Diagrammatic representation of RS perturbation theory

first used in QE by R. Feynman
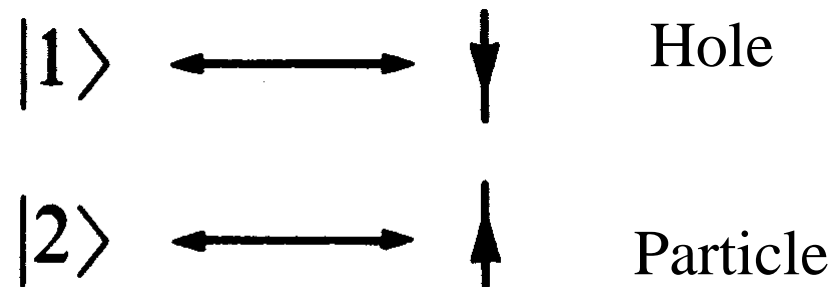
Diagrammatic Perturbation Theory for Two States

• lowest eigenvalue of two state problem

Perturbation V is presented by dot.

$V \longleftrightarrow \bullet$

Two zero order states |1> and |2>
are lines with arrows

$|1\rangle \longleftrightarrow \downarrow$ Hole

$|2\rangle \longleftrightarrow \uparrow$ Particle

Simple representation of matrix elements V

$$\langle 1 | \mathscr{V} | 1 \rangle = V_{11}$$

$$\langle 1 | \mathscr{V} | 2 \rangle = V_{12}$$

$$\langle 2 | \mathscr{V} | 1 \rangle = V_{21}$$

$$\langle 2 | \mathscr{V} | 2 \rangle = V_{22}$$

<label of line *in* | V | label of line *out* >

N-th order energy, N=1,..4 is product of n matrix elements V, each matrix elements is dot with line going into it and line coming out of it => algebraic representation by pictures containing N dot connected in some way.

Rules:
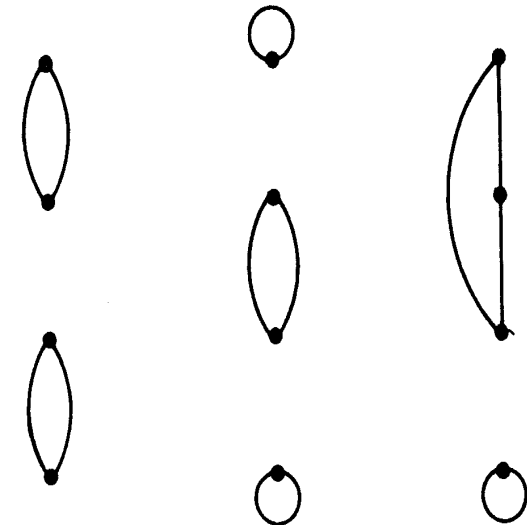
1)   N dot vertically
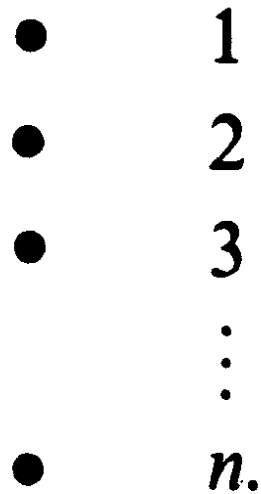
2) Connect all n dots together with **continuous** line

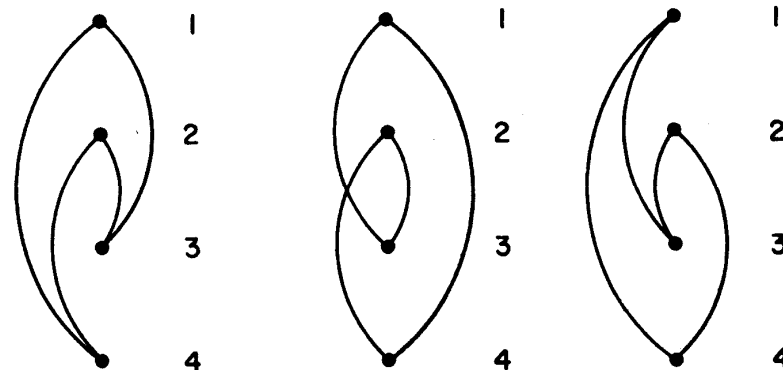3) Do it in all possible distinct ways. Two diagram are equivalent if each and every dot is connected to an identical pair of dots

IDENTICAL   →

"rubber bands" glued to dots
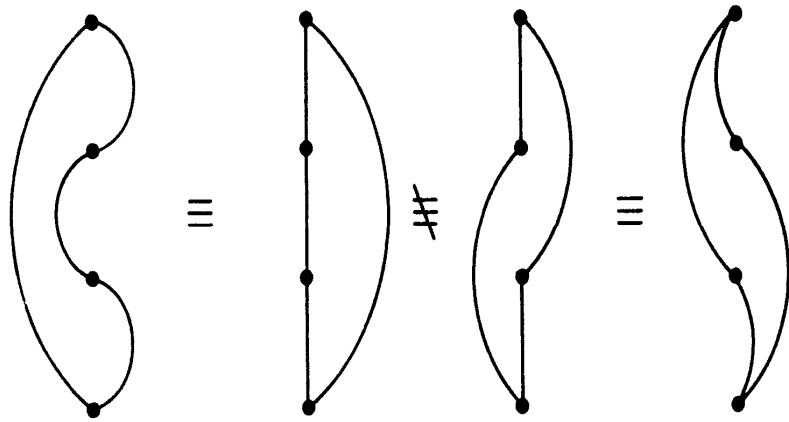
Diagrams to 4th order

Only distinct diagrams

$\equiv$ $\not\equiv$ $\equiv$

$n = 1$

$n = 2$

Arrows (1 is label for down line, 2 for up line)

$n = 3$

2

1

1

2

N = 3
two possibility
of labeling

1

2

2

$n = 4$
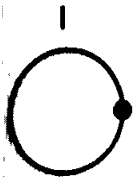
$n = 1$

Circular lines
are hole lines
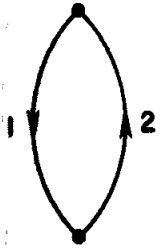
$n = 2$
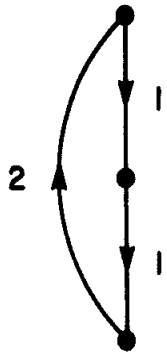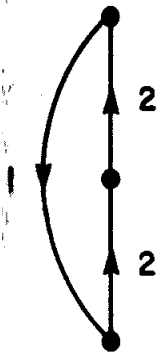
$n = 3$
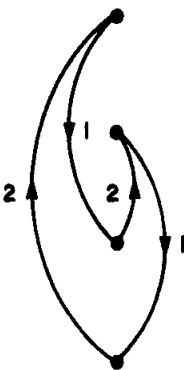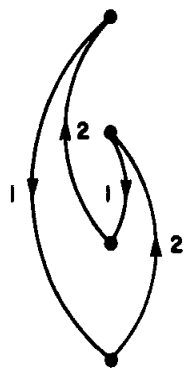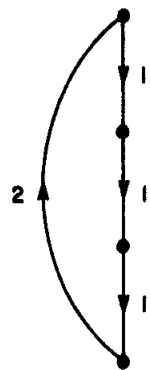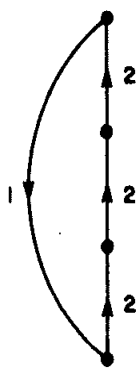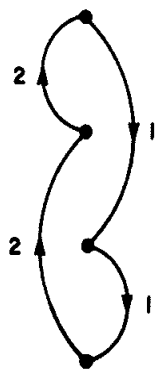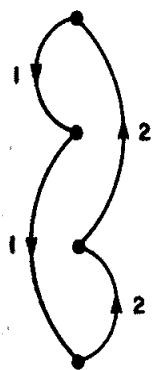
$n = 4$

Correspondence between pictures and n^{th} order of energy

Rules to translating pictures to algebraic expression:

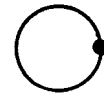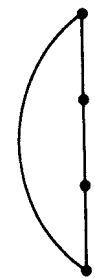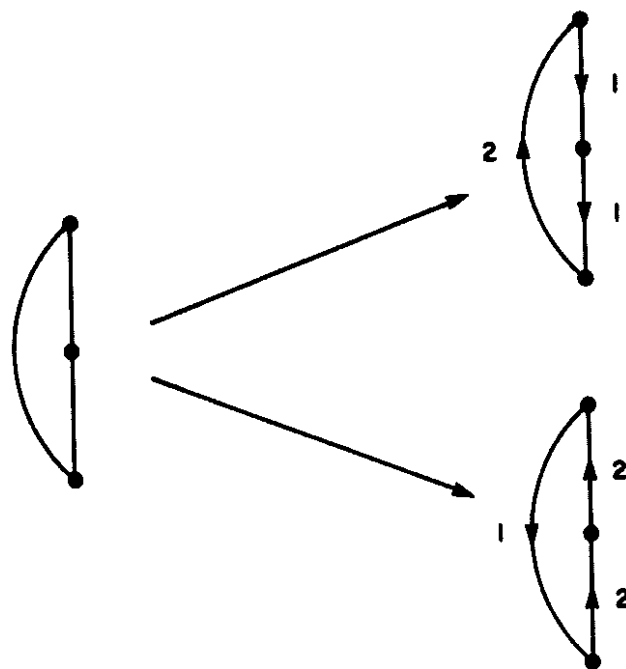a) Each dot contributes a factor $<$ label *in* $|V|$ label *out*$>$ to numerator

b) Each pair of adjaced dots contributes to the denominator factor $\sum E_{hole}^{(0)} - \sum E_{particule}^{(0)}$

where the sums runs over label of all holes and particle lines crossing an imaginary

horizontal line separating two adjacent dots

c) The sign of expression is $(-)^{h+l}$,where h is number of hole lines and l is number of closed

loops
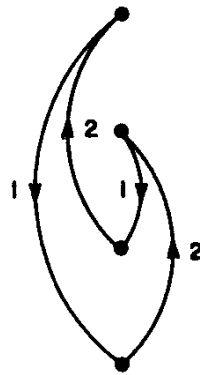
Ex.
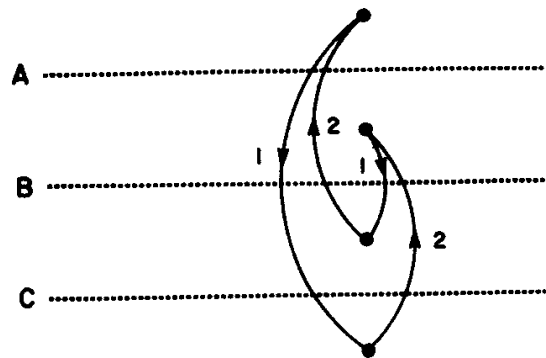
Upper two dots contribute by factor $\langle 2|V|1 \rangle = V_{21}$

remaining by factor $\langle 1|V|2 \rangle = V_{12}$ to the numerator.

Line A and C contributes by factor $E_1^{(0)} - E_2^{(0)}$

line B by $\left(2E_1^{(0)} - 2E_2^{(0)}\right)$

Since we have two holes (h = 2) and one closed
loop (l = 1) => $(-1)^3$

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

Algebraic expression for following pair in diagram
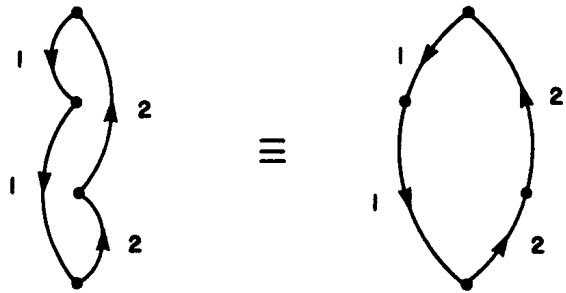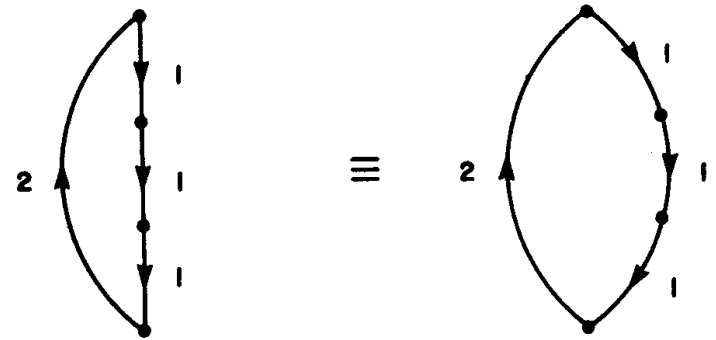
We can distort given diagram as long as we don't change the vertical ordering of dots.

