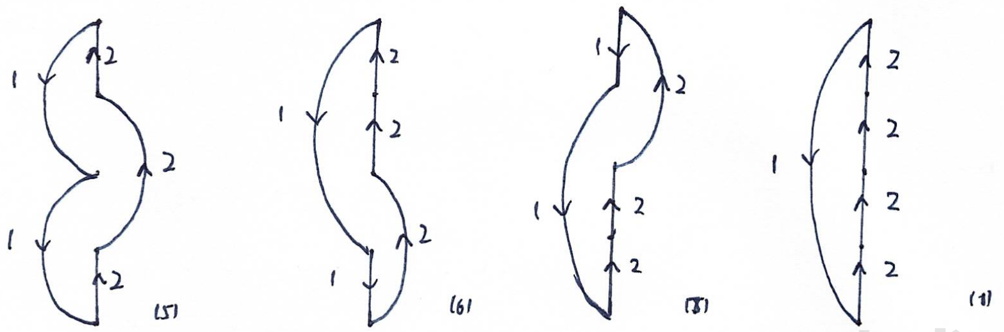
$\therefore\lim_{N\to\infty}\frac{E_R(SCI)}{N^{1/2}}=\frac{1}{4}\beta$

6.2.1节（双态下的图解摄动理论）习题解析

习题6.1　在五阶图中满足任一横线穿过仅有一洞线及一孔线的情形有以下8种. 对应能量为



$(-1)^{4+1}\frac{V_{21}V_{11}^{3}V_{12}}{(E_1^{(0)}-E_2^{(0)})^4}$　$(-1)^{3+1}\frac{V_{21}V_{11}^{2}V_{12}V_{22}}{(E_1^{(0)}-E_2^{(0)})^4}$　$(-1)^{3+1}\frac{V_{21}V_{11}^{2}V_{12}V_{22}}{(E_1^{(0)}-E_3^{(0)})^4}$　$(-1)^{3+1}\frac{V_{21}V_{11}^{2}V_{12}V_{22}}{(E_1^{(0)}-E_2^{(0)})^4}$



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

$$\therefore E(5阶)=\frac{-V_{21}V_{11}^{3}V_{12}+3V_{11}^{2}V_{12}V_{21}V_{22}-3V_{11}V_{12}V_{21}V_{22}^{2}+V_{21}V_{12}V_{22}^{3}}{(E_1^{(0)}-E_2^{(0)})^4}=\frac{V_{12}V_{21}(V_{22}-V_{11})^3}{(E_1^{(0)}-E_2^{(0)})^4}.$$

如何做到不重不落，个人认为遵循以下顺序

(1). 记$N'=N-1$，N为摄动图阶数.

(2) 首先有如图(1)这种从上到下全是相邻点洞线的，~~之后~~最大连接长$i=1$；之后递增最大连接长$i=2$.

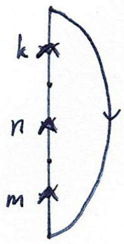
(3)讨论有一段最大连接长，两段最大连接长，…，$[N'/i]$段最大连接长情形，如图(2)-(4)是最大连接长$i=2$且数目为1的情形；(5)为最大连接长为2且数目为2情形($4\div2=2$)；

(4) 再递增最大连接长，重复(3)，到最大连接长$=N'$时，即图(8)情形时，讨论终止.

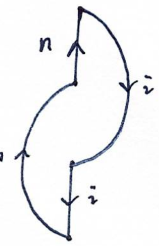
此做法则适用于任一横线穿过且仅穿过一对洞线及孔线情形

6.2.2节(N态的图解摄动理论)习题解析

练习6.2　计算相应的费曼图如下：



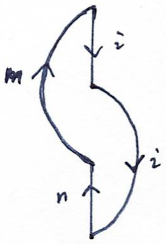
(1)



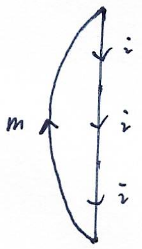
(2)

$$(-1)^{1+1}\sum_{k=1}^{+\infty}{}'\sum_{n=1}^{+\infty}{}'\sum_{m=1}^{+\infty}{}'\frac{V_{ki}V_{im}V_{mn}V_{nk}}{(E_i^{(0)}-E_k^{(0)})(E_i^{(0)}-E_m^{(0)})(E_i^{(0)}-E_n^{(0)})}$$

$$(-1)^{2+1}\sum_{m=1}^{+\infty}{}'\sum_{n=1}^{+\infty}\frac{V_{ni}V_{ii}V_{im}V_{mn}}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_m^{(0)})^2}$$



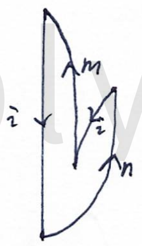
(3)



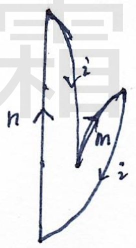
(4)

$$(-1)^{2+1}\sum_{m=1}^{+\infty}{}'\sum_{n=1}^{+\infty}{}'\frac{V_{mi}V_{ii}V_{in}V_{nm}}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_m^{(0)})^2}$$

$$(-1)^{3+1}\sum_{m=1}^{+\infty}{}'\frac{V_{mi}V_{ii}^2V_{im}}{(E_i^{(0)}-E_m^{(0)})^3}$$



(5)



(6)

$$(-1)^{2+1}\sum_{m=1}^{+\infty}{}'\sum_{n=1}^{+\infty}{}'\frac{V_{mi}V_{in}V_{ni}V_{im}}{(E_i^{(0)}-E_m^{(0)})(2E_i^{(0)}-E_m^{(0)}-E_n^{(0)})(E_i^{(0)}-E_n^{(0)})}$$

$$(-1)^{2+1}\sum_{m=1}^{+\infty}{}'\sum_{n=1}^{+\infty}{}'\frac{V_{in}V_{ni}V_{im}V_{mi}}{(E_i^{(0)}-E_n^{(0)})(2E_i^{(0)}-E_m^{(0)}-E_n^{(0)})}$$

以上这6个摄动能分别用E_1到E_6表示，下用6.1节方法解~~题~~四阶摄动总能量，由教材式(6.7d)，

$$\mathcal{H}_0|\psi_i^{(3)}\rangle+\mathcal{V}|\psi_i^{(2)}\rangle=E_i^{(0)}|\psi_i^{(3)}\rangle+E_i^{(1)}|\psi_i^{(2)}\rangle+E_i^{(2)}|\psi_i^{(1)}\rangle+E_i^{(3)}|\psi_i^{(0)}\rangle$$

两边同乘$\langle n|(n\neq i)$，得

$$E_n^{(0)}\langle n|\psi_i^{(3)}\rangle+\langle n|\mathcal{V}|\psi_i^{(2)}\rangle=E_i^{(0)}\langle n|\psi_i^{(3)}\rangle+E_i^{(1)}\langle n|\psi_i^{(2)}\rangle+E_i^{(2)}\langle n|\psi_i^{(1)}\rangle$$

从而

$$\langle n|\psi_i^{(3)}\rangle=\frac{\langle n|\mathcal{V}|\psi_i^{(2)}\rangle-E_i^{(1)}\langle n|\psi_i^{(2)}\rangle-E_i^{(2)}\langle n|\psi_i^{(1)}\rangle}{\cancel{E}\,E_i^{(0)}-E_n^{(0)}}$$

由教材式(6.8b)，~~猜~~类比 $E_i^{(4)}=\langle i|\mathcal{V}|\psi_i^{(3)}\rangle$，证明如下~~：将式(6.7)两边同乘⟨i|，之得~~同式(6.7)的获取，比较λ^4

$\cancel{E_i^{(4)}=}$　　$\cancel{\langle i|\mathcal{V}|\psi_i^{(3)}\rangle=E_4}$

的情形，得

$$\mathcal{H}_0|\psi_i^{(4)}\rangle+\mathcal{V}|\psi_i^{(3)}\rangle=E_i^{(0)}|\psi_i^{(4)}\rangle+E_i^{(1)}|\psi_i^{(3)}\rangle+E_i^{(2)}|\psi_i^{(2)}\rangle+E_i^{(3)}|\psi_i^{(1)}\rangle+E_i^{(4)}|\psi_i^{(0)}\rangle$$

两边同乘$\langle i|$，之得

$$E_i^{(4)}=\langle i|\mathcal{V}|\psi_i^{(3)}\rangle.$$

证明完成，从而 $E_i^{(4)}=\langle i|V|\Psi_i^{(3)}\rangle$。同6.1节式(6.15)推导，代入 $\langle n|\Psi_i^{(3)}\rangle$ 表达式，再代入式(6.11),(6.14)

$$E_i^{(4)}=\langle i|V|\Psi_i^{(3)}\rangle=\sum_{n=1}^{+\infty}{}'_i\langle i|V|n\rangle\langle n|\Psi_i^{(3)}\rangle.$$

