课堂练习

练习1：推导以下结论：$E_0+\delta E_0^{(1)}=\langle\Phi_0|\hat{H}|\Phi_0\rangle\equiv E_0^{(\mathrm{HF})}$

解：零阶基态能量为$E_0=\langle\Phi_0|\hat{H}_0|\Phi_0\rangle=\sum\limits_a\varepsilon_a$，一阶能量修正为

$\delta E_0^{(1)}=\langle\Phi_0|\hat{V}|\Phi_0\rangle=-\frac{1}{2}\sum\limits_{a,b}\langle ab||ab\rangle$，两者相加得

$$E_0+\delta E_0^{(1)}=\sum_a\varepsilon_a-\frac{1}{2}\sum_{a,b}\langle ab||ab\rangle=\sum_a\Big(h_{aa}+\sum_b\langle ab||ab\rangle\Big)-\frac{1}{2}\sum_{a,b}\langle ab||ab\rangle=\sum_a h_{aa}+\frac{1}{2}\sum_{a,b}\langle ab||ab\rangle=\langle\Phi_0|\hat{H}|\Phi_0\rangle$$

练习2：从$\delta E_0^{(2)}=\frac{1}{4}\sum\limits_{a,b}\sum\limits_{r,s}\frac{|\langle ab||rs\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}$推导出下式

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

解：显然

$$\begin{aligned}
\delta E_0^{(2)}&=\frac{1}{4}\sum_{a,b}\sum_{r,s}\frac{|\langle ab||rs\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}=\frac{1}{4}\sum_{a,b}\sum_{r,s}\frac{\langle ab||rs\rangle\langle rs||ab\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}\\
&=\frac{1}{4}\sum_{a,b}\sum_{r,s}\frac{(\langle ab|rs\rangle-\langle ab|sr\rangle)(\langle rs|ab\rangle-\langle rs|ba\rangle)}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}\\
&=\frac{1}{4}\sum_{a,b}\sum_{r,s}\frac{\langle ab|rs\rangle\langle rs|ab\rangle-\langle ab|sr\rangle\langle rs|ab\rangle-\langle ab|rs\rangle\langle rs|ba\rangle+\langle ab|sr\rangle\langle rs|ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}\\
&=\frac{1}{4}\sum_{a,b}\sum_{r,s}\frac{\langle ab|rs\rangle\langle rs|ab\rangle-\langle ba|rs\rangle\langle rs|ab\rangle-\langle ab|rs\rangle\langle rs|ba\rangle+\langle ab|sr\rangle\langle sr|ab\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}\text{（交换哑标）}\\
&=\frac{1}{2}\sum_{a,b}\sum_{r,s}\Big[\frac{\langle ab|rs\rangle\langle rs|ab\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}-\frac{\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}\Big]
\end{aligned}$$