First order

$$= V_{11}$$
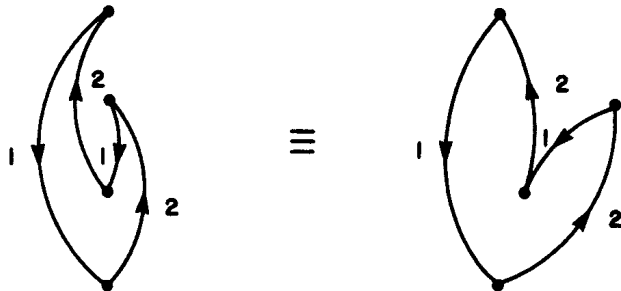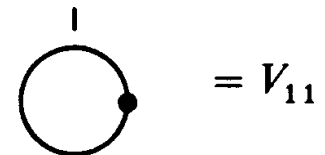
Translation diagram into formulas
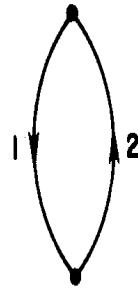
$$(-)^{1+1} \frac{\langle 1|\mathcal{V}|2\rangle\langle 2|\mathcal{V}|1\rangle}{E_1^{(0)} - E_2^{(0)}} = \frac{V_{12}V_{21}}{E_1^{(0)} - E_2^{(0)}}$$

$$(-)^{1+1} \frac{\langle 1|\mathcal{V}|2\rangle\langle 2|\mathcal{V}|2\rangle\langle 2|\mathcal{V}|1\rangle}{(E_1^{(0)} - E_2^{(0)})^2} = \frac{V_{12}V_{22}V_{21}}{(E_1^{(0)} - E_2^{(0)})^2}$$
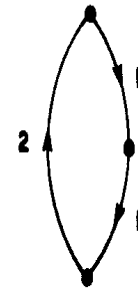
$$(-)^{2+1} \frac{\langle 1|\mathcal{V}|2\rangle\langle 2|\mathcal{V}|1\rangle\langle 1|\mathcal{V}|1\rangle}{(E_1^{(0)} - E_2^{(0)})^2} = -\frac{V_{12}V_{21}V_{11}}{(E_1^{(0)} - E_2^{(0)})^2}$$
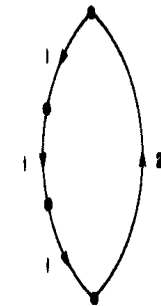
$$(-)^{3+1} \frac{\langle 1|\mathcal{V}|2\rangle\langle 2|\mathcal{V}|1\rangle\langle 1|\mathcal{V}|1\rangle\langle 1|\mathcal{V}|1\rangle}{(E_1^{(0)} - E_2^{(0)})^3} = \frac{V_{12}V_{21}V_{11}^2}{(E_1^{(0)} - E_2^{(0)})^3}$$
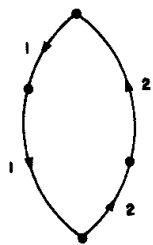
$$(-)^{2+1} \frac{\langle 1|\mathscr{V}|2\rangle\langle 2|\mathscr{V}|2\rangle\langle 2|\mathscr{V}|1\rangle\langle 1|\mathscr{V}|1\rangle}{(E_1^{(0)} - E_2^{(0)})^3} = -\frac{V_{12}V_{22}V_{21}V_{11}}{(E_1^{(0)} - E_2^{(0)})^3}$$
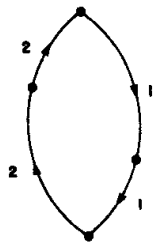
$$(-)^{2+1} \frac{\langle 1|\mathscr{V}|2\rangle\langle 2|\mathscr{V}|2\rangle\langle 2|\mathscr{V}|1\rangle\langle 1|\mathscr{V}|1\rangle}{(E_1^{(0)} - E_2^{(0)})^3} = -\frac{V_{12}V_{22}V_{21}V_{11}}{(E_1^{(0)} - E_2^{(0)})^3}$$
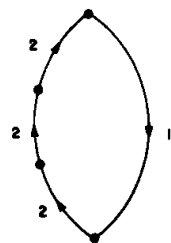
$$(-)^{1+1} \frac{\langle 1|\mathscr{V}|2\rangle\langle 2|\mathscr{V}|2\rangle\langle 2|\mathscr{V}|2\rangle\langle 2|\mathscr{V}|1\rangle}{(E_1^{(0)} - E_2^{(0)})^3} = \frac{V_{12}V_{22}^2 V_{21}}{(E_1^{(0)} - E_2^{(0)})^3}$$
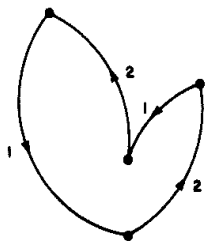
$$(-)^{2+1} \frac{\langle 1|\mathscr{V}|2\rangle\langle 2|\mathscr{V}|1\rangle\langle 1|\mathscr{V}|2\rangle\langle 2|\mathscr{V}|1\rangle}{(E_1^{(0)} - E_2^{(0)})^2(2E_1^{(0)} - 2E_2^{(0)})} = -\frac{(V_{12}V_{21})^2}{2(E_1^{(0)} - E_2^{(0)})^3}$$
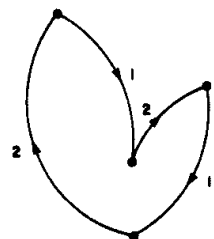
$$(-)^{2+1} \frac{\langle 1|\mathscr{V}|2\rangle\langle 2|\mathscr{V}|1\rangle\langle 1|\mathscr{V}|2\rangle\langle 2|\mathscr{V}|1\rangle}{(E_1^{(0)} - E_2^{(0)})^2(2E_1^{(0)} - 2E_2^{(0)})} = -\frac{(V_{12}V_{21})^2}{2(E_1^{(0)} - E_2^{(0)})^3}$$

Ex. Write down and evaluate all fifth-order diagrams that have property that imaginary horizontal line crosses only one hole and one particle line. Show that the sum of such diagrams is $\dfrac{V_{12}V_{21}(V_{22}-V_{11})^3}{(E_1^{(0)}-E_2^{(0)})^4}$

Hint: there are eight such diagrams and they can be generated by adding three dots to the second-order diagram

Diagrammatic perturbation theory for N states

N-state system, still only one hole state |1> but N-1 particle states |n>, n=2,3, ..,4.

Any particle line can be labeled by index n. So
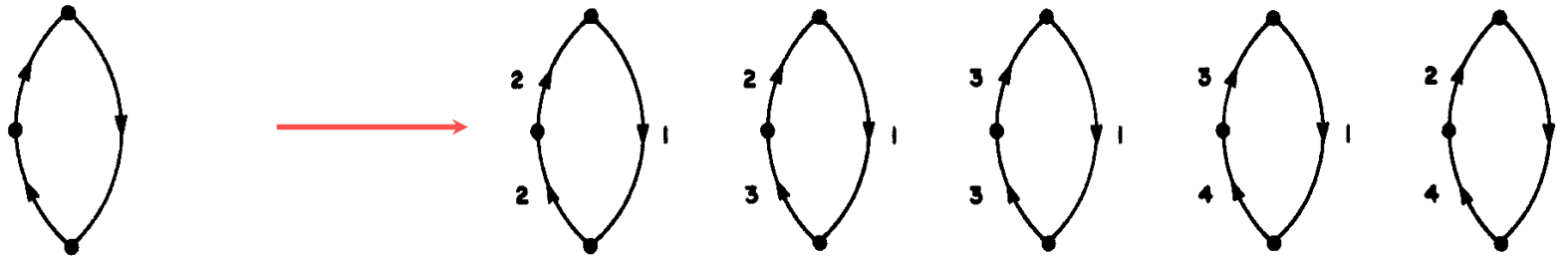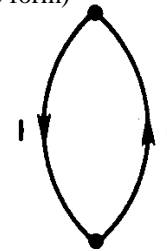
or generally, *m* and *n* is in depended from 2, ..N

$$n = 2, \ldots, N$$
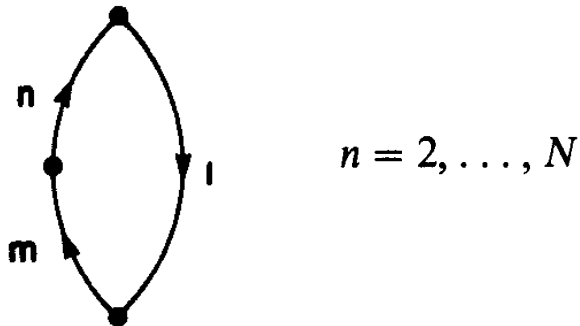
Subset of diagrams where m=n is called *diagonal*
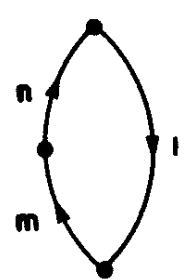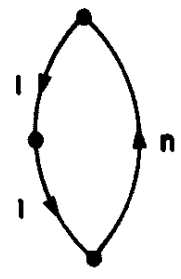
Second order energy (klick on the form)

$$\bigcirc = \sum_{n \neq 1} \frac{V_{1n}V_{n1}}{E_1^{(0)} - E_n^{(0)}} = {\sum_n}' \frac{V_{1n}V_{n1}}{E_1^{(0)} - E_n^{(0)}}$$

Third order of energy

$$\bigcirc + \bigcirc = {\sum_{nm}}' \frac{V_{1m}V_{mn}V_{n1}}{(E_1^{(0)} - E_m^{(0)})(E_1^{(0)} - E_n^{(0)})} - {\sum_n}' \frac{V_{11}V_{1n}V_{n1}}{(E_1^{(0)} - E_n^{(0)})^2}$$

What if we want expression for some state i, which is not necessary the lowest?

Label hole line by i and particle line as k, m,n from 1, 2,...,i-1, i+1, ..,N

$\longrightarrow$ Diagrammatic RS

Ex. Using diagrammatic techniques to obtain 4th order perturbation theory of a particular state i of N-state system. That is evaluate the diagrams
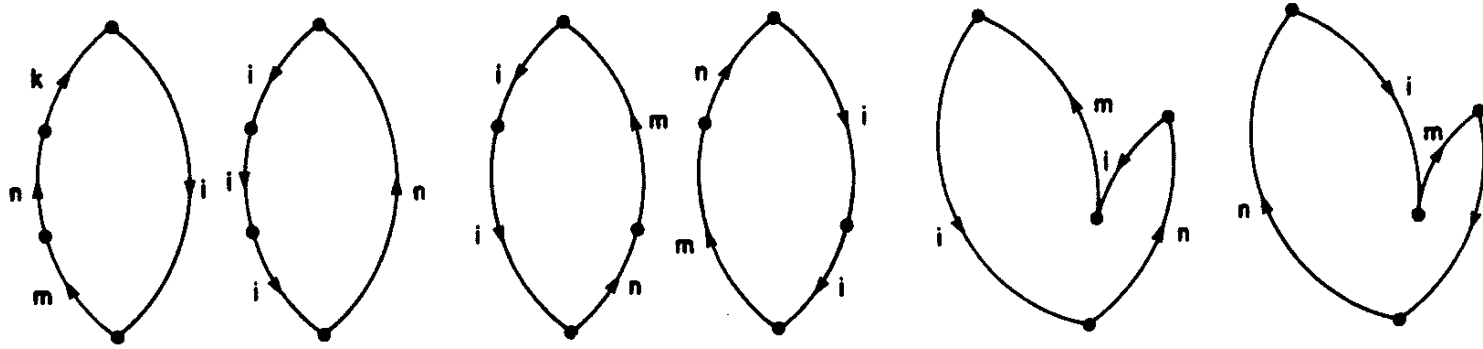
Where m, n, k exclude i. Obtain also result from algebraic expression and compare it together