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

$$=\sum_{n=1}^{+\infty}{}'_i\frac{\langle i|V|n\rangle\langle n|V|\Psi_i^{(2)}\rangle}{E_i^{(0)}-E_n^{(0)}}-E_i^{(1)}\sum_{n=1}^{+\infty}{}'_i\frac{\langle i|V|n\rangle\langle n|\Psi_i^{(2)}\rangle}{E_i^{(0)}-E_n^{(0)}}-E_i^{(2)}\sum_{n=1}^{+\infty}{}'_i\frac{\langle i|V|n\rangle\langle n|\Psi_i^{(1)}\rangle}{E_i^{(0)}-E_n^{(0)}}$$

$$=\sum_{n=1}^{+\infty}{}'_i\sum_{m=1}^{+\infty}{}'_i\frac{\langle i|V|n\rangle\langle n|V|m\rangle\langle m|\Psi_i^{(2)}\rangle}{E_i^{(0)}-E_n^{(0)}}-E_i^{(1)}\sum_{n=1}^{+\infty}{}'_i\frac{\langle i|V|n\rangle\langle n|\Psi_i^{(2)}\rangle}{E_i^{(0)}-E_n^{(0)}}-E_i^{(2)}\sum_{n=1}^{+\infty}\frac{\langle i|V|n\rangle\langle n|\Psi_i^{(1)}\rangle}{E_i^{(0)}-E_n^{(0)}}$$

$$=\sum_{n=1}^{+\infty}{}'_i\sum_{m=1}^{+\infty}{}'_i\frac{\langle i|V|n\rangle\langle n|V|m\rangle}{E_i^{(0)}-E_n^{(0)}}\frac{\langle m|V|\Psi_i^{(1)}\rangle-E_i^{(1)}\langle m|\Psi_i^{(1)}\rangle}{E_i^{(0)}-E_m^{(0)}}$$

$$-\sum_{n=1}^{+\infty}{}'_i\frac{\langle i|V|n\rangle}{E_i^{(0)}-E_n^{(0)}}\frac{\langle n|V|\Psi_i^{(1)}\rangle-E_i^{(1)}\langle n|\Psi_i^{(1)}\rangle}{E_i^{(0)}-E_n^{(0)}}-E_i\sum_{n=1}^{+\infty}{}'_i\frac{\langle i|V|n\rangle\langle n|\Psi_i^{(1)}\rangle}{E_i^{(0)}-E_n^{(0)}}$$

$$=\sum_{n=1}^{+\infty}{}'_i\sum_{m=1}^{+\infty}{}'_i\frac{\langle i|V|n\rangle\langle n|V|m\rangle\langle m|V|\Psi_i^{(1)}\rangle}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_m^{(0)})}-E_i^{(1)}\sum_{n=1}^{+\infty}{}'_i\sum_{m=1}^{+\infty}{}'_i\frac{\langle i|V|n\rangle\langle n|V|m\rangle\langle m|\Psi_i^{(1)}\rangle}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_m^{(0)})}.$$

$$-E_i^{(1)}\sum_{n=1}^{+\infty}{}'_i\frac{\langle i|V|n\rangle\langle n|V|\Psi_i^{(1)}\rangle}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_n^{(0)})}+(E_i^{(1)})^2\sum_{n=1}^{+\infty}{}'_i\frac{\langle i|V|n\rangle\langle n|\Psi_i^{(1)}\rangle}{E_i^{(0)}-E_n^{(0)}}-E_i^{(2)}\sum_{n=1}^{+\infty}{}'_i\frac{\langle i|V|n\rangle\langle n|\Psi_i^{(1)}\rangle}{E_i^{(0)}-E_n^{(0)}}.$$

$$=\sum_{n=1}^{+\infty}{}'_i\sum_{m=1}^{+\infty}{}'_i\sum_{k=1}^{+\infty}{}'_i\frac{V_{in}V_{nm}V_{mk}V_{ki}}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_m^{(0)})(E_i^{(0)}-E_k^{(0)})}-E_i^{(1)}\sum_{n=1}^{+\infty}{}'_i\sum_{m=1}^{+\infty}\frac{V_{in}V_{nm}V_{mi}}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_m^{(0)})^2}$$

$$-E_i^{(1)}\sum_{n=1}^{+\infty}{}'_i\sum_{m=1}^{+\infty}{}'_i\frac{V_{in}V_{nm}V_{mi}}{(E_i^{(0)}-E_n^{(0)})^2(E_i^{(0)}-E_m^{(0)})}+(E_i^{(1)})^2\sum_{n=1}^{+\infty}{}'_i\frac{V_{ni}V_{in}}{(E_i^{(0)}-E_n^{(0)})^3}-E_i^{(2)}\sum_{n=1}^{+\infty}\frac{V_{in}V_{ni}}{(E_i^{(0)}-E_n^{(0)})^2}$$

$$=\sum_{n=1}^{+\infty}{}'_i\sum_{m=1}^{+\infty}{}'_i\sum_{k=1}^{+\infty}{}'_i\frac{V_{ki}V_{in}V_{nm}V_{mk}}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_m^{(0)})(E_i^{(0)}-E_k^{(0)})}-\sum_{m=1}^{+\infty}{}'_i\sum_{n=1}^{+\infty}{}'_i\frac{V_{ii}V_{in}V_{nm}V_{mi}}{(E_i^{(0)}-E_n^{(0)})(E_i^{(0)}-E_m^{(0)})^2}$$

$$-\sum_{n=1}^{+\infty}{}'_i\sum_{m=1}^{+\infty}{}'_i\frac{V_{ii}V_{im}V_{mn}V_{ni}}{(E_i^{(0)}-E_m^{(0)})^2(E_i^{(0)}-E_n^{(0)})}+\sum_{m=1}^{+\infty}{}'_i\frac{V_{im}V_{mi}V_{ii}^2}{(E_i^{(0)}-E_m^{(0)})^3}-\sum_{n=1}^{+\infty}{}'_i\frac{V_{in}V_{ni}}{(E_i^{(0)}-E_n^{(0)})^2}\sum_{m=1}^{+\infty}{}'_i\frac{V_{mi}V_{im}}{E_i^{(0)}-E_m^{(0)}}$$

此式中的第一项即为 E_1，第二项为 E_3，第三项为 E_2，第四项为 E_4。而第五、六项无直接归属。实际上，它们等于上式最后一项，证明如下：

$$E_5+E_6=-\sum_{m=1}^{+\infty}{}'_i\sum_{n=1}^{+\infty}{}'_i\frac{V_{mi}V_{in}V_{ni}V_{im}}{(E_i^{(0)}-E_m^{(0)})(2E_i^{(0)}-E_m^{(0)}-E_n^{(0)})(E_i^{(0)}-E_n^{(0)})}-\sum_{m=1}^{+\infty}{}'_i\sum_{n=1}^{+\infty}{}'_i\frac{V_{in}V_{ni}V_{im}V_{mi}}{(E_i^{(0)}-E_n^{(0)})^2(2E_i^{(0)}-E_m^{(0)}-E_n^{(0)})}$$

$$=-\sum_{m=1}^{+\infty}{}'_i\sum_{n=1}^{+\infty}{}'_i\frac{V_{mi}V_{in}V_{ni}V_{im}}{(E_i^{(0)}-E_m^{(0)})(2E_i^{(0)}-E_m^{(0)}-E_n^{(0)})(E_i^{(0)}-E_n^{(0)})^2}\left[E_i^{(0)}-E_n^{(0)}+E_2^{(0)}-E_m^{(0)}\right]$$

$$=-\sum_{m=1}^{+\infty}{}'_i\sum_{n=1}^{+\infty}{}'_i\frac{V_{mi}V_{in}V_{ni}V_{im}}{(E_i^{(0)}-E_m^{(0)})(E_i^{(0)}-E_n^{(0)})^2}=-\sum_{m=1}^{+\infty}{}'_i\frac{V_{mi}V_{im}}{E_i^{(0)}-E_m^{(0)}}\cdot\sum_{n=1}^{+\infty}{}'_i\frac{V_{in}V_{ni}}{(E_i^{(0)}-E_n^{(0)})^2}$$，此即上式尾项。

从而用分析法得到的结果与图解法相同

6.3节（轨道摄动理论：单粒子摄动）习题解析

练习6.3

$$E_0^{(2)}=\sum_{n\in singlets}\frac{|\langle\Psi_0|\boxed{\sum_i} v(i)|n\rangle|^2}{E_0^{(0)}-E_n^{(0)}}=\sum_{a=1}^{N}\sum_{r=1}^{+\infty}{}'_{a}\frac{\langle a|v|r\rangle\langle r|v|a\rangle}{\varepsilon_a^{(0)}-\varepsilon_r^{(0)}}=\sum_{a=1}^{N}\sum_{b=1}^{N}{}'_{a}\frac{V_{ab}V_{ba}}{\varepsilon_a^{(0)}-\varepsilon_b^{(0)}}+\sum_{a=1}^{N}\sum_{r=N+1}^{+\infty}\frac{V_{ar}V_{ra}}{\varepsilon_a^{(0)}-\varepsilon_r^{(0)}}=\sum_{a=1}^{N}\sum_{r=N+1}^{+\infty}\frac{V_{a\cdots}}{\varepsilon_a^{(0)}-\cdots}$$