练习3：证明对于闭壳层体系，练习1的结论还可进一步化简为

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

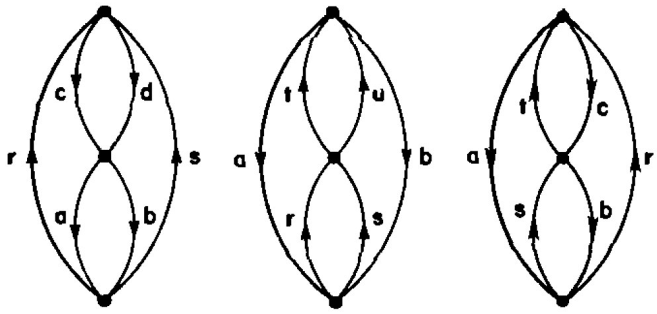
证明：若为闭壳层体系，则

$$\begin{aligned}
\delta E_0^{(2)}&=\frac{1}{2}\sum_{a,b}\sum_{r,s}\frac{\langle ab|rs\rangle\langle rs|ab\rangle-\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}\text{（此处不考虑自旋轨道）}\\
&=\frac{1}{2}\sum_{a,b}\sum_{r,s}\frac{\langle ab|rs\rangle\langle rs|ab\rangle+\langle\bar{a}b|\bar{r}s\rangle\langle\bar{r}s|\bar{a}b\rangle+\langle a\bar{b}|r\bar{s}\rangle\langle r\bar{s}|a\bar{b}\rangle+\langle\bar{a}\bar{b}|\bar{r}\bar{s}\rangle\langle\bar{r}\bar{s}|\bar{a}\bar{b}\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}\\
&\quad-\frac{1}{2}\sum_{a,b}\sum_{r,s}\frac{\langle ab|rs\rangle\langle rs|ba\rangle+\langle\bar{a}\bar{b}|\bar{r}\bar{s}\rangle\langle\bar{r}\bar{s}|\bar{b}\bar{a}\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}\text{（此处考虑自旋轨道）}\\
&=\sum_{a,b}\sum_{r,s}\frac{2\langle ab|rs\rangle\langle rs|ab\rangle-\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}
\end{aligned}$$

练习4：推导如下的三阶能量修正表达式

$$
\begin{aligned}
\delta E_0^{(3)} = &\frac{1}{8}\sum_{a,b,c,d}\sum_{r,s}\frac{\langle ab||rs\rangle\langle rs||cd\rangle\langle cd||ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_c+\varepsilon_d-\varepsilon_r-\varepsilon_s)} \\
&+\frac{1}{8}\sum_{a,b}\sum_{r,s,t,u}\frac{\langle ab||rs\rangle\langle rs||tu\rangle\langle tu||ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_a+\varepsilon_b-\varepsilon_t-\varepsilon_u)} \\
&+\sum_{a,b,c}\sum_{r,s,t}\frac{\langle ab||rs\rangle\langle rt||ac\rangle\langle cs||tb\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_a+\varepsilon_c-\varepsilon_r-\varepsilon_t)}
\end{aligned}
$$

解：直接使用三阶修正的一般表达式，推导过于繁琐，现采用Hugenholtz图加以说明。对于三阶能量修正，仅有如下三种Hugenholtz图是合理的（满足一笔画条件）



对于图1，其等价的线对有三组（a与b，c与d，r与s），因此对称性系数为$(\frac{1}{2})^3=\frac{1}{8}$；其空穴线有4条，子图中闭环有2个（$a\to r\to c\to a$，$b\to s\to d\to b$），因此符号系数为$(-1)^{4+2}=1$，从而这部分能量写作

$$
\begin{aligned}
\delta E_{\text{part1}}^{(3)} &= (\frac{1}{2})^3(-1)^{4+2}\sum_{a,b,c,d}\sum_{r,s}\frac{\langle ab||rs\rangle\langle rs||cd\rangle\langle cd||ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_c+\varepsilon_d-\varepsilon_r-\varepsilon_s)} \\
&= \frac{1}{8}\sum_{a,b,c,d}\sum_{r,s}\frac{\langle ab||rs\rangle\langle rs||cd\rangle\langle cd||ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_c+\varepsilon_d-\varepsilon_r-\varepsilon_s)}
\end{aligned}
$$

对于图2，其等价的线对有三组（a与b，r与s，t与u），因此对称性系数为$(\frac{1}{2})^3=\frac{1}{8}$；其空穴线有2条，子图中闭环有2个（$a\to r\to t\to a$，$b\to s\to u\to b$），因此符号系数为$(-1)^{4+2}=1$，

$$
\begin{aligned}
\delta E_{\text{part2}}^{(3)} &= (\frac{1}{2})^3(-1)^{2+2}\sum_{a,b}\sum_{r,s,t,u}\frac{\langle ab||rs\rangle\langle rs||tu\rangle\langle tu||ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_a+\varepsilon_b-\varepsilon_t-\varepsilon_u)} \\
&= \frac{1}{8}\sum_{a,b}\sum_{r,s,t,u}\frac{\langle ab||rs\rangle\langle rs||tu\rangle\langle tu||ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_a+\varepsilon_b-\varepsilon_t-\varepsilon_u)}
\end{aligned}
$$