Summation of diagrams

Two state system , 2nd order of energy

All diagram by adding dots
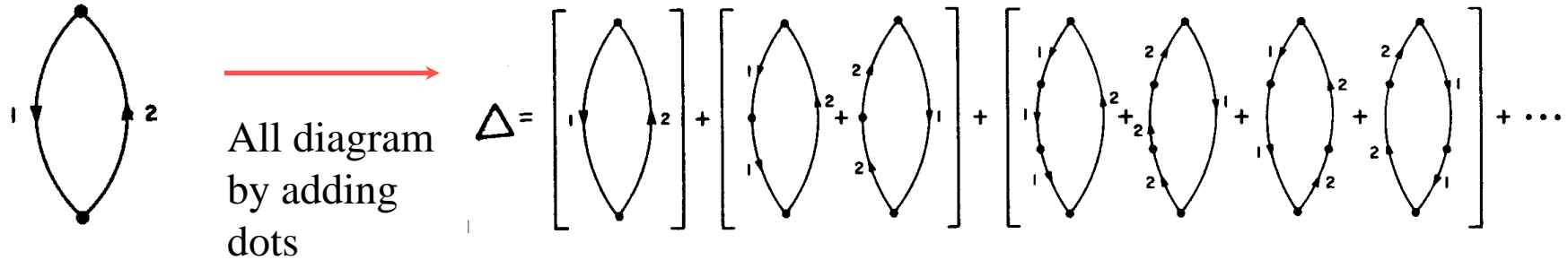
then

$$\Delta = \left[\frac{V_{12}V_{21}}{E_1^{(0)} - E_2^{(0)}} \right] + \left[\frac{V_{12}V_{21}(V_{22} - V_{11})}{(E_1^{(0)} - E_2^{(0)})^2} \right] + \left[\frac{V_{12}V_{21}(V_{22} - V_{11})^2}{(E_1^{(0)} - E_2^{(0)})^3} \right] + \left[\frac{V_{12}V_{21}(V_{22} - V_{11})^3}{(E_1^{(0)} - E_2^{(0)})^4} \right] + \ldots$$

or

$$\Delta = \frac{V_{12}V_{21}}{E_1^{(0)} - E_2^{(0)}} \left[1 + \left(\frac{V_{22} - V_{11}}{E_1^{(0)} - E_2^{(0)}} \right) + \left(\frac{V_{22} - V_{11}}{E_1^{(0)} - E_2^{(0)}} \right)^2 + \left(\frac{V_{22} - V_{11}}{E_1^{(0)} - E_2^{(0)}} \right)^3 + \ldots \right]$$

with

$$(1 - x)^{-1} = 1 + x + x^2 + x^3 + \ldots$$

$V_{22} - V_{11} < E_1 - E_2$!

$$\Delta = \frac{V_{12}V_{21}}{E_1^{(0)} - E_2^{(0)}} \left[\frac{1}{1 - \dfrac{V_{22} - V_{11}}{E_1^{(0)} - E_2^{(0)}}} \right] = \frac{V_{12}V_{21}}{(E_1^{(0)} + V_{11}) - (E_2^{(0)} + V_{22})}$$

like 2nd order of perturbation but with shifted energy denominator

Summing to infinite order can be obtained by finite order – different partitioning into perturbated and unperturbated part:

$$H_0 = \begin{pmatrix} E_1^{(0)} & 0 \\ 0 & E_2^{(0)} \end{pmatrix}$$

$$H_0' = \begin{pmatrix} E_1^{(0)} + V_{11} & 0 \\ 0 & E_2^{(0)} + V_{22} \end{pmatrix}$$

$$V = \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix}$$

$$V' = \begin{pmatrix} 0 & V_{12} \\ V_{21} & 0 \end{pmatrix}$$

Then geometric sum of diagrams is simply 2nd order PT in new partitioning.

For N-state system, adding dots to second order diagram

$$\Delta = \sum_n \frac{V_{1n}V_{n1}}{(E_1^{(0)} + V_{11}) - (E_n^{(0)} + V_{nn})}$$

n=1 term excluded

Orbital perturbation theory: one particle perturbations

Special case where unperturbed Hamiltonian is sum of one-particle Hamiltonians. $H_0 = \sum_i h_0(i)$

HF have such form, so we are interested in improving by PT.

First consider case where $V = \sum_i v(i)$ (not really) (ex. Molecule in electric field F =>perturbation

is $\vec{F}\sum_i r(i)$ where r(i) is position of ith electron.

Set of spin orbitals and orbital energies that are eigenfunction and eigenvalues of h_0

$$h_0 \chi_i^{(0)} = \varepsilon_i^{(0)} \chi_i^{(0)}$$
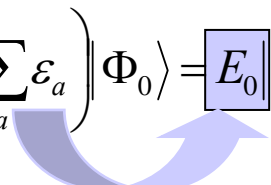
Ground state wave function ($|\Psi_0>$) : $\left|\Psi_0\right\rangle = \left|\chi_1^{(0)} \cdots \chi_a^{(0)} \cdots \chi_N^{(0)}\right\rangle$

Occupied (hole) spin orbitals a, b, c and unoccupied (particle) spin orbitals r, s, t

$$H_0\left|\Psi_0\right\rangle = \left(\sum_a \varepsilon_a^{(0)}\right)\left|\Psi_0\right\rangle \xrightarrow{\quad V \quad} E_0 = \left\langle\Psi_0\left|H\right|\Psi_0\right\rangle = \left\langle\Psi_0\left|H_0 + V\right|\Psi_0\right\rangle = \sum_a \varepsilon_a^{(0)} + \sum_a \left\langle a|v|a\right\rangle = \sum_a \varepsilon_a^{(0)} + \sum_a v_{aa}$$

In our case: $H = H_0 + V = \sum_i (h_0(i) + v(i)) = \sum_i h(i) \xrightarrow{\text{1 e}^- \text{ terms}} h\chi_i = (h_0 + v)\chi_i = \varepsilon_i \chi_i$

Exact wf $\left|\Phi_0\right\rangle = \left|\chi_1 \cdots \chi_a \cdots \chi_N\right\rangle$ and $H\left|\Psi_0\right\rangle = \left(\sum_a \varepsilon_a\right)\left|\Phi_0\right\rangle = E_0\left|\Phi_0\right\rangle$

Perturbation expansion of exact E_0 can be generally written): $\quad E_0 = E_0^{(0)} + E_0^{(1)} + E_0^{(2)} + \ldots$

and for orbital energy ε_a holds:

$$\varepsilon_a = \varepsilon_a^{(0)} + \langle a|v|a\rangle + \sum_i \frac{\langle a|v|i\rangle\langle i|v|a\rangle}{\varepsilon_a^{(0)} - \varepsilon_i^{(0)}} + \ldots$$
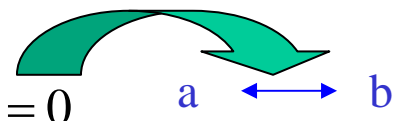
$$\varepsilon_a = \varepsilon_a^{(0)} + v_{aa} + \sum_i \frac{v_{ai} v_{ia}}{\varepsilon_a^{(0)} - \varepsilon_i^{(0)}} + \ldots$$

Two parts of summation over particle orbitals and over holes (except a).

$$\varepsilon_a = \varepsilon_a^{(0)} + v_{aa} + \sum_r \frac{v_{ar} v_{ra}}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}} + \sum_{b \neq a} \frac{v_{ab} v_{ba}}{\varepsilon_a^{(0)} - \varepsilon_b^{(0)}} + \ldots$$

Total energy

Term X $\quad X = \sum_{\substack{ab \\ b \neq a}} \frac{v_{ab} v_{ba}}{\varepsilon_a^{(0)} - \varepsilon_b^{(0)}} = 0$ $\qquad$ a $\longleftrightarrow$ b

Second order

$$E_0 = \sum_a \varepsilon_a = \underbrace{\sum_a \varepsilon_a^{(0)}}_{E_0^{(0)}} + \underbrace{\sum_a v_{aa}}_{E_0^{(1)}} + \underbrace{\sum_{ar} \frac{v_{ar} v_{ra}}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}}}_{E_0^{(2)}} + \ldots$$

Matrix element v_{ij} is non-zero is spinorbitals i and j have same spin, than for closed systems:

$$E_0^{(0)} = 2 \sum_a^{N/2} \varepsilon_a$$

$$E_0^{(1)} = 2 \sum_a^{N/2} v_{aa}$$

$$E_0^{(2)} = 2 \sum_{ar}^{N/2} \frac{v_{ar} v_{ra}}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}}$$

Ex. Derive

$$E_0^{(2)} = \sum_{ar} \frac{v_{ar} v_{ra}}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}}$$

Starting with general expression for second-order energy applied to N-electron system

$$E_0^{(2)} = \sum_n{}' \frac{\left| \left\langle \Psi_0 \left| \sum_i v(i) \right| n \right\rangle \right|^2}{E_0^{(0)} - E_n^{(0)}}$$

where sum runs over all stages of system except ground state

Hint: The states |n> must be single excitations of type $\left| \Psi_a^r \right\rangle = \left| \chi_1^{(0)} \cdots \chi_{a-1}^{(0)} \chi_r^{(0)} \chi_{a+1}^{(0)} \cdots \chi_N^{(0)} \right\rangle$

Ex. Calculate the third-order energy $E_0^{(3)}$ using the general expression.

a) Show that

$$B_0^{(3)} = -E_0^{(1)} \sum_n {}' \frac{\left|\langle \Psi_0 |V| n \rangle\right|^2}{(E_0^{(0)} - E_n^{(0)})^2} = -\sum_{abr} \frac{v_{aa} v_{rb} v_{br}}{(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})^2}$$

b) Show that

$$A_0^{(3)} = \sum_{nm} {}' \frac{\langle \Psi_0 |V| n \rangle \langle n |V| m \rangle \langle m |V| \Psi_0 \rangle}{(E_0^{(0)} - E_n^{(0)})(E_0^{(0)} - E_m^{(0)})} = \sum_{abrs} \frac{v_{ar} v_{sb} \langle \Psi_a^r |V| \Psi_b^s \rangle}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_s^{(0)})}$$

c) Show that

$$\langle \Psi_a^r |V| \Psi_b^s \rangle = v_{rs} \qquad \text{if } a = b \ \ r \neq s$$

$$= -v_{ba} \qquad \text{if } a \neq b \ \ r = s$$

$$= \sum_c v_{cc} - v_{aa} + v_{rr} \qquad \text{if } a = b \ \ r = s$$

and zero otherwise.

d) Finally combine two term to obtain

$$E_0^{(3)} = A_0^{(3)} + B_0^{(3)} = \sum_{ars} \frac{v_{ar} v_{rs} v_{sa}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})} - \sum_{abr} \frac{v_{ra} v_{ab} v_{br}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})}$$

e) Show that for close-shell system

$$E_0^{(3)} = 2\sum_{ars}^{N/2} \frac{v_{ar} v_{rs} v_{sa}}{(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} - 2\sum_{abr}^{N/2} \frac{v_{ra} v_{ab} v_{br}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})}$$

Cyclic polyene with N carbon atoms (N=2n=4v+2), v=1, 2, 3, ..)

Resonance energy- difference between exact total energy and energy of N/2=n localized ethylenic units.

Occupied (hole) and unoccupied (particle) orbitals in the ith unit are denoted by $|i>$ or $|i*>$

Hamiltonian is

$$H = H_0 + V = \sum_i h_0(i) + \sum_i v(i)$$

$$\varepsilon_i^{(0)} - \varepsilon_{j*}^{(0)} = 2\beta \text{ independent of } i \text{ and } j$$

Non zero matrix elements

$$\langle i|v|(i\pm1)*\rangle = \pm\beta/2$$

$$\langle i|v|(i\pm1)\rangle = \beta/2$$

$$\langle i*|v|(i\pm1)^*\rangle = -\beta/2$$

Since polyene is cyclic, 0th ethylen unit is same as n^{th}, $(n+1)^{th}$ is first

In this model exact resonance energy of benzene is 2β, asymptotically exact energy is

$$\lim_{N\to\infty} E_R = (4/\pi - 1)N\beta = 0.2732\, N\beta$$

We need to known only matrix elements of perturbation v

Second-order energy (close-shell)

$$E_0^{(2)} = 2\sum_{ar}^{N/2} \frac{v_{ar}v_{ra}}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}} = 2\sum_{ar}^{N/2} \frac{\langle a|v|r\rangle\langle r|v|a\rangle}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}}$$

a runs over all *n* occupied $|i>$, *r* over all *n* unoccupied $|j^* >$

$$E_0^{(2)} = 2\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{\langle i|v|j^*\rangle\langle j^*|v|i\rangle}{\varepsilon_i^{(0)} - \varepsilon_{j^*}^{(0)}} = \frac{1}{\beta}\sum_{i=1}^{n}\sum_{j=1}^{n}\langle i|v|j^*\rangle\langle j^*|v|i\rangle$$

Using fact hat the difference between orbitals is always 2β

For fixed *i* summation over *j* is easy : matrix elements are non-zero onlu when $j = i \pm 1$

thus
$$E_0^{(2)} = \frac{1}{\beta}\sum_{i=1}^{n}\langle i|v|(i+1)^*\rangle\langle (i+1)^*|v|i\rangle + \langle i|v|(i-1)^*\rangle\langle (i-1)^*|v|i\rangle$$

$$= \frac{1}{\beta}\sum_{i=1}^{n}\left[(\beta/2)^2 + (-\beta/2)^2\right] = \frac{n\beta}{2} = \frac{N\beta}{4} = 0.25N\beta$$

For benzene second-order resonance energy is 1.5β, exact value is 2β, in larger systems is agreements even better- for large N energy approach 91.5% exact results.