第二个等号的转化在于必定得有一个占据轨道受激与一个轨道作用，所以对所有占据轨道求和，再对所有轨道求和，再利用占据轨道不接受其他电子使 $\sum_{a=1}^{N}\sum_{b=1}^{N}{}'_{a}\frac{V_{ab}V_{ba}}{\varepsilon_a^{(0)}-\varepsilon_b^{(0)}}=0$（根本是Pauli不相容原理，操作/证明同式(6.41)－式(6.42)间 $X=0$ 的证明）进行化简即得原结论。

练习6.4

(a). $$B_0^{(3)}=-E_0^{(1)}\sum_{n\in singlets}\frac{|\langle\Psi_0|\mathscr{V}|n\rangle|^2}{(E_0^{(0)}-E_n^{(0)})^2}=-\sum_{a=1}^{N}V_{aa}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\frac{V_{br}V_{rb}}{(\varepsilon_b^{(0)}-\varepsilon_r^{(0)})^2}=-\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\frac{V_{aa}V_{br}V_{rb}}{(\varepsilon_b^{(0)}-\varepsilon_r^{(0)})^2}$$

(b) $$A_0^{(3)}=\sum_{m\in singlets}\sum_{n\in singlets}\frac{\langle\Psi_0|\mathscr{V}|n\rangle\langle n|\mathscr{V}|m\rangle\langle m|\mathscr{V}|\Psi_0\rangle}{(E_0^{(0)}-E_n^{(0)})(E_0^{(0)}-E_m^{(0)})}$$，做与练习6.3相同的转化。

$$=\sum_{a=1}^{N}\sum_{r=1}^{+\infty}{}'_{a}\sum_{b=1}^{N}\sum_{s=1}^{+\infty}{}'_{b}\frac{\langle\Psi_0|\mathscr{V}|\Psi_a^r\rangle\langle\Psi_a^r|\mathscr{V}|\Psi_b^s\rangle\langle\Psi_b^s|\mathscr{V}|\Psi_0\rangle}{(E_0^{(0)}-E_n^{(0)})(E_0^{(0)}-E_m^{(0)})}$$，利用反对称性化简

$$=\sum_{a=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{b=1}^{N}\sum_{s=N+1}^{+\infty}\frac{V_{ar}V_{bs}\langle\Psi_a^r|\mathscr{V}|\Psi_b^s\rangle}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_b^{(0)}-\varepsilon_s^{(0)})}$$

(c) 当 $a\neq b$，$r\neq s$ 时，$\langle\Psi_a^r|\mathscr{V}|\Psi_b^s\rangle=0$，因为相差两个轨道；

当 $a=b$，$r\neq s$ 时，$\langle\Psi_a^r|\mathscr{V}|\Psi_a^s\rangle=\langle r|v|s\rangle=V_{rs}$；

当 $a\neq b$，$r=s$ 时，$\langle\Psi_a^r|\mathscr{V}|\Psi_b^r\rangle=-\langle b|v|a\rangle=-V_{ba}$；方法是对换左矢中b与r位置，同上立得；

当 $a=b$，$r=s$ 时，$\langle\Psi_a^r|\mathscr{V}|\Psi_a^r\rangle=\sum_{c=1}^{N}V_{cc}-V_{aa}+V_{rr}$。

(d) $E_0^{(3)}=A_0^{(3)}+B_0^{(3)}$（按 $a=b\wedge r\neq s$，$a\neq b\wedge r=s$，$a=b\wedge r=s$ 三种情形展开 $A_0^{(3)}$，代入 $B^{(3)}$ 进行整理）。

$$=\sum_{a=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}{}'_{r}\frac{V_{ar}V_{rs}V_{sa}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_a^{(0)}-\varepsilon_s^{(0)})}+\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\frac{V_{ar}(-V_{ba})V_{rb}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_b^{(0)}-\varepsilon_r^{(0)})}$$

$$+\sum_{a=1}^{N}\sum_{r=N+1}^{+\infty}\frac{V_{ar}V_{ra}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})^2}\left(\sum_{c=1}^{N}V_{cc}+V_{rr}-V_{aa}\right)-\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\frac{V_{aa}V_{br}V_{rb}}{(\varepsilon_b^{(0)}-\varepsilon_r^{(0)})^2}$$

$$=\sum_{a=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}{}'_{r}\frac{V_{ar}V_{rs}V_{sa}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_a^{(0)}-\varepsilon_s^{(0)})}-\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\frac{V_{aa}V_{br}V_{rb}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_b^{(0)}-\varepsilon_r^{(0)})}+\sum_{c=1}^{N}\sum_{a=1}^{N}\sum_{r=N+1}^{+\infty}\frac{V_{cc}V_{ar}V_{ra}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})^2}$$

$$+V_{rr}\sum_{a=1}^{N}\sum_{r=N+1}^{+\infty}\frac{V_{ar}V_{ra}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})^2}-V_{aa}\sum_{a=1}^{N}\sum_{r=N+1}^{+\infty}\frac{V_{ar}V_{ra}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})^2}-\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\frac{V_{aa}V_{br}V_{rb}}{(\varepsilon_b^{(0)}-\varepsilon_r^{(0)})^2}$$

$$=\sum_{a=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\frac{V_{ar}V_{rs}V_{sa}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_a^{(0)}-\varepsilon_s^{(0)})}-\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\frac{V_{ar}V_{rb}V_{ba}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_b^{(0)}-\varepsilon_r^{(0)})}.$$

(e). 对闭壳层体系，$\sum_{a=1}^{N}=\sum_{a=1}^{N/2}+\sum_{\bar{a}=1}^{N/2}$，记 $A_0^{(3)'}=\sum_{a=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\frac{V_{ar}V_{rs}V_{sa}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_a^{(0)}-\varepsilon_s^{(0)})}$，$B_0^{(3)'}=\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\frac{V_{ar}V_{rb}V_{ba}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_b^{(0)}-\varepsilon_r^{(0)})}$。

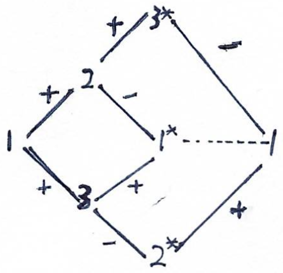
$$\therefore A_0^{(3)'}=\sum_{a=1}^{N/2}\sum_{r=\frac{N}{2}+1}^{+\infty}\sum_{s=\frac{N}{2}+1}^{+\infty}\frac{V_{ar}V_{rs}V_{sa}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_a^{(0)}-\varepsilon_s^{(0)})}+\sum_{\bar{a}=1}^{N/2}\sum_{\bar{r}=\frac{N}{2}+1}^{+\infty}\sum_{\bar{s}=\frac{N}{2}+1}^{+\infty}\frac{V_{\bar{a}\bar{r}}V_{\bar{r}\bar{s}}V_{\bar{s}\bar{a}}}{(\varepsilon_{\bar{a}}^{(0)}-\varepsilon_{\bar{r}}^{(0)})(\varepsilon_{\bar{a}}^{(0)}-\varepsilon_{\bar{s}}^{(0)})}=2\sum_{a=1}^{N/2}\sum_{r=\frac{N}{2}+1}^{+\infty}\sum_{s=\frac{N}{2}+1}^{+\infty}\frac{V_{ar}V_{rs}V_{sa}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_a^{(0)}-\varepsilon_s^{(0)})}.$$

$$B_0^{(3)'}=\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}\sum_{r=\frac{N}{2}+1}^{+\infty}\frac{V_{ar}V_{rb}V_{ba}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_b^{(0)}-\varepsilon_r^{(0)})}+\sum_{\bar{a}=1}^{N/2}\sum_{\bar{b}=1}^{N/2}\sum_{\bar{r}=\frac{N}{2}+1}^{+\infty}\frac{V_{\bar{a}\bar{r}}V_{\bar{r}\bar{b}}V_{\bar{b}\bar{a}}}{(\varepsilon_{\bar{a}}^{(0)}-\varepsilon_{\bar{r}}^{(0)})(\varepsilon_{\bar{b}}^{(0)}-\varepsilon_{\bar{r}}^{(0)})}=2\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}\sum_{r=\frac{N}{2}+1}^{+\infty}\frac{V_{ar}V_{rb}V_{ba}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_b^{(0)}-\varepsilon_r^{(0)})}$$