对于图3，其无等价的线，因此对称性系数为$(\frac{1}{2})^0=1$；其空穴线有3条，子图中闭环有3个（$a\to r\to a$，$b\to s\to b$，$c\to t\to c$），因此符号系数为$(-1)^{3+3}=1$，

$$
\begin{aligned}
\delta E_{\text{part3}}^{(3)} &= (\frac{1}{2})^0(-1)^{3+3}\sum_{a,b,c}\sum_{r,s,t}\frac{\langle ab||rs\rangle\langle rt||ac\rangle\langle cs||tb\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_a+\varepsilon_c-\varepsilon_r-\varepsilon_t)} \\
&= \sum_{a,b,c}\sum_{r,s,t}\frac{\langle ab||rs\rangle\langle rt||ac\rangle\langle cs||tb\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)(\varepsilon_a+\varepsilon_c-\varepsilon_r-\varepsilon_t)}
\end{aligned}
$$

以上三部分能量相加，即可得到题目中三阶能量修正的表达式。

练习5：推导H_2最小基组的三阶能量修正的表达式（直接使用三阶修正的一般表达式）为

$$
\delta E_0^{(3)} = \frac{K_{12}^2[J_{11}+J_{22}+2K_{12}-4J_{12}]}{4(\varepsilon_1-\varepsilon_2)^2}
$$

解：根据三阶修正的一般表达式，我们有：

$$\delta E_0^{(3)}=\sum_{k\neq 0}\sum_{m\neq 0}\frac{V_{0k}V_{km}V_{m0}}{(E_0^{(0)}-E_k^{(0)})(E_0^{(0)}-E_m^{(0)})}-\delta E_0^{(1)}\sum_{k\neq 0}\frac{|V_{k0}|^2}{(E_0^{(0)}-E_k^{(0)})^2}=\frac{V_{11}|V_{10}|^2-\delta E_0^{(1)}|V_{10}|^2}{(E_0^{(0)}-E_1^{(0)})^2}$$

其中

$$\begin{cases}(E_0^{(0)}-E_1^{(0)})^2=(2\varepsilon_1-2\varepsilon_2)^2=4(\varepsilon_1-\varepsilon_2)^2\\ \delta E_0^{(1)}=\langle\Phi_0|\hat{V}|\Phi_0\rangle=-\frac{1}{2}\sum\limits_{a,b}\langle ab||ab\rangle=-\langle 1\bar{1}||1\bar{1}\rangle=-J_{11}\\ V_{10}=\langle\Phi_1|\hat{V}|\Phi_0\rangle=\langle\Phi_1|(\hat{H}-\hat{H}_0)|\Phi_0\rangle=K_{12}\\ V_{11}=\langle\Phi_1|\hat{V}|\Phi_1\rangle=\langle\Phi_1|(\hat{H}-\hat{H}_0)|\Phi_1\rangle=(2h_{22}+J_{22})-2\varepsilon_2\\ \qquad=(2h_{22}+J_{22})-2(h_{22}+2J_{12}-K_{12})=J_{22}-4J_{12}+2K_{12}\end{cases}$$

代入原式得

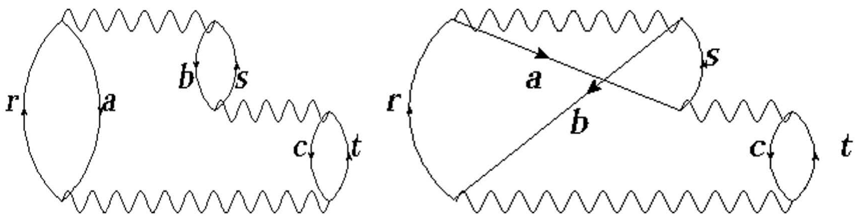
$$\delta E_0^{(3)}=\frac{(J_{22}-4J_{12}+2K_{12})K_{12}^2-(-J_{11})K_{12}^2}{4(\varepsilon_1-\varepsilon_2)^2}=\frac{K_{12}^2[J_{11}+J_{22}+2K_{12}-4J_{12}]}{4(\varepsilon_1-\varepsilon_2)^2}$$