Summation *i* over fixed *j*: orbital *i* can interact only with orbital $(i\pm1)^*$ .See picture:

$i \rightarrow j^* \rightarrow i \leftrightarrow$ $\leftrightarrow \sum_{j}\langle i|v|j^*\rangle\langle j^*|v|i\rangle$
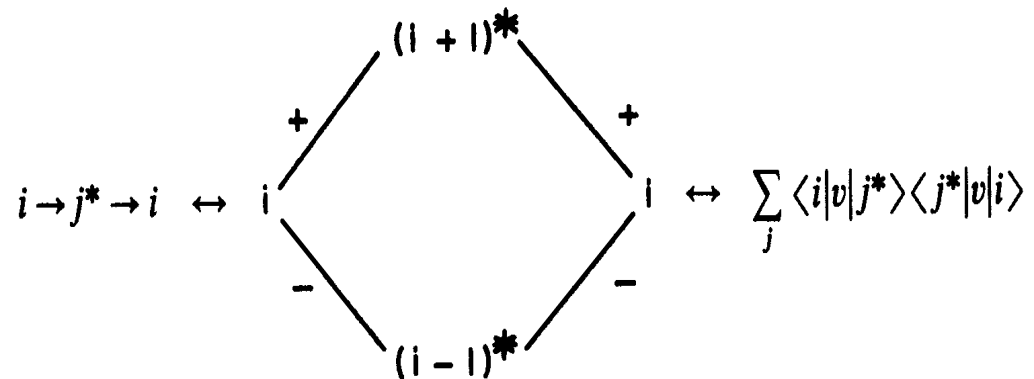
Plus and minus indicate that the matrix elements between the two orbitals $\pm\beta/2$

Sum over j can be evaluated-start at i on the left and go to i on the right by all possible paths. Add all contributions. Illustration-value of path $i \to (i+1)^* \to i$ is $(+\beta/2)(+\beta/2)=\beta^2/4$ while
value of path $i \to (i-1)^* \to i$ is $(-\beta/2)(-\beta/2)=\beta^2/4$
So the summation over j is just $\beta^2/4$ for each value of i.

Calculation of **third order** of energy (close shell):

$$E_0^{(3)} = 2\sum_{ars}^{N/2} \frac{v_{ar}v_{rs}v_{sa}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} - 2\sum_{abr}^{N/2} \frac{v_{ra}v_{ab}v_{br}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})}$$

Proceeding same way as in $E_0^{(2)}$, the first term is
$$\frac{2}{(2\beta)^2}\sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n}\langle i|v|j^*\rangle\langle j^*|v|k^*\rangle\langle k^*|v|i\rangle$$

Evaluation of expression over j and k

$i \longrightarrow j^* \longrightarrow k^* \longrightarrow i \longleftrightarrow$
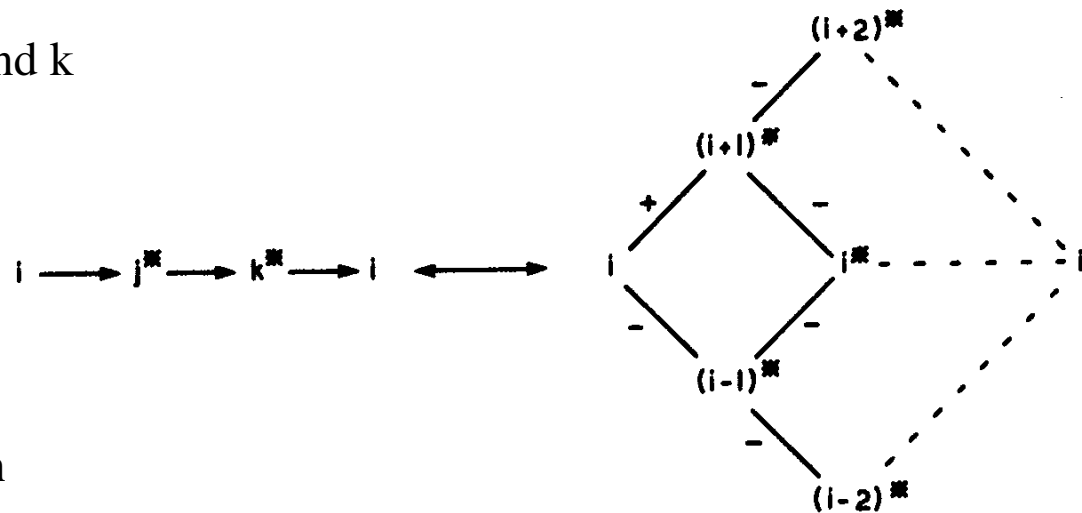
Note since i cannot interact with i^* or $(i+2)^*$ or $(i-2)^*$ the value of this sum must be zero. Similar in second term, so third-order energy is zero.

But don't be hasty. In benzene orbitals $(i \pm 2)^*$ is same as $(i \mp 1)^*$, thus pictorial representation of the sum over j and k with i is:
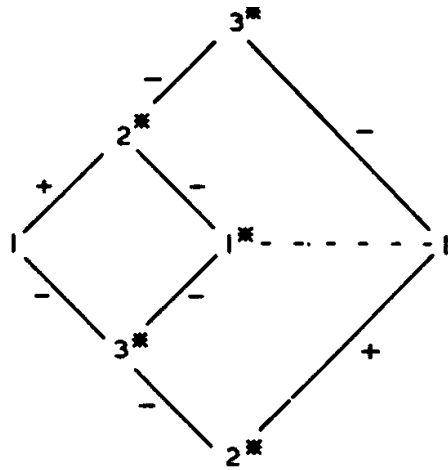
So there are two paths 1) $1 \to 2^* \to 3^* \to 1$ with value $(\beta/2)(-\beta/2)$ $(-\beta/2)= \beta^3/8$

2) $1 \to 3^* \to 2^* \to 1$ with value $(-\beta/2)(-\beta/2)$ $(\beta/2)= \beta^3/8$

Than the first term $E_0^{(3)}$ is $\dfrac{2}{(2\beta)^2}\sum_{i=1}^{3}\left[(\beta^3/8)+(\beta^3/8)\right]=\dfrac{3\beta}{8}$

Total third energy $E_0^{(3)}$ for benzene is $E_0^{(3)}(benzene)=\dfrac{3\beta}{4}$

Resonance energy up to third order is 2.25β (113% of exact value).

In excise the fourth order energy is $E_0^{(4)}=\dfrac{N\beta}{64}$, thus resonance nergy up to fourth order is 2.34 β (117% of exact value). Perturbation expression does not converge. But works better for larger systems.

The energy up to fourth level is 0.2656 Nβ i.e. $\left(\dfrac{1}{4}+\dfrac{1}{64}\right)N\beta$

Compare with asymptotic exact value 0.2732 Nβ (i.e. 97% of exact value).

Ex. Show that the second term in

$$E_0^{(3)} = 2\sum_{ars}^{N/2} \frac{v_{ar}v_{rs}v_{sa}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_a^{(0)} - \varepsilon_s^{(0)})} - 2\sum_{abr}^{N/2} \frac{v_{ra}v_{ab}v_{br}}{(\varepsilon_a^{(0)} - \varepsilon_r^{(0)})(\varepsilon_b^{(0)} - \varepsilon_r^{(0)})}$$

is equal to $\dfrac{3}{8}\beta$ for benzene.

___

Ex. Consider a cyclic polyene with $N = 4v+2$, $v=1, 2, 3, ..$ Carbons. Instead that all bonds are identical suppose that they alternate in length. In context of Hückel theory this means that resonance integrals alternate between β_1 and β_2. For example for benzene we have
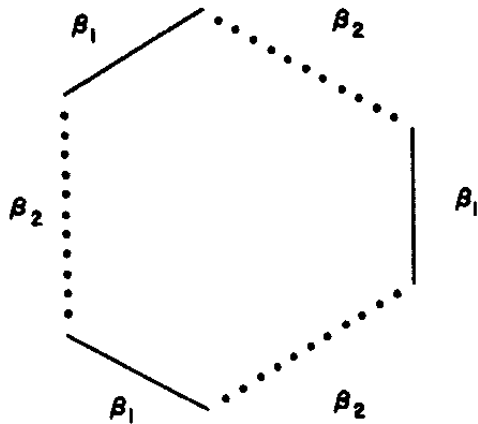
Now it can be shown that the exact energy in this case is

$$\varepsilon_0 = N\alpha - 2\sum_{j=-v}^{v}(\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos\frac{2j\pi}{2v+1})$$

Note that when $\beta_1 = \beta_2 = \beta$, since $2\cos^2\theta = (1 + \cos 2\theta)$ and

β is negative we recover $\varepsilon_0 = N\alpha + 4\beta\sum_{j=-v}^{v}\cos\frac{j\pi}{2v+1}$

And if $\beta_1 = \beta$ and $\beta_2 = 0$ than $E_0 = N\alpha + N\beta$ (total energy in localized ethylenic description)

Purpose of this excise is to obtain the exact energy in power of $\beta_{2/}\beta_1$.

a) Show that for benzene (v = 1) in alternating short and long bond model is

$$\varepsilon_0 = 6\alpha + 2(\beta_1 + \beta_2) - 4\left(\beta_1^2 + \beta_2^2 - \beta_1\beta_2\right)^{1/2}$$

Do this first by using general expression and then by setting up the Hückel matrix, diagonalizing it and then adding up the occupied orbital energies. Note that for $\beta_1 = \beta_2 = \beta$ we obtain old result $6\alpha + 8\beta$.

b) Setting $\beta_1 = \beta$ and $\beta_2/\beta_1 = x$ show that the resonance energy of benzene can be written as

$$E_R = 4\beta(\frac{1}{2}x - 1 + (1 + x^2 - x)^{1/2})$$

Note that when x = 0, $E_R = 0$ and when x = 1, $E_R = 2\beta$ which is exact.

c) Using relation $(1+y)^{1/2} = 1 + \frac{1}{2}y - \frac{1}{8}y^2 + \frac{1}{16}y^3 - \frac{5}{128}y^4 + \dots \quad |y| < 1$ expand E_R to fourth order in x

and thus show that $E_R = \beta(\frac{3}{2}x^2 + \frac{3}{4}x^3 + \frac{3}{32}x^4 + \dots)$ identifying coefficient of x^n with nth-

order perturbation results, we have $\quad E_0^{(2)} = \frac{3}{2}\beta$

$$E_0^{(3)} = \frac{3}{4}\beta$$

$$E_0^{(4)} = \frac{3}{32}\beta$$

Note that $E_0^{(2)}$ and $E_0^{(3)}$ agree with previous results. Small insight into poor convergence of perturbation expansion of the resonance energy of benzene. When x is small, then rapid convergence. However for our problem is x $= 1$.
Resonance energy calculated to Mth-order as function of M is below. Converging to exact value of 2β. Above method for obtaining $E_0^{(n)}$ for n= 2, 3, 4 is extremely laborious.
Results below were calculated by first showing that

$$E_0^{(n)} = 4\beta C_n^{-1/2}(\tfrac{1}{2}), \text{ where } C_n^{-1/2}(x) \text{ is GegenBauer polynomial.}$$