其中，$\sum_{a=1}^{N}=\sum_{a=1}^{N/2}+\sum_{\bar{a}=1}^{N/2}$，$\sum_{r=N+1}^{+\infty}=\sum_{r=\frac{N}{2}+1}^{+\infty}+\sum_{\bar{r}=\frac{N}{2}+1}^{+\infty}$ 分别为占据求和与非占求和裂分，但 $A_0^{(3)'}$ 中化简只有两项因为 $V_{a\bar{r}}=V_{\bar{a}r}=0$，所以干脆不写这种加项；同理，$B_0^{(3)'}$ 中省略了 $V_{a\bar{b}}$、$V_{a\bar{s}}$ 这种加项，从而在只写有效（非零）加项下化简出了 $A_0^{(3)'}$ 与 $B_0^{(3)'}$。从而

$$E_0^{(3)}(\text{closed-shell})=A_0^{(3)'}-B_0^{(3)'}=2\sum_{a=1}^{N/2}\sum_{r=\frac{N}{2}+1}^{+\infty}\sum_{s=\frac{N}{2}+1}^{+\infty}\frac{V_{ar}V_{rs}V_{sa}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_a^{(0)}-\varepsilon_s^{(0)})}-2\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}\sum_{r=\frac{N}{2}+1}^{+\infty}\frac{V_{ar}V_{rb}V_{ba}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_b^{(0)}-\varepsilon_r^{(0)})}.$$

练习6.5



Vab Vbr Vra

$$-2\sum_{a=1}^{3}\sum_{b=1}^{3}\sum_{r=4}^{6}\frac{V_{ra}V_{ab}V_{br}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_b^{(0)}-\varepsilon_r^{(0)})}$$

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

$$=-\frac{1}{2\beta^2}\sum_{i=1}^{3}\left(-\frac{3}{8}\beta^3-\frac{3}{8}\beta^3\right)=\frac{3}{8}\beta$$

即式(6.52)中第二项为$3\beta/8$.

练习6.6

(a) $$\varepsilon_0=6\alpha-2\sum_{j=-1}^{1}\left(\beta_1^2+\beta_2^2+2\beta_1\beta_2\cos\frac{2j\pi}{2N+1}\right)^{1/2}-$$

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

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

如求解下面矩阵之本征值,并进度求和亦可得此结果.

$$H=\begin{pmatrix}\alpha & \beta_2 & 0 & 0 & 0 & \beta_1\\ \beta_2 & \alpha & \beta_1 & 0 & 0 & 0\\ 0 & \beta_1 & \alpha & \beta_2 & 0 & 0\\ 0 & 0 & \beta_2 & \alpha & \beta_1 & 0\\ 0 & 0 & 0 & \beta_1 & \alpha & \beta_2\\ \beta_1 & 0 & 0 & 0 & \beta_2 & \alpha\end{pmatrix}$$

(b) $E_R=\varepsilon_0-E_0=2(\beta_1+\beta_2)-4(\beta_1^2+\beta_2^2-\beta_1\beta_2)^{1/2}-6\beta_1=\beta_1[4(1-x+x^2)^{\frac{1}{2}}+2(1+x)-6]=4\beta[\sqrt{1-x+x^2}-1+\frac{1}{2}x]$.

$\therefore E_R|_{x=0}=0.\quad E_R|_{x=1}=2\beta.$

(c). $E_R=\beta\left(\frac{3}{2}x^2+\frac{3}{4}x^3+\frac{3}{32}x^4+\frac{15}{64}x^5+o(x^5)\right)$

$\therefore E_0^{(2)}=\frac{3}{2}\beta.\quad E_0^{(3)}=\frac{3}{4}\beta.\quad E_0^{(4)}=\frac{3}{32}\beta.,\cdots$

利用特殊函数的知识. Gegenbauer多项式的生成函数给出

$$(1-2xt+t^2)^{-\lambda}=\sum_{n=0}^{+\infty}C_n^{\lambda}(x)t^n.\quad |t|<1.\ |x|<1.$$

令$x=\frac{1}{2}$. $\lambda=-\frac{1}{2}$.得

$$\sqrt{1-t+t^2}=\sum_{n=0}^{+\infty}C_n^{-\frac{1}{2}}(x)t^n\quad.\ |t|<1$$

Gegenbauer多项式有递推关系

$$(n+1)C_{n+1}^{\lambda}-2(\lambda+n)xC_n^{\lambda}+(2\lambda+n-1)C_{n-1}^{\lambda}=0$$

令$x=1/2$. $\lambda=-1/2$得.

$$(n+1)C_{n+1}^{-\frac{1}{2}}\left(\tfrac{1}{2}\right)=(n-\tfrac{1}{2})C_n^{-\frac{1}{2}}\left(\tfrac{1}{2}\right)-(n-2)C_{n-1}^{-\frac{1}{2}}\left(\tfrac{1}{2}\right).$$

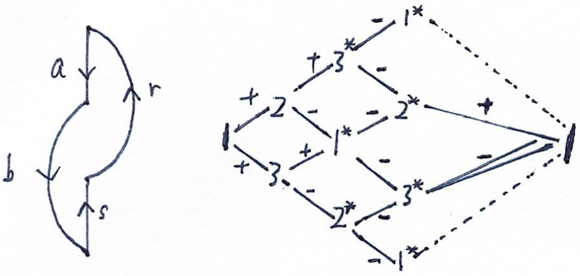
从而

$$(n+1)E_0^{(n+1)}=(n-\tfrac{1}{2})E_0^{(n)}-(n-2)E_0^{(n-1)}.$$

注:关于Gegenbauer多项式 可参考王竹溪.郭敦仁编著《特殊函数概论》5.23节.

6.4节(轨道微扰理论的图形表示)习题解析

练习6.7 a)

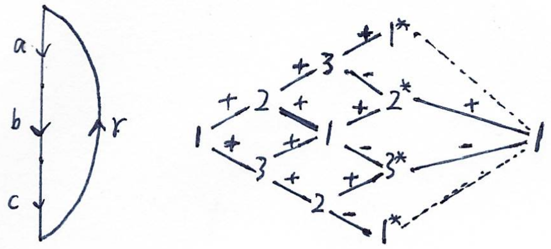


$$(-1)^{2+1}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\frac{V_{ra}V_{ab}V_{bs}V_{sr}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_b^{(0)}-\varepsilon_r^{(0)})(\varepsilon_b^{(0)}-\varepsilon_s^{(0)})}$$

$$=-\frac{2}{(2\beta)^3}\sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{k^*=1}^{3}\sum_{l^*=1}^{3}V_{ij}V_{jk^*}V_{k^*l^*}V_{l^*i}$$

$$=-\frac{1}{4\beta^3}\sum_{i=1}^{3}\left(-\frac{\beta^4}{16}+\frac{\beta^4}{16}-\frac{\beta^4}{16}-\frac{\beta^4}{16}+\frac{\beta^4}{16}-\frac{\beta^4}{16}\right)$$

$$=-\frac{3}{4\beta^3}\cdot\left(-\frac{1}{8}\beta^4\right)=\frac{3}{32}\beta=\frac{6}{64}\beta=\frac{N}{64}\beta.$$

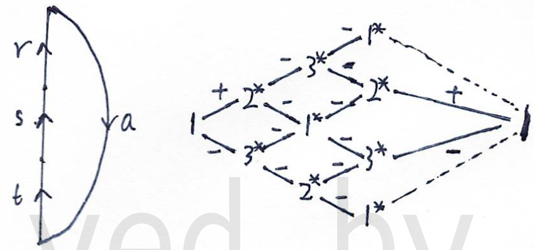


$$(-1)^{3+1}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{c=1}^{N}\sum_{r=N+1}^{+\infty}\frac{V_{ra}V_{ab}V_{bc}V_{cr}}{(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_b^{(0)}-\varepsilon_r^{(0)})(\varepsilon_c^{(0)}-\varepsilon_r^{(0)})}$$

$$=\frac{2}{(2\beta)^3}\sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{k=1}^{3}\sum_{l^*=1}^{3}V_{l^*i}V_{ij}V_{jk}V_{kl^*}$$

$$=\frac{2}{(2\beta)^3}\sum_{i=1}^{3}\left(-\frac{\beta^4}{16}+\frac{\beta^4}{16}+\frac{\beta^4}{16}+\frac{\beta^4}{16}+\frac{\beta^4}{16}-\frac{\beta^4}{16}\right)$$

$$=\frac{3}{4\beta^3}\cdot\frac{1}{8}\beta^4=\frac{3}{32}\beta=\frac{6}{64}\beta=\frac{N}{64}\beta.$$