练习6：利用闭壳层体系的二阶能量修正公式，直接写出N个无相互作用的H_2分子的二阶能量修正

解：由$\delta E_0^{(2)}=\sum\limits_{a,b}\sum\limits_{r,s}\frac{2\langle ab|rs\rangle\langle rs|ab\rangle-\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}$，得N个无相互作用的$H_2$分子的二阶能量修正为

$$\delta E_0^{(2)}=\sum_{i=1}^{N}\frac{2\langle 1_i1_i|2_i2_i\rangle\langle 2_i2_i|1_i1_i\rangle-\langle 1_i1_i|2_i2_i\rangle\langle 2_i2_i|1_i1_i\rangle}{\varepsilon_1+\varepsilon_1-\varepsilon_2-\varepsilon_2}=\sum_{i=1}^{N}\frac{\langle 1_i1_i|2_i2_i\rangle\langle 2_i2_i|1_i1_i\rangle}{2(\varepsilon_1-\varepsilon_2)}=\frac{NK_{12}^2}{2(\varepsilon_1-\varepsilon_2)}$$

练习7：写出如下Goldstone图对应的相关能代数表达式



解：对左图，其相关能的表达式为

$$E_{x1}^{(3)}=(-1)^{3+3}\sum_{a,b,c}\sum_{r,s,t}\frac{\langle ac|rt\rangle\langle bt|sc\rangle\langle rs|ab\rangle}{(\varepsilon_a+\varepsilon_c-\varepsilon_r-\varepsilon_t)(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)}$$

对右图，其相关能的表达式为

$$E_{x2}^{(3)}=(-1)^{3+2}\sum_{a,b,c}\sum_{r,s,t}\frac{\langle bc|rt\rangle\langle at|sc\rangle\langle rs|ab\rangle}{(\varepsilon_b+\varepsilon_c-\varepsilon_r-\varepsilon_t)(\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)}$$

练习8：对于CCD方法，请用双重激发的系数，推导出四重激发的系数的表达式

$$\begin{aligned}c_{ab}^{rs}*c_{cd}^{tu}\equiv{}& c_{ab}^{rs}c_{cd}^{tu}-\overline{c_{ab}^{rs}*c_{cd}^{tu}}\\ \equiv{}& c_{ab}^{rs}c_{cd}^{tu}-c_{ac}^{rs}c_{bd}^{tu}+c_{ad}^{rs}c_{bc}^{tu}-c_{ab}^{rt}c_{cd}^{su}+c_{ac}^{rt}c_{bd}^{su}-c_{ad}^{rt}c_{bc}^{su}\\ &+c_{ab}^{ru}c_{cd}^{st}-c_{ac}^{ru}c_{bd}^{st}+c_{ad}^{ru}c_{bc}^{st}+c_{ab}^{tu}c_{cd}^{rs}-c_{ac}^{tu}c_{bd}^{rs}+c_{ad}^{tu}c_{bc}^{rs}\\ &-c_{ab}^{su}c_{cd}^{rt}+c_{ac}^{su}c_{bd}^{rt}-c_{ad}^{su}c_{bc}^{rt}+c_{ab}^{st}c_{cd}^{ru}-c_{ac}^{st}c_{bd}^{ru}+c_{ad}^{st}c_{bc}^{ru}\end{aligned}$$

解：显然，用团簇算符$\hat{T}_2$两次作用于基态波函数$|\Phi_0\rangle$，可得四重激发，即

$$\frac{1}{2}\hat{T}_2^2|\Phi_0\rangle=\frac{1}{2}\sum_{\substack{a<b\\ r<s}}\sum_{\substack{c<d\\ t<u}}c_{ab}^{rs}c_{cd}^{tu}\hat{a}_r^\dagger\hat{a}_s^\dagger\hat{a}_b\hat{a}_a\hat{a}_t^\dagger\hat{a}_u^\dagger\hat{a}_d\hat{a}_c|\Phi_0\rangle=\sum_{\substack{a<b<c<d\\ r<s<t<u}}c_{ab}^{rs}*c_{cd}^{tu}|\Phi_{abcd}^{rstu}\rangle$$