And using recursive properties of these polynomials to shown that

$$\left(n+1\right)E_0^{(n+1)} = (n-\tfrac{1}{2})E_0^{(n)} - (n-2)E_0^{(n-1)}$$
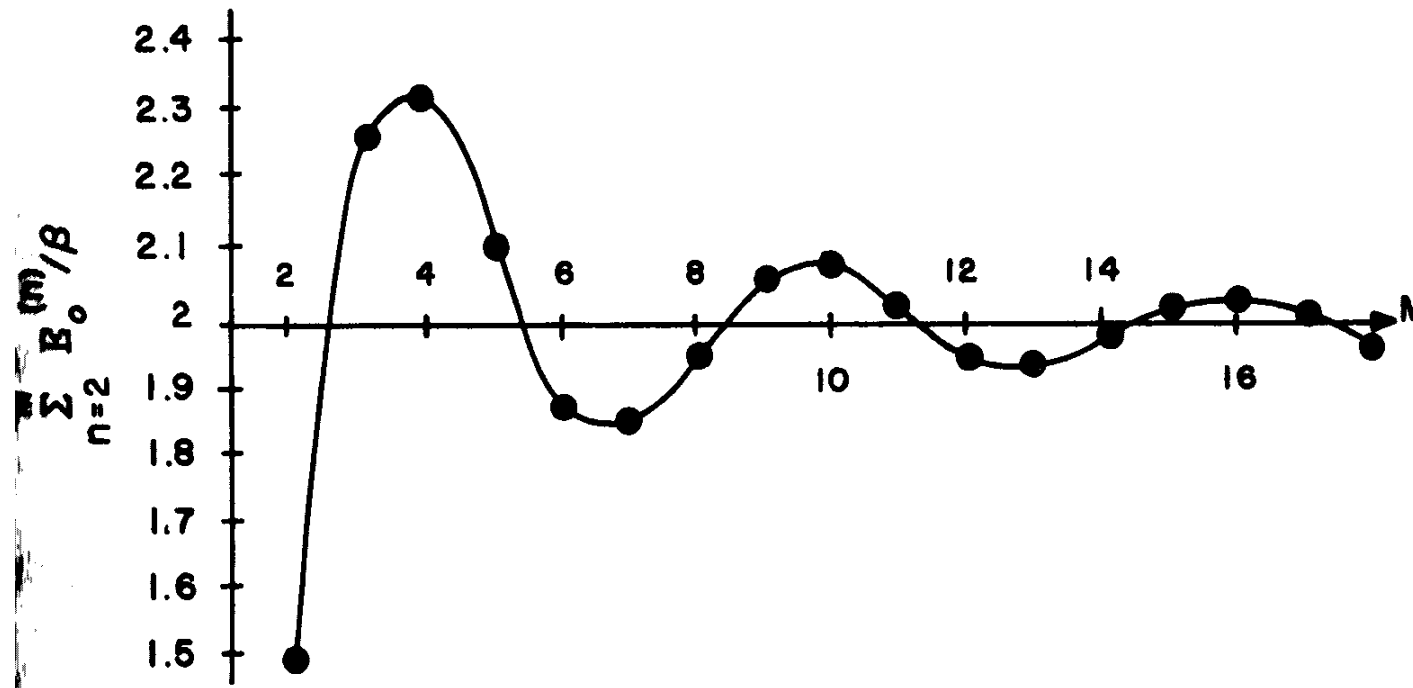
Diagrammatic representation of orbital perturbation theory

Holes – a, b, …
Particles - r, s,

$n = 1$

$n = 2$

$n = 3$

$n = 4$
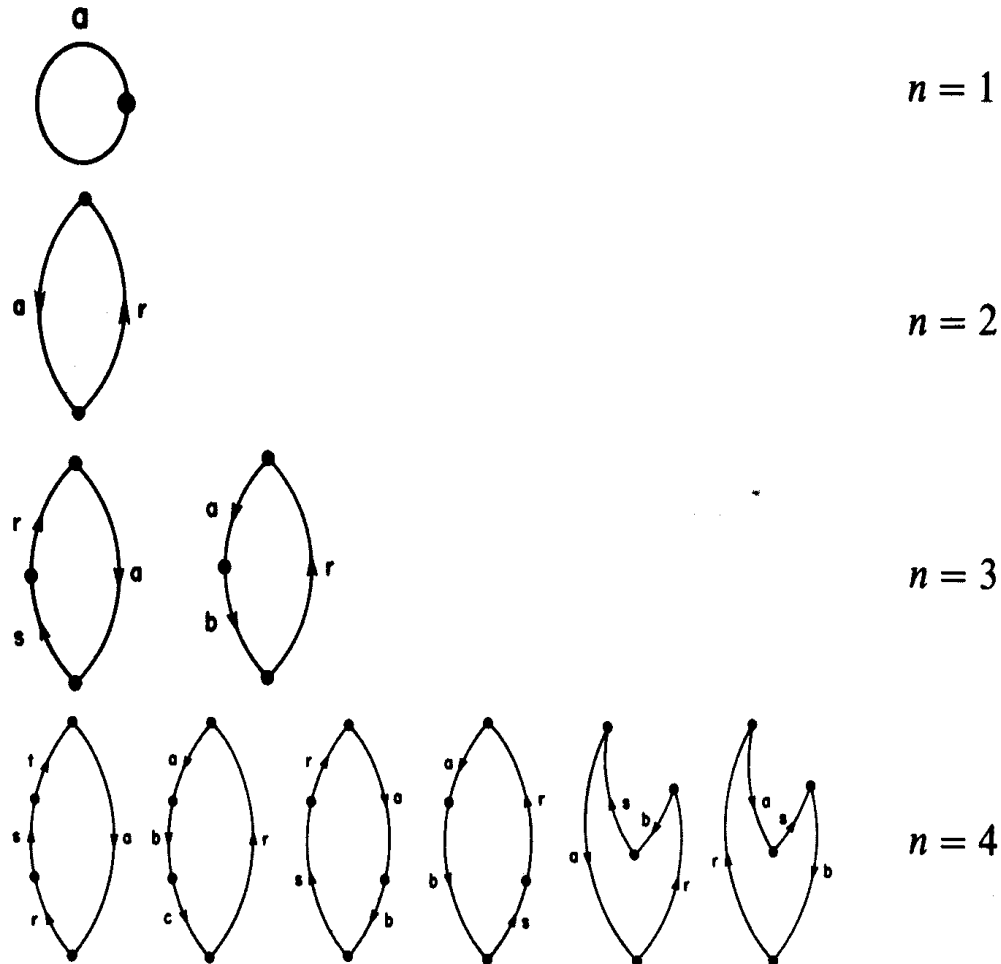
Fourth rule: Sum the expression over all particle and hole indices.

Using these rules:

$$E_0^{(1)} = \bigcirc\!\!\bullet = \sum_a v_{aa}$$

$$E_0^{(2)} = \bigcirc = \sum_{ar} \frac{v_{ar} v_{ra}}{\varepsilon_a^{(0)} - \varepsilon_r^{(0)}}$$

$$E_0^{(3)} = \bigcirc + \bigcirc$$

$$= \sum_{ars} \frac{v_{as} v_{sr} v_{ra}}{\left(\varepsilon_a^{(0)} - \varepsilon_s^{(0)}\right)\left(\varepsilon_a^{(0)} - \varepsilon_r^{(0)}\right)} - \sum_{abr} \frac{v_{ra} v_{ab} v_{br}}{\left(\varepsilon_a^{(0)} - \varepsilon_r^{(0)}\right)\left(\varepsilon_b^{(0)} - \varepsilon_r^{(0)}\right)}$$

For close shell systems:

$$\sum^{N} = 2 \sum^{N/2}$$

Ex. Find fourth order energy for closed-shell cyclic polyene

a)   Show that

 $= \dfrac{N\beta}{64}$

and   so that $E_0^{(4)} = \dfrac{N\beta}{64}$

 $= -\dfrac{3N\beta}{128}$

Thus the resonance energy calculated for cyclic polyene with N>6 up to fourth order is (1/4+1/64) Nβ = 0.2656 Nβ, which compares with asymptotically exact value of 0.2732 Nβ (97% of exact).

b) For benzene, show that the diagrammatic result for the fourth-order energy agrees with the independently calculated results from previous exercise (with short and long bonds).

Perturbation expansion of the correlation energy

Improving of HF of N-electron system $\qquad H = H_0 + V$

HF $\quad H_0 \left| \Psi_0 \right\rangle = E_0^{(0)} \Psi_0 \qquad\qquad E_0^{(0)} = \sum_a \varepsilon_a$

$$E_0^{(1)} = \left\langle \Psi_0 \left| V \right| \Psi_0 \right\rangle = -\frac{1}{2} \sum_{ab} \left\langle ab \| ab \right\rangle$$

HF energy is $\quad E_0 = E_0^{(0)} + E_0^{(1)} = \sum_a \varepsilon_a - \tfrac{1}{2} \sum_{ab} \left\langle ab \| ab \right\rangle$

First correlation from $\qquad E_0^{(2)} = {\sum_n}' \dfrac{\left| \left\langle 0 \left| V \right| n \right\rangle \right|^2}{E_0^{(0)} - E_n^{(0)}} \qquad$ Summation over but the ground state of system

$\left| 0 \right\rangle = \left| \Psi_0 \right\rangle \qquad\qquad$ |n> these states cannot be single excitation due to

$$\left\langle \Psi_0 \left| V \right| \Psi_a^r \right\rangle = \left\langle \Psi_0 \left| H - H_0 \right| \Psi_a^r \right\rangle = \left\langle \Psi_0 \left| H \right| \Psi_a^r \right\rangle - f_{ar} = 0$$

Brillouin's theorem

Spinorb. are eigenfunction of Fock op.

Triply excited states do not mix with $|\Psi_0 >$ due to two-particle nature of perturbation!

Double excitation $\left|\Psi_{ab}^{rs}\right\rangle$ $\qquad H_0\left|\Psi_{ab}^{rs}\right\rangle = (E_0^{(0)} - (\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s))\left|\Psi_{ab}^{rs}\right\rangle$

Summing over all possible double excitation

$$E_0^{(2)} = \sum_{\substack{a<b \\ r<s}} \frac{\left|\left\langle \Psi_0 \left| \sum_{i<j} r_{ij}^{-1} \right| \Psi_{ab}^{rs} \right\rangle\right|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} = \sum_{\substack{a<b \\ r<s}} \frac{\left|\langle ab\|rs\rangle\right|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

Sum of contribution from each pair of electron in occupied orbitals

$$E_0^{(2)} = \sum_{a<b} e_{ab}^{FO}$$

$$e_{ab}^{FO} = \sum_{r<s} \frac{\left|\langle ab\|rs\rangle\right|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \qquad \text{"Pair theory"}$$

At level of first-order pairs, pair theory gives same correlation as 2nd PT.

$$a = b \quad \text{or} \ \ r=s \quad \longrightarrow \quad 0 \qquad E_0^{(2)} = \frac{1}{4}\sum_{abrs} \frac{\left|\langle ab\|rs\rangle\right|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

$$E_0^{(2)} = \frac{1}{2}\sum_{abrs} \frac{\langle ab|rs\rangle\langle rs|ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \frac{1}{2}\sum_{abrs} \frac{\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

close shell $\qquad E_0^{(2)} = 2\sum_{abrs}^{N/2} \frac{\langle ab|rs\rangle\langle rs|ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \sum_{abrs}^{N/2} \frac{\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$

Ex.Derive

$$E_0^{(2)} = \frac{1}{2}\sum_{abrs}\frac{\langle ab|rs\rangle\langle rs|ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \frac{1}{2}\sum_{abrs}\frac{\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

and

$$E_0^{(2)} = 2\sum_{abrs}^{N/2}\frac{\langle ab|rs\rangle\langle rs|ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \sum_{abrs}^{N/2}\frac{\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

from

$$E_0^{(2)} = \frac{1}{4}\sum_{abrs}\frac{\left|\langle ab\|rs\rangle\right|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

third order of energy

$$E_0^{(3)} = \frac{1}{8} \sum_{abcdrs} \frac{\langle ab \| rs \rangle \langle cd \| ab \rangle \langle rs \| cd \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)(\varepsilon_c + \varepsilon_d - \varepsilon_r - \varepsilon_s)}$$

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

$$+ \sum_{abcrst} \frac{\langle ab \| rs \rangle \langle cs \| tb \rangle \langle rt \| ac \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)(\varepsilon_a + \varepsilon_c - \varepsilon_r - \varepsilon_t)}$$