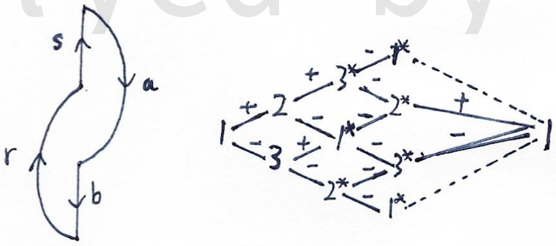


$$(-1)^{1+1}\sum_{a=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\sum_{t=N+1}^{+\infty}\frac{V_{ra}V_{at}V_{ts}V_{sr}}{(\varepsilon_a^{(0)}-\varepsilon_t^{(0)})(\varepsilon_a^{(0)}-\varepsilon_s^{(0)})(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})}$$

$$=\frac{2}{(2\beta)^3}\sum_{i=1}^{3}\sum_{j^*=1}^{3}\sum_{k^*=1}^{3}\sum_{l^*=1}^{3}V_{ij^*}V_{j^*k^*}V_{k^*l^*}V_{l^*i}$$

$$=\frac{1}{4\beta^3}\sum_{i=1}^{3}\left(\frac{\beta^4}{16}+\frac{\beta^4}{16}-\frac{\beta^4}{16}-\frac{\beta^4}{16}+\frac{\beta^4}{16}+\frac{\beta^4}{16}\right)$$

$$=\frac{3}{4\beta^3}\cdot\frac{1}{8}\beta^4=\frac{3}{32}\beta=\frac{6}{64}\beta=\frac{N}{64}\beta.$$

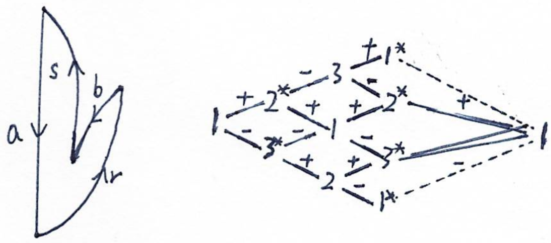


$$(-1)^{2+1}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\frac{V_{sa}V_{ab}V_{br}V_{rs}}{(\varepsilon_a^{(0)}-\varepsilon_s^{(0)})(\varepsilon_a^{(0)}-\varepsilon_r^{(0)})(\varepsilon_b^{(0)}-\varepsilon_r^{(0)})}$$

$$=-\frac{2}{(2\beta)^3}\sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{k^*=1}^{3}\sum_{l^*=1}^{3}V_{ij}V_{jk^*}V_{k^*l^*}V_{l^*i}$$

$$=+\frac{1}{4\beta^3}\sum_{i=1}^{3}\left(-\frac{\beta^4}{16}+\frac{\beta^4}{16}-\frac{\beta^4}{16}-\frac{\beta^4}{16}+\frac{\beta^4}{16}-\frac{\beta^4}{16}\right)$$

$$=\frac{3}{4\beta^3}\cdot\frac{1}{8}\beta^4=\frac{3}{32}\beta=\frac{6}{64}\beta=\frac{N}{64}\beta.$$

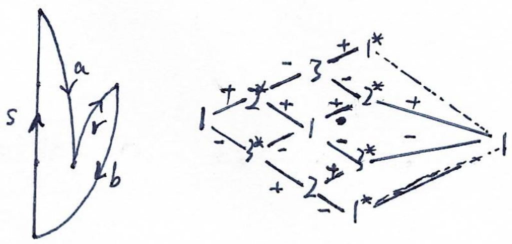


$$(-1)^{2+1}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\frac{V_{sa}V_{ar}V_{rb}V_{bs}}{(\varepsilon_a^{(0)}-\varepsilon_s^{(0)})(\varepsilon_a^{(0)}+\varepsilon_b^{(0)}-\varepsilon_r^{(0)}-\varepsilon_s^{(0)})(\varepsilon}$$

$$=-\frac{2}{(2\beta)^2\cdot4\beta}\sum_{i=1}^{3}\sum_{j^*=1}^{3}\sum_{k=1}^{3}\sum_{l^*=1}^{3}V_{ij^*}V_{j^*k}V_{kl^*}V_{l^*i}$$

$$=-\frac{1}{8\beta^3}\sum_{i=1}^{3}\left(\frac{1}{16}\beta^4+\frac{1}{16}\beta^4+\frac{1}{16}\beta^4+\frac{1}{16}\beta^4+\frac{1}{16}\beta^4+\frac{1}{16}\right.$$

$$=-\frac{3}{8\beta^3}\cdot\frac{6}{16}\beta^4=-\frac{18}{128}\beta=-\frac{3N}{128}\beta.$$



$$(-1)^{2+1}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\frac{V_{sa}V_{ar}V_{rb}V_{bs}}{(\varepsilon_a^{(0)}-\varepsilon_s^{(0)})(\varepsilon_a^{(0)}+\varepsilon_b^{(0)}-\varepsilon_r^{(0)}-\varepsilon_s^{(0)})(\varepsilon_b^{(0)}-\varepsilon_s^{(0)})}$$

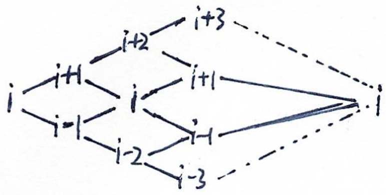
$$=-\frac{2}{(2\beta)^2\cdot4\beta}\sum_{i=1}^{3}\sum_{j^*=1}^{3}\sum_{k=1}^{3}\sum_{l^*=1}^{3}V_{ij^*}V_{j^*k}V_{kl^*}V_{l^*i}$$

$$=-\frac{1}{8\beta^3}\sum_{i=1}^{3}\left(\frac{1}{16}\beta^4+\frac{1}{16}\beta^4+\frac{1}{16}\beta^4+\frac{1}{16}\beta^4+\frac{1}{16}\beta^4+\frac{1}{16}\beta^4\right)$$

$$=-\frac{3}{8\beta^3}\cdot\frac{6}{16}\beta^4=-\frac{18}{128}\beta=-\frac{3N}{128}\beta.$$

从而对 $N=6$ 的环状多烯结构(即苯)，$E_0^{(4)}=\frac{N}{64}\beta\cdot4-\frac{3N}{128}\beta\cdot2=\frac{N}{64}.$

而对于$N>6$的体系，做普适分析图，可以看到，即使对$N>6$体系，图的形状与$N=6$并无分别，从而若就



具体的项分析，得到的正负项分布亦同，从而结果也应为

$$E_0^{(4)}=\frac{N}{64}\beta$$

从而计算$N>6$的环状多烯体系基态的共振能为$\left(\frac{1}{4}+\frac{1}{64}\right)N\beta=0.2656N\beta$.

(b). 对苯，令$N=6$，由(a)，得 $E_0^{(4)}=\frac{3}{32}\beta$.

6.5节(振动扩张及相关能)习题解析.

练习6.8 $E_0^{(2)}=\frac{1}{4}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\frac{|\langle ab\|rs\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}=\frac{1}{4}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\frac{(\langle ab|rs\rangle-\langle ab|sr\rangle)(\langle rs|ab\rangle-\langle rs|ba\rangle)}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}$

$$=\frac{1}{4}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\frac{\langle ab|rs\rangle\langle rs|ab\rangle+\langle ab|sr\rangle\langle rs|ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}-\frac{\langle ab|sr\rangle\langle rs|ab\rangle+\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}$$

$$=\frac{1}{4}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\frac{\langle ab|rs\rangle\langle rs|ab\rangle+\langle ab|rs\rangle\langle sr|ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}-\frac{\langle ab|rs\rangle\langle sr|ab\rangle+\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}$$

$$=\frac{1}{4}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\frac{\langle ab|rs\rangle\langle rs|ab\rangle+\langle ab|rs\rangle\langle rs|ab\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}-\frac{\langle ab|rs\rangle\langle rs|ba\rangle+\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}$$

$$=\frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\frac{\langle ab|rs\rangle\langle rs|ab\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}-\frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\frac{\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}$$

从而式(6.73)得证.

对于闭壳层体系,应有 $\sum_{a=1}^{N}=\sum_{a=1}^{N/2}+\sum_{\bar a=1}^{N/2}$, $\sum_{b=1}^{N}=\sum_{b=1}^{N/2}+\sum_{\bar b=1}^{N/2}$, $\sum_{r=N+1}^{+\infty}=\sum_{r=\frac{N}{2}+1}^{+\infty}+\sum_{\bar r=\frac{N}{2}+1}^{+\infty}$, $\sum_{s=N+1}^{+\infty}=\sum_{s=\frac{N}{2}+1}^{+\infty}+\sum_{\bar s=\frac{N}{2}+1}^{+\infty}$

而对于如 $\sum_{a=1}\sum_{b=1}\sum_{r=\frac{N}{2}+1}\sum_{s=\frac{N}{2}+1}$ 这种四求和指标只有一个取β向和 $\sum_{\bar a=1}^{N/2}\sum_{\bar b=1}^{N/2}\sum_{\bar r=\frac{N}{2}+1}^{+\infty}\sum_{\bar s=\frac{N}{2}+1}^{+\infty}$ 这种只有三个取β的和式

必然每一加项均为0.从而不计入此 $C_4^1=8$ 项之贡献;对于剩余项,则有.