现在我们通过观察哑标来求出$c_{ab}^{rs}*c_{cd}^{tu}$，显然右边的哑标限制较大，因此对于同一个波函数，可能存在多种哑标的组合形式，它等价于左边只用一种系数表示的波函数。对于右边的a,b,c,d这四个哑标，当限制条件从$a<b<c<d$放宽为$a<b,c<d$时，其等价于左边ab,cd的哑标组合有ab,cd，ac,bd，ad,bc，bc,ad，bd,ac，cd,ab，共计6种；同理，对于右边的r,s,t,u这四个哑标，其其等价于左边rs,tu的哑标组合有rs,tu，rt,su，ru,st，st,ru，su,rt，tu,rs，共计6种。
看起来，这两种哑标组合相互拼合，可以得到$6\times 6=36$种系数写法，但请注意，在这36种系数写法中，可以划出18组，每一组的系数写法是等价的（如ab,cd与rs,tu拼合成$c_{ab}^{rs}c_{cd}^{tu}$，而cd,ab与tu,rs拼合成$c_{cd}^{tu}c_{ab}^{rs}$，两者是等价的），因此最后可以写出18组不同的系数（写法可参照题面给出的等式）。
接下来我们要写出这些系数前面的符号，显然右边的$c_{ab}^{rs}c_{cd}^{tu}$与左边的$c_{ab}^{rs}c_{cd}^{tu}$符号一致，均为"$+$"，且代表的波函数变换过程均为$|\dots abcd\dots\rangle\to|\dots rstu\dots\rangle$，接下来只需要看其余的系数对应的激发前波函数和激发后波函数，即可确定符号。对于哑标组合ab,cd，ac,bd，ad,bc，bc,ad，bd,ac，cd,ab，其对应的激发前波函数为$|\dots abcd\dots\rangle$，$|\dots acbd\dots\rangle$，$|\dots adbc\dots\rangle$，$|\dots bcad\dots\rangle$，$|\dots bdac\dots\rangle$，$|\dots cdab\dots\rangle$，它们变换到$|\dots abcd\dots\rangle$需要的交换次数为0，1，2，2，3，4；同理，对于哑标组合rs,tu，rt,su，ru,st，st,ru，su,rt，tu,rs，其对应的激发后波函数为$|\dots rstu\dots\rangle$，$|\dots rtsu\dots\rangle$，$|\dots rust\dots\rangle$，$|\dots stru\dots\rangle$，$|\dots surt\dots\rangle$，$|\dots turs\dots\rangle$，它们变换到$|\dots rstu\dots\rangle$需要的交换次数为0，1，2，2，3，4。从而，我们得到如下等式：

$$\begin{aligned}
c_{ab}^{rs}*c_{cd}^{tu}=&(-1)^{0+0}c_{ab}^{rs}c_{cd}^{tu}+(-1)^{1+0}c_{ac}^{rs}c_{bd}^{tu}+(-1)^{2+0}c_{ad}^{rs}c_{bc}^{tu}+(-1)^{0+1}c_{ab}^{rt}c_{cd}^{su}+(-1)^{1+1}c_{ac}^{rt}c_{bd}^{su}+(-1)^{2+1}c_{ad}^{rt}c_{bc}^{su}\\
&+(-1)^{0+2}c_{ab}^{ru}c_{cd}^{st}+(-1)^{1+2}c_{ac}^{ru}c_{bd}^{st}+(-1)^{2+2}c_{ad}^{ru}c_{bc}^{st}+(-1)^{0+4}c_{ab}^{tu}c_{cd}^{rs}+(-1)^{1+4}c_{ac}^{tu}c_{bd}^{rs}+(-1)^{2+4}c_{ad}^{tu}c_{bc}^{rs}\\
&+(-1)^{0+3}c_{ab}^{su}c_{cd}^{rt}+(-1)^{1+3}c_{ac}^{su}c_{bd}^{rt}+(-1)^{2+3}c_{ad}^{su}c_{bc}^{rt}+(-1)^{0+2}c_{ab}^{st}c_{cd}^{ru}+(-1)^{1+2}c_{ac}^{st}c_{bd}^{ru}+(-1)^{2+2}c_{ad}^{st}c_{bc}^{ru}\\
=&c_{ab}^{rs}c_{cd}^{tu}-c_{ac}^{rs}c_{bd}^{tu}+c_{ad}^{rs}c_{bc}^{tu}-c_{ab}^{rt}c_{cd}^{su}+c_{ac}^{rt}c_{bd}^{su}-c_{ad}^{rt}c_{bc}^{su}\\
&+c_{ab}^{ru}c_{cd}^{st}-c_{ac}^{ru}c_{bd}^{st}+c_{ad}^{ru}c_{bc}^{st}+c_{ab}^{tu}c_{cd}^{rs}-c_{ac}^{tu}c_{bd}^{rs}+c_{ad}^{tu}c_{bc}^{rs}\\
&-c_{ab}^{su}c_{cd}^{rt}+c_{ac}^{su}c_{bd}^{rt}-c_{ad}^{su}c_{bc}^{rt}+c_{ab}^{st}c_{cd}^{ru}-c_{ac}^{st}c_{bd}^{ru}+c_{ad}^{st}c_{bc}^{ru}
\end{aligned}$$