Illustration - Second and third order of H_2 in minimal basis

Exact correlation is $\quad E_{corr} = \Delta - (\Delta^2 + K_{12}^2)^{1/2}$

where $\quad 2\Delta = 2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12}$

$$= 2(\varepsilon_2 - \varepsilon_1) + \langle 11|11 \rangle + \langle 22|22 \rangle - 4\langle 12|12 \rangle + 2\langle 11|22 \rangle$$

Expansion of correlation energy to Taylor series up to third order $\quad E_{corr} = E_0^{(2)} + E_0^{(3)} + \ldots$

where $\quad E_0^{(2)} = \dfrac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)} \qquad E_0^{(3)} = \dfrac{K_{12}^2(J_{11} + J_{22} - 4J_{12} + 2K_{12})}{4(\varepsilon_1 - \varepsilon_2)^2}$

Single hole orbitals a = b = 1, similarly r = s = 2 then

$$E_0^{(2)} = 2 \sum_{abrs}^{N/2} \frac{\langle ab|rs \rangle \langle rs|ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \sum_{abrs}^{N/2} \frac{\langle ab|rs \rangle \langle rs|ba \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

becomes

$$E_0^{(2)} = 2 \frac{\langle 11|22 \rangle \langle 22|11 \rangle}{2(\varepsilon_1 - \varepsilon_2)} - \frac{\langle 11|22 \rangle \langle 22|11 \rangle}{2(\varepsilon_1 - \varepsilon_2)} = \frac{|\langle 11|22 \rangle^2|}{2(\varepsilon_1 - \varepsilon_2)} = \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}$$

Ex. Derive

$$E_0^{(2)} = \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}$$

and

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

from

$$E_{corr} = \Delta - (\Delta^2 + K_{12}^2)^{1/2}$$

The N-dependence of RS perturbation expansion

Proof that PT is proportional to number of particles:
Supermolecule N noninteracting H_2 (in DCI was proportional to $N^{1/2}$ in limit of large N
Label the orbitals:

All two electron integrals involving orbitals from different units are zero. HF wave function is

$$\left| \Psi_0 \right\rangle = \left| 1_1 \bar{1}_1 1_2 \bar{1}_2 \cdots 1_N \bar{1}_N \right\rangle$$

Zeroth-order

$$E_0^{(0)} = \left\langle \Psi_0 \left| H_0 \right| \Psi_0 \right\rangle = 2\sum_{i=1}^{N} \left\langle 1_i \left| f \right| 1_i \right\rangle = 2N\varepsilon_1$$

First order

$$E_0^{(1)} = \left\langle \Psi_0 \left| V \right| \Psi_0 \right\rangle = -\sum_{i=1}^{N} \left\langle 1_i 1_i \left| 1_i 1_i \right. \right\rangle = -NJ_{11}$$

HF energy of supermolecule $E_0 = \langle \Psi_0 | H_0 + V | \Psi_0 \rangle = E_0^{(0)} + E_0^{(1)} = N(2\varepsilon_1 - J_{11})$

is indeed simply N times HF of one subunit. Expression for 2nd order energy is

$$E_0^{(2)} = {\sum_n}' \frac{\left| \langle 0 | V | n \rangle \right|^2}{E_0^{(0)} - E_n^{(0)}}$$

Clearly $|0> = |\Psi_0>$ and the state $|n>$ must be a double excitation of type $\left| \Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i} \right\rangle$

For these excitation $E_0^{(0)} - E_n^{(0)} = 2(\varepsilon_1 - \varepsilon_2)$

$$\langle \Psi_0 | V | \Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i} \rangle = \langle 1_i \bar{1}_i | 2_i \bar{2}_i \rangle - \langle 1_i \bar{1}_i | \bar{2}_i 2_i \rangle = \langle 11 | 22 \rangle = K_{12}$$

Summation over n can be replaced by summation over i

$$E_0^{(2)} = \sum_{i=1}^{N} \frac{\left| \langle \Psi_0 | V | \Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i} \rangle \right|^2}{2(\varepsilon_1 - \varepsilon_2)} = \frac{N K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)} \qquad \longleftarrow \qquad$$ N times energy of one unit

General expression of third order energy is $\qquad E_0^{(3)} = A_0^{(3)} + B_0^{(3)}$

where $A_0^{(3)} = {\sum_n}' {\sum_m}' \frac{\langle 0 | V | n \rangle \langle n | V | m \rangle \langle m | V | 0 \rangle}{(E_0^{(0)} - E_n^{(0)})(E_0^{(0)} - E_m^{(0)})}$

and $\qquad B_0^{(3)} = -E_0^{(1)} {\sum_n}' \frac{\left| \langle 0 | V | n \rangle \right|^2}{(E_0^{(0)} - E_n^{(0)})^2}$

$B_0^{(3)}$ doesn't appear to have N dependence, since *$B_0^{(3)}$ is proportional to N^2* :

$$B_0^{(3)} = -(-NJ_{11})\sum_{i=1}^{N}\frac{K_{12}^2}{(2\varepsilon_1 - 2\varepsilon_2)^2} = \frac{N^2 J_{11} K_{12}^2}{4(\varepsilon_1 - \varepsilon_2)^2}$$

But this term is cancelled by part of term $A_0^{(3)}$.

In $A_0^{(3)}$ both |n> and |m> must be states of type $\left|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\right\rangle$ so that

$$A_0^{(3)} = \sum_{i=1}^{N}\frac{\left\langle\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\left|V\right|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\right\rangle K_{12}^2}{4(\varepsilon_1 - \varepsilon_2)^2}$$

Only diagonal term because integral involving different units are zero.

$$\left\langle\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\left|V\right|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\right\rangle = \left\langle\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\left|H - H_0\right|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\right\rangle$$

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

so we have
$$A_0^{(3)} = -\frac{N^2 J_{11} K_{12}^2}{4(\varepsilon_1 - \varepsilon_2)^2} + \frac{NK_{12}^2(J_{11} + J_{22} - 4J_{12} + 2K_{12})}{4(\varepsilon_1 - \varepsilon_2)^2}$$

or
$$E_0^{(3)} = A_0^{(3)} + B_0^{(3)} = \frac{NK_{12}^2(J_{11} + J_{22} - 4J_{12} + 2K_{12})}{4(\varepsilon_1 - \varepsilon_2)^2}$$

Ex.Derive and

$$\left\langle\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\left|V\right|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\right\rangle = \left\langle\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\left|H - H_0\right|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\right\rangle$$

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

$$E_0^{(1)} = \left\langle\Psi_0\left|V\right|\Psi_0\right\rangle = -\sum_{i=1}^{N}\left\langle 1_i 1_i\left|1_i 1_i\right.\right\rangle = -NJ_{11}$$

Diagrammatic representation of the perturbation expansion of the correlation energy

Nth order of energy (zero order is HF), HF is good for start, due to Brillouin theorem.

Hugenholtz diagram

In
$$E_0^{(2)} = \frac{1}{4} \sum_{abrs} \frac{\left|\langle ab \| rs \rangle\right|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$
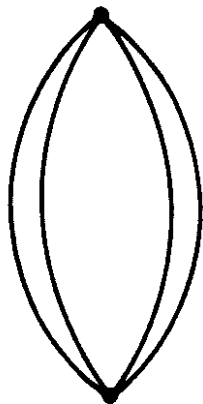the numerator have four indices – result of two particle nature of perturbation
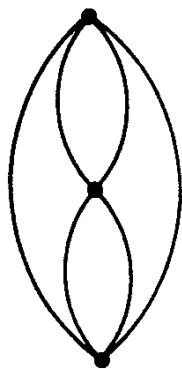
Dot with two line in and two line out

In diagram – connect dots in all possible ways:
1) Each dot has four lines
2) Each diagram is linked
3) Each diagram is distinct
4) Diagram containing more than one dot do not have lines which start and end at the same point.
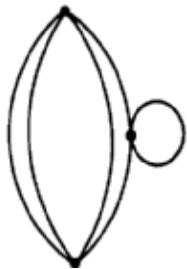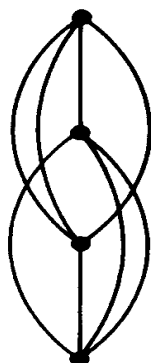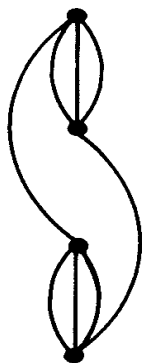

Consequence of Brillouin's

$n = 2$

$n = 3$

Fourth order
(unlabeled)
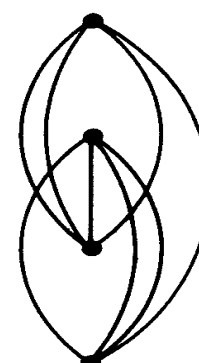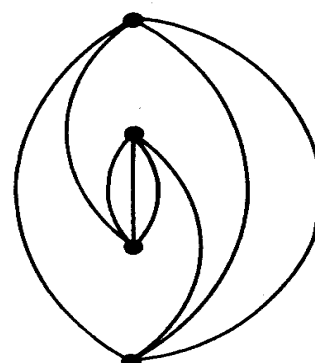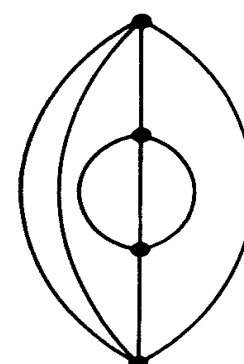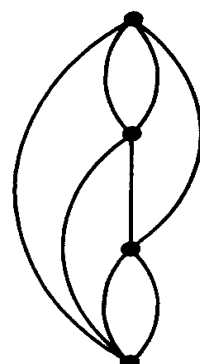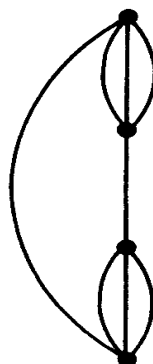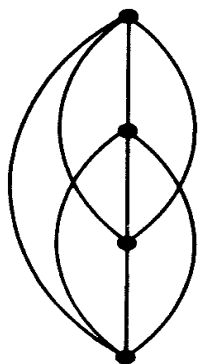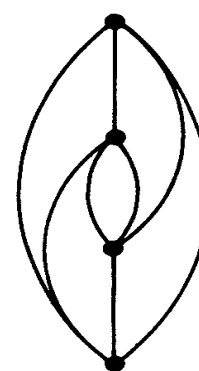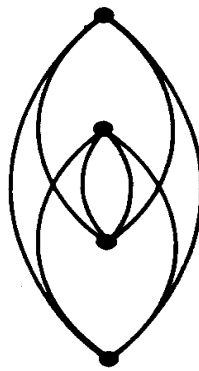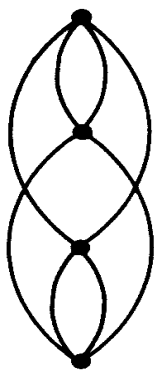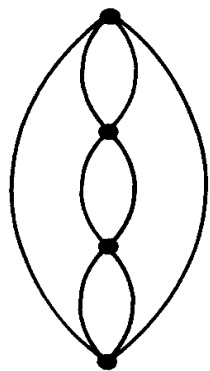
Labeling

$n = 2$

$n = 3$

Hugenholtz diagram

a) *Each dot contributes an antisymmetrized matrix element ⟨label-1 in, label-2 in||label-1 out, label-2 out⟩ to the numerator. The particular labeling 1 and 2 is arbitrary.*

b) *Each pair of adjacent dots contributes the denominator factor*

$$\sum \varepsilon_{\text{holes}} - \sum \varepsilon_{\text{particles}}$$

where the sums run over the labels of all hole and particle lines crossing an imaginary horizontal line separating the two adjacent dots.