$\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}\sum_{r=\frac{N}{2}+1}^{+\infty}\sum_{s=\frac{N}{2}+1}^{+\infty}$: $\langle ab|rs\rangle\langle rs|ab\rangle=[ar|bs][ra|sb]\neq0$, $\langle ab|rs\rangle\langle rs|ba\rangle=[ar|bs][rb|sa]\neq0$.

$\sum_{\bar a=1}^{N/2}\sum_{\bar b=1}^{N/2}\sum_{r=\frac{N}{2}+1}^{+\infty}\sum_{s=\frac{N}{2}+1}^{+\infty}$: $\langle \bar a\bar b|rs\rangle\langle rs|\bar a\bar b\rangle=[\bar ar|\bar bs][r\bar a|s\bar b]=0$, $\langle \bar a\bar b|rs\rangle\langle rs|\bar b\bar a\rangle=[\bar ar|\bar bs][r\bar b|s\bar a]=0$

$\sum_{\bar a=1}^{N/2}\sum_{b=1}^{N/2}\sum_{\bar r=\frac{N}{2}+1}^{+\infty}\sum_{s=\frac{N}{2}+1}^{+\infty}$: $\langle \bar ab|\bar rs\rangle\langle \bar rs|\bar ab\rangle=[\bar a\bar r|bs][\bar r\bar a|sb]\neq0$. $\langle \bar ab|\bar rs\rangle\langle \bar rs|b\bar a\rangle=[\bar a\bar r|bs][\bar rb|s\bar a]=0$.

$\sum_{\bar a=1}^{N/2}\sum_{b=1}^{N/2}\sum_{r=\frac{N}{2}+1}^{+\infty}\sum_{\bar s=\frac{N}{2}+1}^{+\infty}$: $\langle \bar ab|r\bar s\rangle\langle r\bar s|\bar ab\rangle=[\bar ar|b\bar s][r\bar a|\bar sb]=0$, $\langle \bar ab|r\bar s\rangle\langle r\bar s|b\bar a\rangle=[\bar ar|b\bar s][rb|\bar s\bar a]=0$

$\sum_{a=1}^{N/2}\sum_{\bar b=1}^{N/2}\sum_{\bar r=\frac{N}{2}+1}^{+\infty}\sum_{s=\frac{N}{2}+1}^{+\infty}$: $\langle a\bar b|\bar rs\rangle\langle \bar rs|a\bar b\rangle=[a\bar r|\bar bs][\bar ra|s\bar b]=0$. $\langle a\bar b|\bar rs\rangle\langle \bar rs|\bar ba\rangle=[a\bar r|\bar bs][\bar r\bar b|sa]=0$

$\sum_{a=1}^{N/2}\sum_{\bar b=1}^{N/2}\sum_{r=\frac{N}{2}+1}^{+\infty}\sum_{\bar s=\frac{N}{2}+1}^{+\infty}$: $\langle a\bar b|r\bar s\rangle\langle r\bar s|a\bar b\rangle=[ar|\bar b\bar s][ra|\bar s\bar b]\neq0$, $\langle a\bar b|r\bar s\rangle\langle r\bar s|\bar ba\rangle=[ar|\bar b\bar s][r\bar b|\bar sa]=0$.

$\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}\sum_{\bar r=\frac{N}{2}+1}^{+\infty}\sum_{\bar s=\frac{N}{2}+1}^{+\infty}$: $\langle ab|\bar r\bar s\rangle\langle \bar r\bar s|ab\rangle=[a\bar r|b\bar s][\bar ra|\bar sb]=0$. $\langle ab|\bar r\bar s\rangle\langle \bar r\bar s|ba\rangle=[a\bar r|b\bar s][\bar rb|\bar sa]=0$.

$\sum_{\bar a=1}^{N/2}\sum_{\bar b=1}^{N/2}\sum_{\bar r=\frac{N}{2}+1}^{+\infty}\sum_{\bar s=\frac{N}{2}+1}^{+\infty}$: $\langle \bar a\bar b|\bar r\bar s\rangle\langle \bar r\bar s|\bar a\bar b\rangle=[\bar a\bar r|\bar b\bar s][\bar r\bar a|\bar s\bar b]\neq0$. $\langle \bar a\bar b|\bar r\bar s\rangle\langle \bar r\bar s|\bar b\bar a\rangle=[\bar a\bar r|\bar b\bar s][\bar r\bar b|\bar s\bar a]\neq0$.

从而由式(6.73). 第一项化符有4项不为0. 第二项有2项不为0.且分母不变($\varepsilon_{\bar a}=\varepsilon_a$, $\varepsilon_{\bar b}=\varepsilon_b$, $\varepsilon_{\bar r}=\varepsilon_r$, $\varepsilon_{\bar s}=\varepsilon_s$),故

$$E_0^{(2)}=\frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\frac{\langle ab|rs\rangle\langle rs|ab\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}-\frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\frac{\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}$$

$$=\frac{1}{2}\cdot4\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}\sum_{r=\frac{N}{2}+1}^{+\infty}\sum_{s=\frac{N}{2}+1}^{+\infty}\frac{\langle ab|rs\rangle\langle rs|ab\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}-\frac{1}{2}\cdot2\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}\sum_{r=\frac{N}{2}+1}^{+\infty}\sum_{s=\frac{N}{2}+1}^{+\infty}\frac{\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}$$

$$=2\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}\sum_{r=\frac{N}{2}+1}^{+\infty}\sum_{s=\frac{N}{2}+1}^{+\infty}\frac{\langle ab|rs\rangle\langle rs|ab\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}-\sum_{a=1}^{N/2}\sum_{b=1}^{N/2}\sum_{r=\frac{N}{2}+1}^{+\infty}\sum_{s=\frac{N}{2}+1}^{+\infty}\frac{\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}.$$

此即式(6.74).

练习6.9. 注意 $\Delta\sim\varepsilon_2-\varepsilon_1$ $\therefore E_{corr}=\Delta\left(1-\sqrt{1+\frac{K_{12}^2}{\Delta^2}}\right)=\Delta\left(1-\left(1+\frac{K_{12}^2}{2\Delta^2}-\frac{K_{12}^4}{8\Delta^4}+o(\Delta^{-4})\right)\right)\doteq-\frac{K_{12}^2}{2\Delta}+\frac{K_{12}^4}{8\Delta^3}+o(\Delta^{-3})$

$$E_{corr}=-\frac{K_{12}^2}{2(\varepsilon_2-\varepsilon_1)+J_{11}+J_{22}-4J_{12}+2K_{12}}+\frac{K_{12}^4}{[2(\varepsilon_2-\varepsilon_1)+J_{11}+J_{22}-4J_{12}+2K_{12}]^3}+o[(\varepsilon_2-\varepsilon_1)^{-3}]$$

$$=-\frac{K_{12}^2}{2(\varepsilon_2-\varepsilon_1)}\left[1-\frac{J_{11}+J_{22}-4J_{12}+2K_{12}}{2(\varepsilon_2-\varepsilon_1)}+\left(\frac{J_{11}+J_{22}-4J_{12}+2K_{12}}{2(\varepsilon_2-\varepsilon_1)}\right)^2+o[(\varepsilon_2-\varepsilon_1)^{-3}]\right]+o[(\varepsilon_2-\varepsilon_1)^{-3}]$$

$$= -\frac{K_{12}^2}{2(\varepsilon_2-\varepsilon_1)} + \frac{K_{12}^2(J_{11}+J_{22}-4J_{12}+2K_{12})}{4(\varepsilon_2-\varepsilon_1)^2} + o[(\varepsilon_2-\varepsilon_1)^3]$$

从而 $E_0^{(2)} = \frac{K_{12}^2}{2(\varepsilon_1-\varepsilon_2)}$. 此即式(6.77)

$$E_0^{(3)} = \frac{K_{12}^2(J_{11}+J_{22}-4J_{12}+2K_{12})}{4(\varepsilon_1-\varepsilon_2)^2}$$，此即式(6.78).

6.6节（RS 振动扩张对参数 N 的依赖性）习题解析.