练习9：应用以上CCD方程分析N个无相互作用的H_2分子的相关能，验证其满足大小一致性

解：CCD方程组为

$$\begin{cases}
E_{corr}=\sum\limits_{\substack{a<b\\r<s}}c_{ab}^{rs}\langle\Phi_0|\hat{H}|\Phi_{ab}^{rs}\rangle\\
\langle\Phi_{ab}^{rs}|\hat{H}|\Phi_0\rangle+\sum\limits_{\substack{c<d\\t<u}}c_{cd}^{tu}\langle\Phi_{ab}^{rs}|\hat{H}|\Phi_{cd}^{tu}\rangle+\sum\limits_{\substack{a\neq c<d\neq b\\r\neq t<u\neq s}}c_{ab}^{rs}*c_{cd}^{tu}\langle\Phi_0|\hat{H}|\Phi_{cd}^{tu}\rangle=E_{corr}c_{ab}^{rs}
\end{cases}$$

对于题中所述体系，记$|\Phi_0\rangle=|1_1\bar{1}_1\dots 1_N\bar{1}_N\rangle$，$|\Phi_i\rangle=|1_1\bar{1}_1\dots 2_i\bar{2}_i\dots 1_N 1_N\rangle$，其中$i=1,2,\dots,N$，则第一个等式为$E_{corr}=\sum\limits_{i=1}^{N}c_{1_i\bar{1}_i}^{2_i\bar{2}_i}\langle\Phi_0|\hat{H}|\Phi_i\rangle=\sum\limits_{i=1}^{N}c_{1_i\bar{1}_i}^{2_i\bar{2}_i}K_{12}$，记$c_{1_i\bar{1}_i}^{2_i\bar{2}_i}\equiv c$，则$E_{corr}=NcK_{12}$。
接下来看第二个等式，代入可得

$$\langle\Phi_i|\hat{H}|\Phi_0\rangle+\sum_{j=1}^{N}c_{1_j\bar{1}_j}^{2_j\bar{2}_j}\langle\Phi_i|\hat{H}|\Phi_j\rangle+\sum_{\substack{j=1\\j\neq i}}^{N}c_{1_i\bar{1}_i}^{2_i\bar{2}_i}c_{1_j\bar{1}_j}^{2_j\bar{2}_j}\langle\Phi_0|\hat{H}|\Phi_j\rangle=E_{corr}c_{1_i\bar{1}_i}^{2_i\bar{2}_i}$$

根据前面的假设，我们代入得

$$K_{12}+c\cdot 2\Delta+(N-1)c^2\cdot K_{12}=E_{corr}c=Nc^2K_{12}$$

即$K_{12}c^2-(2\Delta)c-K_{12}=0$，解得$c=\frac{\Delta\pm\sqrt{\Delta^2+K_{12}^2}}{K_{12}}$，代入相关能表达式，得$E_{corr}=N(\Delta\pm\sqrt{\Delta^2+K_{12}^2})$，因为相关能为负数，所以N个无相互作用的$H_2$分子的相关能为$E_{corr}(N\ \mathrm{H_2})=N(\Delta-\sqrt{\Delta^2+K_{12}^2})=NE_{corr}(\mathrm{H_2})$，满足大小一致性