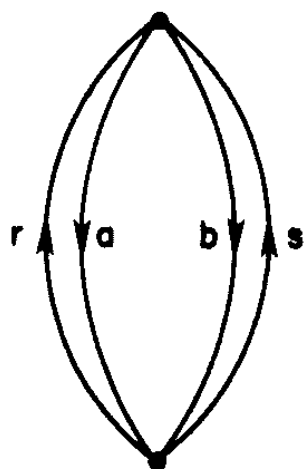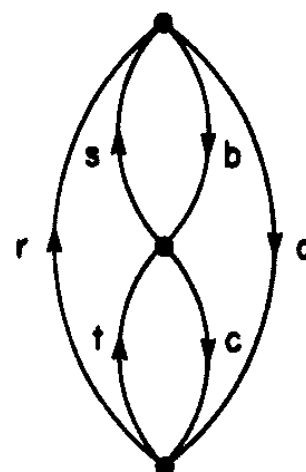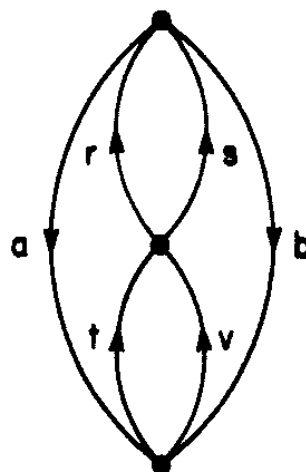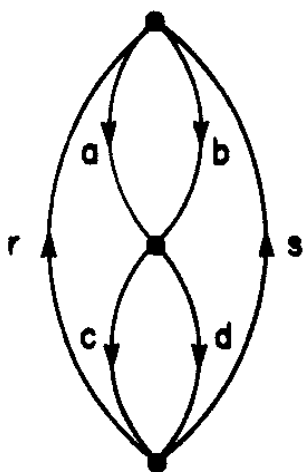c) *The overall sign of the expression is $(-)^{h+l}$, where h and l are the number of hole lines and closed loops, respectively. The number of closed loops cannot be determined by looking at the diagram alone. We will give a prescription below as how to find it from the string of matrix elements written down using rule (H1).*

d) *Sum the expression over all particle and hole indices.*

e) *Multiply the expression by a weight factor 2^{-k}, where k is the number of pairs of equivalent lines in the diagram. Two lines are equivalent when both start and end at the same dot and both go in the same direction.*

Second order

Two equivalent line (r,s) and (a,b)
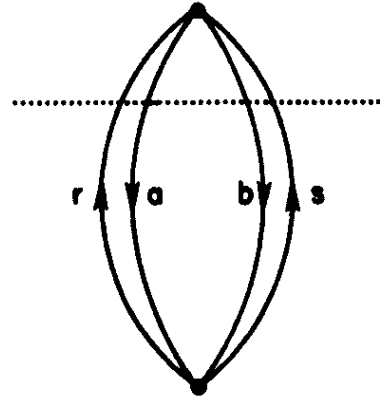
Case A

$$\left(\frac{1}{2}\right)^2 (-)^{2+l_A} \sum_{abrs} \frac{\langle ab\|rs\rangle\langle rs\|ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

Case B

$$\left(\frac{1}{2}\right)^2 (-)^{2+l_B} \sum_{abrs} \frac{\langle ab\|rs\rangle\langle sr\|ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

A and B must be equal – 1 factor. Number of closed loops can be found only after we written down a string of matrix elements

$$\langle ij\|kl\rangle \qquad \text{and} \qquad \langle ij\|kl\rangle$$

Case A

$$\langle ab||rs\rangle\langle rs||ab\rangle \quad : \quad a \xrightarrow{1} r \xrightarrow{2} a$$

$$\langle ab||rs\rangle\langle rs||ab\rangle \quad : \quad b \xrightarrow{1} s \xrightarrow{2} b \qquad \mathbf{l_A = 2}$$

Case B

$$\langle ab||rs\rangle\langle sr||ab\rangle \quad : \quad a \xrightarrow{1} r \xrightarrow{2} b \xrightarrow{3} s \xrightarrow{4} a \qquad \mathbf{l_B = 1}$$
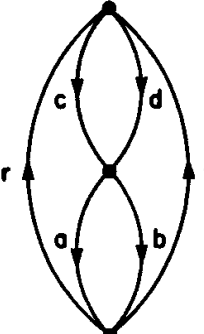
$$\langle rs\|ab\rangle = -\langle sr\|ab\rangle \qquad \longrightarrow \qquad \mathbf{A = B}$$
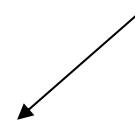
$$E_0^{(2)} = \frac{1}{4}\sum_{abrs}\frac{\langle ab\|rs\rangle\langle rs\|ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$
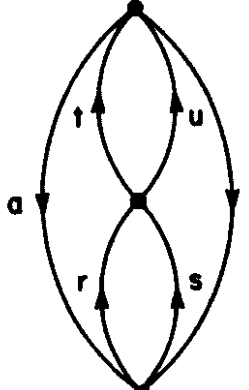
Third order

$$= \left(\frac{1}{2}\right)^3 (-)^{4+l} \sum_{abcdrs} \frac{\langle ab||rs\rangle\langle cd||ab\rangle\langle rs||cd\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)(\varepsilon_c + \varepsilon_d - \varepsilon_r - \varepsilon_s)}$$

$1 = 2$

$a \rightarrow r \rightarrow c \rightarrow a$

$b \rightarrow s \rightarrow d \rightarrow b$

$$= \left(\frac{1}{2}\right)^3 (-)^{2+l} \sum_{abrstu} \frac{\langle ab||rs\rangle\langle rs||tu\rangle\langle tu||ab\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)(\varepsilon_a + \varepsilon_b - \varepsilon_t - \varepsilon_u)}$$

$1 = 2$

$a \rightarrow r \rightarrow t \rightarrow a$

$b \rightarrow s \rightarrow u \rightarrow b$

$$= (-)^{3+l} \sum_{abcrst} \frac{\langle ab||rs\rangle\langle cs||tb\rangle\langle rt||ac\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_r)(\varepsilon_a + \varepsilon_c - \varepsilon_r - \varepsilon_t)}$$

$$l = 3 \qquad \begin{array}{l} a \to r \to a \\ b \to s \to b \\ c \to t \to c \end{array}$$

Total energy $E_0^{(3)}$

$$E_0^{(3)} = \frac{1}{8} \sum_{abcdrs} \frac{\langle ab||rs\rangle\langle cd||ab\rangle\langle rs||cd\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)(\varepsilon_c + \varepsilon_d - \varepsilon_r - \varepsilon_s)}$$

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

$$+ \sum_{abcrst} \frac{\langle ab||rs\rangle\langle cs||tb\rangle\langle rt||ac\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_r)(\varepsilon_a + \varepsilon_c - \varepsilon_r - \varepsilon_t)}$$

Ex. Show that the fourth-order diagram
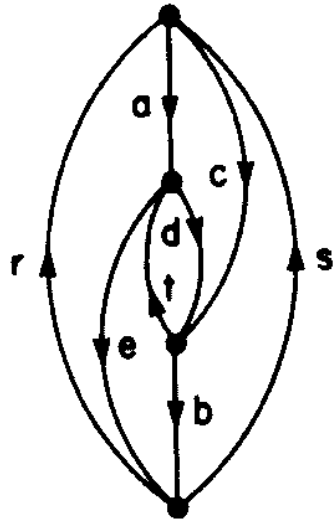
is equal to

$$-\frac{1}{2}\sum_{abcderst}\frac{\langle rs\|ac\rangle\langle at\|de\rangle\langle dc\|tb\rangle\langle eb\|rs\rangle}{(\varepsilon_a+\varepsilon_c-\varepsilon_r-\varepsilon_s)(\varepsilon_c+\varepsilon_d+\varepsilon_e-\varepsilon_r-\varepsilon_t-\varepsilon_s)(\varepsilon_b+\varepsilon_e-\varepsilon_r-\varepsilon_s)}$$

Goldstone diagrams

Two particle interaction is not dot but dashed line
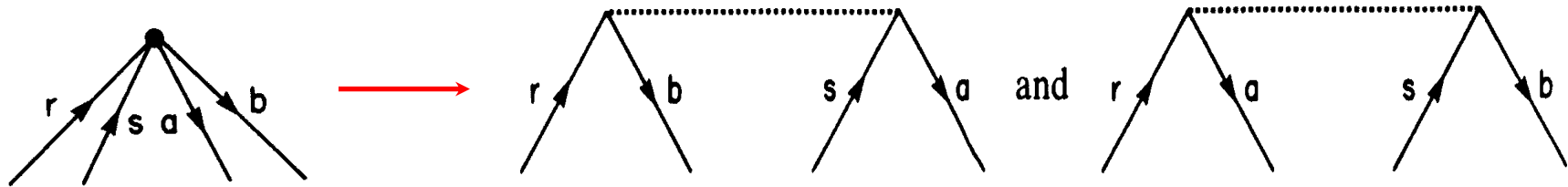
This eliminates the antisymmetric elements.

Direct exchange

Exchange diagram
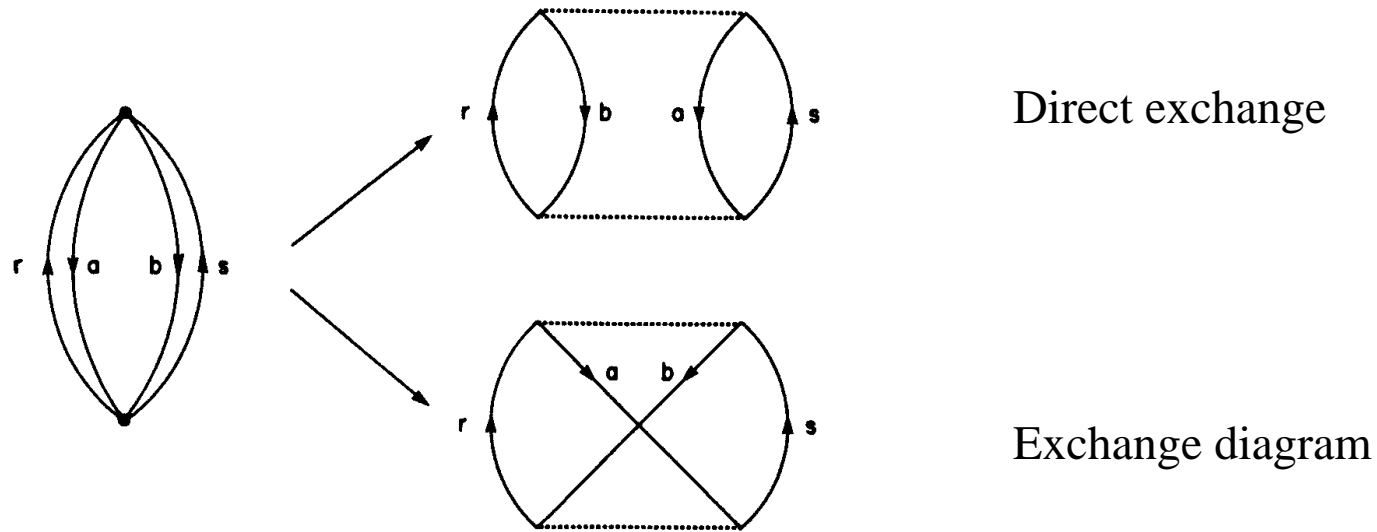
Rules:

Each interaction line
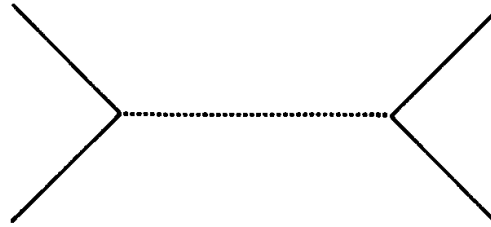
contributes a matrix element factor ⟨label-left in, label-right in | label-left out, label-right out⟩ to the numerator.

Each pair of adjacent interaction lines contributes the denominator factor

$$\sum \varepsilon_{\text{hole}} - \sum \varepsilon_{\text{particle}}$$

where the sums run over the labels of all hole and particle lines crossing an imaginary horizontal line separating the two adjacent interaction lines.

The overall sign of the expression is $(-)^{h+l}$, where h and l are the number of hole lines and closed loops, respectively.

Sum the expression over all particle and hole indices.

Diagrams which have a mirror plane perpendicular to the plane of the paper are multiplied by a factor of 1/2.