练习6.10　由式(6.68)，得

$$E_0^{(1)} = -\frac{1}{2}\sum_{i=1}^{2N}\sum_{j=1}^{2N}\langle ij||ij\rangle$$

$$= -\frac{1}{2}\left[\sum_{i=1}^{N}\langle 1_i 1_i||1_i 1_i\rangle + \sum_{i=1}^{N}\langle 1_i \bar{1}_i||1_i \bar{1}_i\rangle + \sum_{i=1}^{N}\langle \bar{1}_i 1_i||\bar{1}_i 1_i\rangle + \sum_{i=1}^{N}\langle \bar{1}_i \bar{1}_i||\bar{1}_i \bar{1}_i\rangle\right]$$

$$= -\frac{1}{2}\left(0 + \sum_{i=1}^{N}\{[1_i 1_i|\bar{1}_i\bar{1}_i] - [1_i\bar{1}_i|\bar{1}_i 1_i]\} + \sum_{i=1}^{N}\{[\bar{1}_i\bar{1}_i|1_i 1_i] - [\bar{1}_i 1_i|1_i\bar{1}_i]\} + 0\right)$$

$$= -\frac{1}{2}\sum_{i=1}^{N}J_{11} - \frac{1}{2}\sum_{i=1}^{N}J_{11} = -NJ_{11}.$$

此即式(6.86)。

$$\langle\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}|\mathcal{V}|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\rangle = \langle\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}|\mathcal{H}|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\rangle - \langle\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}|\mathcal{H}_0|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\rangle$$

$$= (2N-2)h_{11} + 2h_{22} + \sum_{\substack{j=1 \\ (2_i\bar{2}_i1_i\cdots)}}^{2N}\sum_{\substack{k=1 \\ (2_i\bar{2}_i1_i\cdots)}}^{2N}\langle jk||jk\rangle - [(2N-2)\varepsilon_1 + 2\varepsilon_2]$$

$$= (2N-2)(\varepsilon_1 - J_{11}) + 2(\varepsilon_1 - 2J_{12} + K_{12}) - (2N-2)\varepsilon_1 - 2\varepsilon_2 + \frac{1}{2}\left[\langle 2_i\bar{2}_i||2_i\bar{2}_i\rangle + \langle\bar{2}_i 2_i||\bar{2}_i 2_i\rangle + \sum_{j=1}^{N}{}'_{i}\langle 1_j\bar{1}_j||1_j\bar{1}_j\rangle + \langle\bar{1}_j 1_j||\bar{1}_j 1_j\rangle\right]$$

$$= -(2N-2)J_{11} - 4J_{12} + 2K_{12} + \frac{1}{2}[J_{22} + J_{22} + (N-1)(J_{11} + J_{11})] = -(2N-2)J_{11} - 4J_{12} + 2K_{12} + J_{22} + (N-1)J_{11}$$

$$= -NJ_{11} + J_{11} + J_{22} - 4J_{12} + 2K_{12}$$

此即式(6.90)。

6.7.1节（Hugenholtz图）习题解析

练习6.11　同胚线组结构为(a),(b),(c),(d),(e),(r,s),(t)，从而有因子$(\frac{1}{2})$；

有四个点（四阶），给分子带来$\langle rs||ac\rangle\langle at||de\rangle\langle dc||tb\rangle\langle eb||rs\rangle$（从上到下，由入到出，视左及右可得到

相对的四项乘项为$\langle rs||ac\rangle$，~~cal||~~$\langle ta||ed\rangle = \langle at||de\rangle$，$\langle dc||tb\rangle$，$\langle eb||rs\rangle$）；~~相应~~

相应的置换/对换结构为$(radte)(scb)$，有2个组，从而$l=2$；有5穴线$h=5$；故$(-1)^{5+2}=-1$

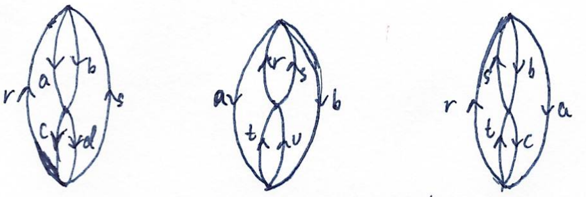
从上到下分母乘项依次为$\varepsilon_a+\varepsilon_c-\varepsilon_s-\varepsilon_r$，$\varepsilon_e+\varepsilon_b-\varepsilon_s-\varepsilon_r$，$\varepsilon_d+\varepsilon_e+\varepsilon_c-\varepsilon_t-\varepsilon_r-\varepsilon_s$；

从而将这些组合起来，这一项代表

$$-\frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{c=1}^{N}\sum_{d=1}^{N}\sum_{e=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\sum_{t=N+1}^{+\infty}\frac{\langle rs||ac\rangle\langle at||de\rangle\langle dc||tb\rangle\langle eb||rs\rangle}{(\varepsilon_a+\varepsilon_c-\varepsilon_s-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_c+\varepsilon_d+\varepsilon_e-\varepsilon_r-\varepsilon_s-\varepsilon_t)}$$

6.7.2节(Goldstone图习题解析.

练习6.12. 数据表6.2中三阶图中仅2、7属第一类个三阶Hugenholtz图;仅1、8属第二个三阶Hugenholtz图.其余都属第三个三阶Hugenholtz图。



第一个三阶Hugenholtz图 第二个三阶Hugenholtz图 第三个三阶Hugenholtz图.

显然,对每种n阶Hugenholtz图,最多有2^n种拓扑不等价情形。对于第三个三阶Hugenholtz图,有8个Goldstone图与之对应,则对第三个三阶Hugenholtz图,其必与这$2^3=8$个Goldstone图等价;对于前二种,内部结构固定,只有等价与不等价如前所示,即分别对应2、7图与1、8图。从而对三阶来说Hugenholtz图的数学价值等于Goldstone图12幅.当然,通过数学表达式进行直接验证也可,下面是证明:

由式(6.75),记第一个Hugenholtz图对应的能量为$E_{01}^{(3)}$,则

$$\cancel{E_{01}^{(3)}=\frac{1}{8}\sum\sum\sum\sum\sum\sum}$$

$$E_{01}^{(3)}=\frac{1}{8}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{c=1}^{N}\sum_{d=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\frac{\langle ab||rs\rangle\langle cd||ab\rangle\langle rs||cd\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_c+\varepsilon_d-\varepsilon_r-\varepsilon_s)}.$$

若验证$E_{01}^{(3)}$等于图2、7所示项之和,则证得第一个三阶Hugenholtz图等于第2、7幅Goldstone图等价.后者和为

$$\frac{1}{2}\sum_{abcdrs}\frac{\langle rs|cb\rangle\langle cb|ad\rangle\langle ad|rs\rangle}{(\varepsilon_c+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_a+\varepsilon_d-\varepsilon_r-\varepsilon_s)}-\frac{1}{2}\sum_{abcdrs}\frac{\langle sr|db\rangle\langle db|ac\rangle\langle ac|rs\rangle}{(\varepsilon_b+\varepsilon_d-\varepsilon_r-\varepsilon_s)(\varepsilon_a+\varepsilon_c-\varepsilon_r-\varepsilon_s)}$$

$$=\frac{1}{2}\sum_{abcdrs}\frac{\langle rs|db\rangle\langle db|ac\rangle\langle ac|rs\rangle}{(\varepsilon_a+\varepsilon_c-\varepsilon_r-\varepsilon_s)(\varepsilon_b+\varepsilon_d-\varepsilon_r-\varepsilon_s)}-\frac{1}{2}\sum_{abcdrs}\frac{\langle ac|rs\rangle\langle db|ac\rangle\langle ac|rs\rangle}{(\varepsilon_b+\varepsilon_d-\varepsilon_r-\varepsilon_s)(\varepsilon_a+\varepsilon_c-\varepsilon_r-\varepsilon_b)}$$

$$=\frac{1}{2}\sum_{abcdrs}\frac{\langle db|ac\rangle\langle ac|rs\rangle[\langle rs|db\rangle-\langle sr|db\rangle]}{(\varepsilon_a+\varepsilon_c-\varepsilon_r-\varepsilon_s)(\varepsilon_b+\varepsilon_d-\varepsilon_r-\varepsilon_s)}=\frac{1}{2}\sum_{abcdrs}\frac{\langle dc|ab\rangle\langle ab|rs\rangle[\langle rs|dc\rangle-\langle sr|dc\rangle]}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_c+\varepsilon_d-\varepsilon_r-\varepsilon_s)}$$

下面化简$E_{01}^{(3)}$:

$$E_{01}^{(3)}=\frac{1}{8}\sum_{abcdrs}\frac{\langle ab||rs\rangle\langle cd||ab\rangle\langle rs||cd\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_c+\varepsilon_d-\varepsilon_r-\varepsilon_s)}$$

$$=\frac{1}{8}\sum_{abcdrs}\frac{1}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_c+\varepsilon_d-\varepsilon_r-\varepsilon_s)}[\langle ab|rs\rangle-\langle ab|sr\rangle][\langle cd|ab\rangle-\langle cd|ba\rangle][\langle rs|cd\rangle-\langle rs|dc\rangle].$$

$$=\frac{1}{8}\sum_{abcdrs}\frac{1}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_c+\varepsilon_d-\varepsilon_r-\varepsilon_s)}[\langle ab|rs\rangle\langle cd|ab\rangle\langle rs|cd\rangle-\langle ab|rs\rangle\langle cd|ab\rangle\langle rs|dc\rangle-\langle ab|rs\rangle\langle cd|ba\rangle\langle rs|cd\rangle$$
$$+\langle ab|rs\rangle\langle cd|ba\rangle\langle rs|dc\rangle-\langle ab|sr\rangle\langle cd|ab\rangle\langle rs|cd\rangle+\langle ab|sr\rangle\langle cd|ab\rangle\langle rs|dc\rangle$$
$$+\langle ab|sr\rangle\langle cd|ba\rangle\langle rs|cd\rangle-\langle ab|sr\rangle\langle cd|ba\rangle\langle rs|dc\rangle]$$

$$=\frac{1}{8}\sum_{abcdrs}\frac{1}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_c+\varepsilon_d-\varepsilon_r-\varepsilon_s)}[\langle ab|rs\rangle\langle dc|ab\rangle\langle rs|dc\rangle-\langle ab|rs\rangle\langle dc|ab\rangle\langle rs|cd\rangle$$
$$-\langle ab|rs\rangle\langle dc|ab\rangle\langle rs|cd\rangle+\langle ab|rs\rangle\langle dc|ab\rangle\langle rs|cd\rangle-\langle ab|sr\rangle\langle dc|ab\rangle\langle rs|dc\rangle$$
$$+\langle ab|sr\rangle\langle dc|ab\rangle\langle rs|cd\rangle+\langle ab|sr\rangle\langle dc|ba\rangle\langle rs|dc\rangle-\langle ab|sr\rangle\langle dc|ba\rangle\langle rs|cd\rangle]$$

$$=\frac{1}{8}\sum_{abcdrs}\frac{1}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_c+\varepsilon_d-\varepsilon_r-\varepsilon_s)}[\langle ab|rs\rangle\langle dc|ab\rangle\langle rs|dc\rangle-\langle ab|rs\rangle\langle dc|ab\rangle\langle sr|dc\rangle$$

$$- \langle ab|rs\rangle\langle dc|ab\rangle\langle rs|cd\rangle + \langle ab|rs\rangle\langle dc|ab\rangle\langle rs|dc\rangle - \langle ab|rs\rangle\langle dc|ab\rangle\langle sr|dc\rangle$$

$$+ \langle ab|rs\rangle\langle dc|ab\rangle\langle sr|dc\rangle + \langle ab|rs\rangle\langle dc|ab\rangle\langle rs|dc\rangle - \langle ab|rs\rangle\langle dc|ab\rangle\langle sr|dc\rangle]$$

$$= \frac{1}{2}\sum_{abcdrs}\frac{\langle ab|rs\rangle\langle dc|ab\rangle[\langle rs|dc\rangle - \langle sr|dc\rangle]}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_c+\varepsilon_d-\varepsilon_r-\varepsilon_s)}.$$

从而第一个三阶图Hugenholtz图与第2.7幅Goldstone图等价.

同理,记第2个三阶Hugenholtz图对应能量为$E^{(3)}_{0\mathrm{II}}$.则

$$E^{(3)}_{0\mathrm{II}} = \frac{1}{8}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{r=N+1}^{+\infty}\sum_{s=N+1}^{+\infty}\sum_{t=N+1}^{+\infty}\sum_{u=N+1}^{+\infty}\frac{\langle ab||rs\rangle\langle rs||tu\rangle\langle tu||ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_a+\varepsilon_b-\varepsilon_t-\varepsilon_u)}.$$

若验证$E^{(3)}_{0\mathrm{II}}$等于图1.8所示项之和,则证得第二个三阶Hugenholtz图与第1.8幅Goldstone图等价.后者和为

$$\frac{1}{2}\sum_{abrstu}\frac{\langle ab|ru\rangle\langle ru|ts\rangle\langle ts|ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_u)(\varepsilon_a+\varepsilon_b-\varepsilon_t-\varepsilon_s)} - \frac{1}{2}\sum_{abrstu}\frac{\langle ab|rt\rangle\langle tr|us\rangle\langle us|ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_u)(\varepsilon_a+\varepsilon_b-\varepsilon_t-\varepsilon_s)}$$

$$= \frac{1}{2}\sum_{abrstu}\frac{\langle ab|rt\rangle\langle rt|us\rangle\langle us|ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_t)(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_s)} - \frac{1}{2}\sum_{abrstu}\frac{\langle ab|rt\rangle\langle tr|us\rangle\langle us|ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_t)(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_s)}$$

$$= \frac{1}{2}\sum_{abrstu}\frac{\langle ab|rt\rangle\langle us|ab\rangle[\langle rt|us\rangle - \langle tr|us\rangle]}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_t)(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_s)}$$

而$E^{(3)}_{0\mathrm{II}}$化简为

$$E^{(3)}_{0\mathrm{II}} = \frac{1}{8}\sum_{abrstu}\frac{\langle ab||rs\rangle\langle rs||tu\rangle\langle tu||ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_a+\varepsilon_b-\varepsilon_t-\varepsilon_u)}$$

$$= \frac{1}{8}\sum_{abrstu}\frac{[\langle ab|rs\rangle - \langle ab|sr\rangle][\langle rs|tu\rangle - \langle rs|ut\rangle][\langle tu|ab\rangle - \langle tu|ba\rangle]}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_t)(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_s)}$$

$$= \frac{1}{8}\sum_{abrstu}\frac{1}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_t)(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_s)}[\langle ab|rs\rangle\langle rs|tu\rangle\langle tu|ab\rangle - \langle ab|rs\rangle\langle rs|tu\rangle\langle tu|ba\rangle$$

$$- \langle ab|rs\rangle\langle rs|ut\rangle\langle tu|ab\rangle + \langle ab|rs\rangle\langle rs|ut\rangle\langle tu|ba\rangle - \langle ab|sr\rangle\langle rs|tu\rangle\langle tu|ab\rangle$$

$$+ \langle ab|sr\rangle\langle rs|tu\rangle\langle tu|ba\rangle + \langle ab|sr\rangle\langle rs|ut\rangle\langle tu|ab\rangle - \langle ab|sr\rangle\langle rs|ut\rangle\langle tu|ba\rangle]$$

$$= \frac{1}{8}\sum_{abrstu}\frac{1}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_t)(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_s)}[\langle ab|rt\rangle\langle rt|su\rangle\langle su|ab\rangle - \langle ab|rt\rangle\langle rt|su\rangle\langle su|ba\rangle$$

$$- \langle ab|rt\rangle\langle rt|us\rangle\langle su|ab\rangle + \langle ab|rt\rangle\langle rt|us\rangle\langle su|ba\rangle - \langle ab|tr\rangle\langle rt|su\rangle\langle su|ab\rangle$$

$$+ \langle ab|tr\rangle\langle rt|su\rangle\langle su|ba\rangle + \langle ab|tr\rangle\langle rt|us\rangle\langle su|ab\rangle - \langle ab|tr\rangle\langle rt|us\rangle\langle su|ba\rangle]$$

$$= \frac{1}{8}\sum_{abrstu}\frac{1}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_t)(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_s)}[\langle ab|rt\rangle\langle rt|us\rangle\langle us|ab\rangle - \langle ab|rt\rangle\langle rt|su\rangle\langle su|ba\rangle$$

$$- \langle ab|rt\rangle\langle rt|su\rangle\langle us|ab\rangle + \langle ab|rt\rangle\langle us|ab\rangle\langle rt|us\rangle - \langle ab|tr\rangle\langle rt|su\rangle\langle su|ab\rangle$$

$$+ \langle ab|rt\rangle\langle tr|su\rangle\langle us|ab\rangle + \langle ab|rt\rangle\langle tr|su\rangle\langle us|ab\rangle - \langle ab|rt\rangle\langle tr|us\rangle\langle us|ab\rangle]$$

$$= \frac{1}{2}\sum_{abrstu}\frac{\langle ab|rt\rangle\langle us|ab\rangle[\langle rt|us\rangle - \langle tr|us\rangle]}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_t)(\varepsilon_a+\varepsilon_b-\varepsilon_u-\varepsilon_s)}$$

从而第二个三阶Hugenholtz图与第1.8幅Goldstone图等价.

同样去验证第三个Hugenholtz图与3.4.5.6.9.10.11.12幅Goldstone图等价,但这个比较简单:打开教材P361第三个Hugenholtz图对应到相应Goldstone中项即可.不再单独验证.

6.7.4节(何为连接图定理?)习题解析

练习6.13. 注意到H_2间无相互作用,因此诸如$\langle 1_i 1_i | 2_j 2_j \rangle = 0$, $i \neq j$. 从而多重求和化为对每个H_2单独运算后求和. 从而必然每幅Goldstone图都得到N倍单H_2结果, 从而$E_0^{(n)} \propto N$得证.