For *closed-shell* *systems,* *a* *summation* *over* *spin* *orbitals* *is* *equal* *to* 2^l *times* *a* *summation* *over* *spatial* *orbitals,* *i.e.,*

$$\sum^{N} = (2)^l \sum^{N/2}.$$

Table: Second and third order of Goldstone diagrams
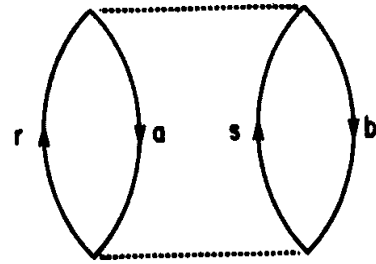
$$(-)^{2+2} \quad \left(\frac{1}{2}\right) \sum_{abrs} \frac{\langle ab|rs\rangle\langle rs|ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$
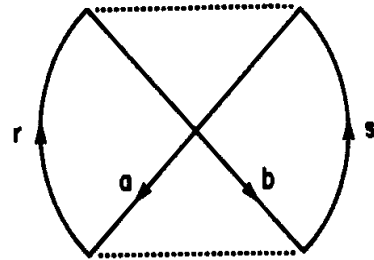
$$(-)^{2+1} \quad \left(\frac{1}{2}\right) \sum_{abrs} \frac{\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$
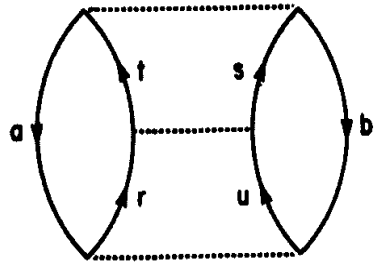
$$(-)^{2+2} \quad \left(\frac{1}{2}\right) \sum_{abrsut} \frac{\langle ab|ru\rangle\langle ru|ts\rangle\langle ts|ab\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_u)(\varepsilon_a + \varepsilon_b - \varepsilon_t - \varepsilon_s)}$$
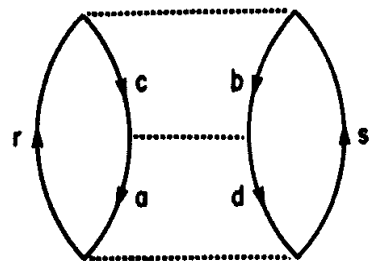
$$(-)^{4+2} \quad \left(\frac{1}{2}\right) \sum_{abcdrs} \frac{\langle ad|rs\rangle\langle cb|ad\rangle\langle rs|cb\rangle}{(\varepsilon_a + \varepsilon_d - \varepsilon_r - \varepsilon_s)(\varepsilon_c + \varepsilon_b - \varepsilon_r - \varepsilon_s)}$$
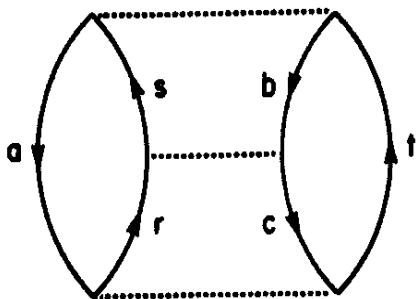
$$(-)^{3+2} \sum_{abcrst} \frac{\langle ac|rt\rangle\langle rb|sc\rangle\langle st|ab\rangle}{(\varepsilon_a + \varepsilon_c - \varepsilon_r - \varepsilon_t)(\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t)}$$

$$(-)^{3+2} \sum_{abcrst} \frac{\langle bc|rt\rangle\langle ra|sb\rangle\langle st|ac\rangle}{(\varepsilon_b + \varepsilon_c - \varepsilon_r - \varepsilon_t)(\varepsilon_a + \varepsilon_c - \varepsilon_s - \varepsilon_t)}$$

$$(-)^{3+3} \sum_{abcrst} \frac{\langle ac|rt\rangle\langle bt|sc\rangle\langle rs|ab\rangle}{(\varepsilon_a + \varepsilon_c - \varepsilon_r - \varepsilon_t)(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)}$$

$$(-)^{3+1} \sum_{abcrst} \frac{\langle cb|rt\rangle \langle at|sc\rangle \langle rs|ab\rangle}{(\varepsilon_c + \varepsilon_b - \varepsilon_r - \varepsilon_t)(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)}$$

$$(-)^{4+1} \left(\frac{1}{2}\right) \sum_{abcdrs} \frac{\langle ac|rs\rangle \langle db|ac\rangle \langle sr|db\rangle}{(\varepsilon_a + \varepsilon_c - \varepsilon_r - \varepsilon_s)(\varepsilon_d + \varepsilon_b - \varepsilon_r - \varepsilon_s)}$$

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

$$(-)^{3+1} \sum_{abcrst} \frac{\langle bc|rt\rangle \langle ar|bs\rangle \langle ts|ac\rangle}{(\varepsilon_c + \varepsilon_b - \varepsilon_r - \varepsilon_t)(\varepsilon_a + \varepsilon_c - \varepsilon_s - \varepsilon_t)}$$
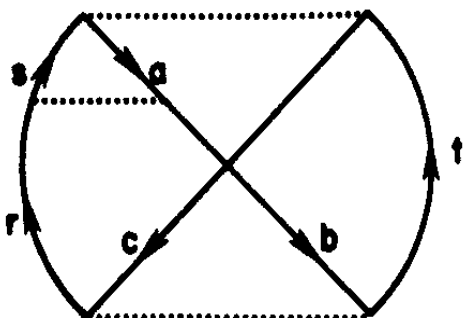
$$(-)^{3+1} \sum_{abcrst} \frac{\langle cb|rt\rangle \langle ra|sb\rangle \langle st|ac\rangle}{(\varepsilon_c + \varepsilon_b - \varepsilon_r - \varepsilon_t)(\varepsilon_a + \varepsilon_c - \varepsilon_s - \varepsilon_t)}$$
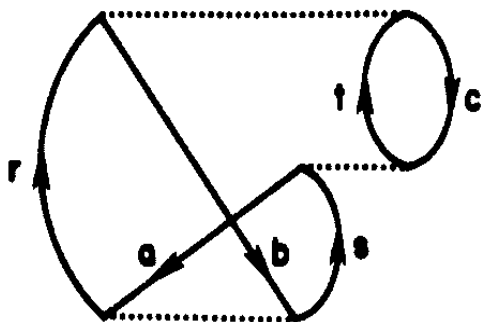
$$(-)^{3+2} \sum_{abcrst} \frac{\langle ab|rs\rangle \langle sc|at\rangle \langle rt|bc\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)(\varepsilon_c + \varepsilon_b - \varepsilon_r - \varepsilon_t)}$$
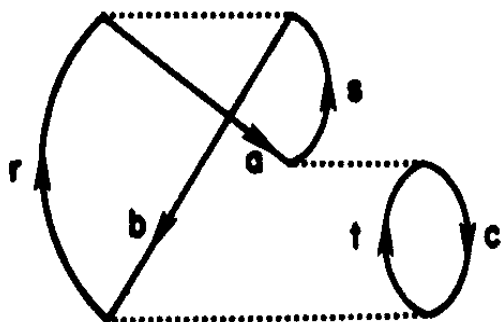
$$(-)^{3+2} \sum_{abcrst} \frac{\langle bc|rt\rangle \langle at|sc\rangle \langle rs|ab\rangle}{(\varepsilon_b + \varepsilon_c - \varepsilon_t - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)}$$

Second order of energy

Direct: Reflecting in perpendicular plane – diagram remains invariant to reflection

Weight factor

$\equiv$

$\longrightarrow$ 1/2
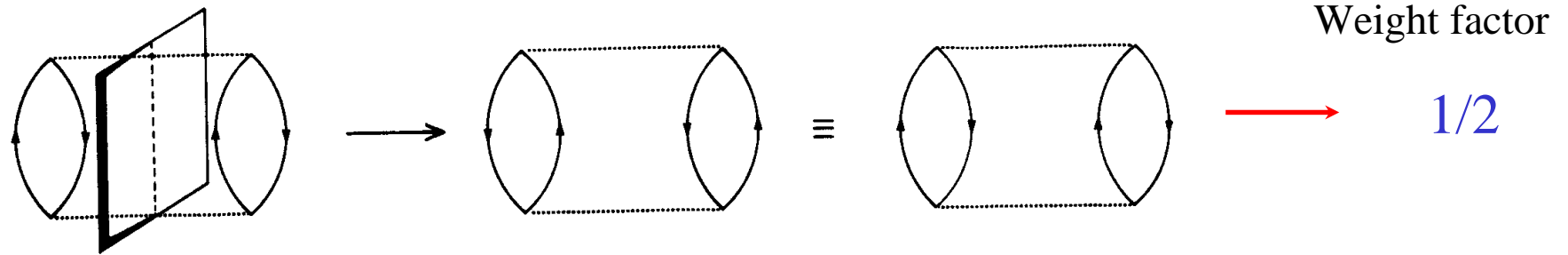
Two holes + two closed loop

$$= \frac{1}{2}(-)^4 \sum_{abrs} \frac{\langle ab|rs \rangle \langle rs|ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$
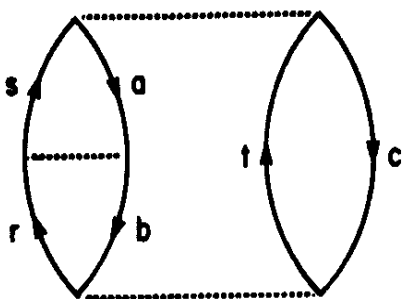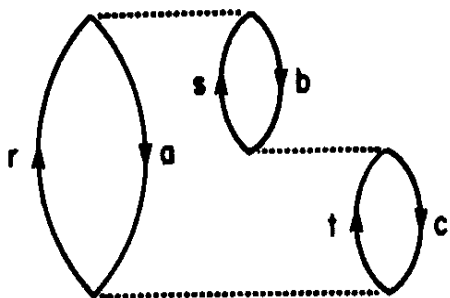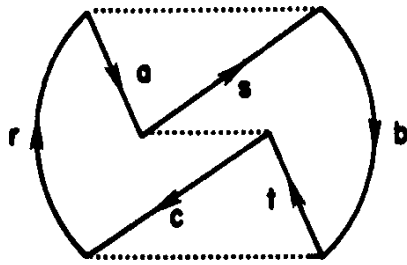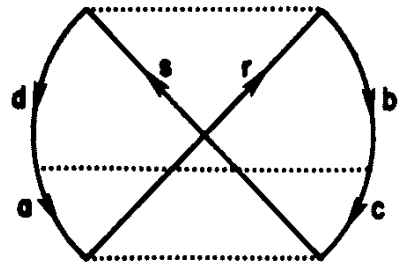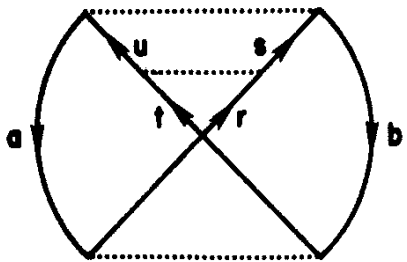
Exchange

$\longrightarrow$ 1/2
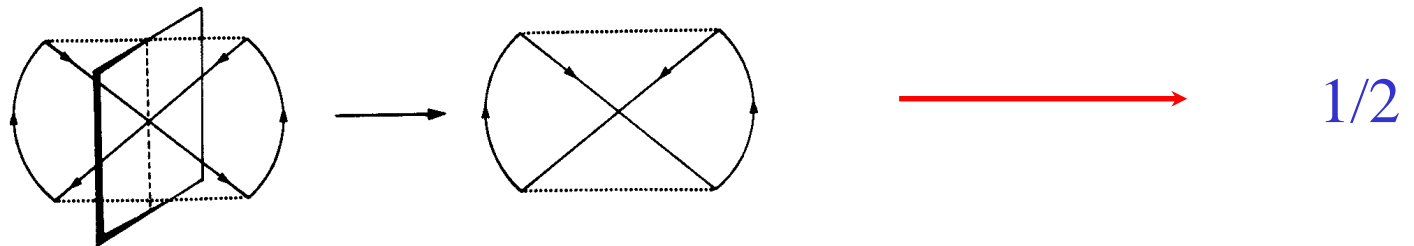
Two holes, but only one loop
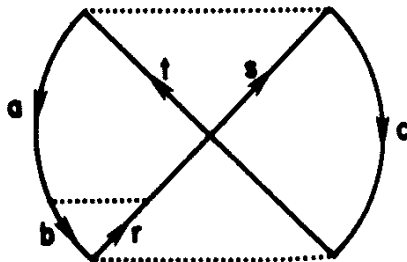
$r \rightarrow b \rightarrow s \rightarrow a \rightarrow r$

$$= \frac{1}{2}(-)^{2+1} \sum_{abrs} \frac{\langle ab|rs \rangle \langle rs|ba \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

Close shell – converting from spin orbital to spatial: direct multiplied by 2^2

exchange   by 2^1

Ex. Goldstone diagrams in Table can be obtained by "pulling apart: the second and third-order Hugenholtz diagrams. For example if we push
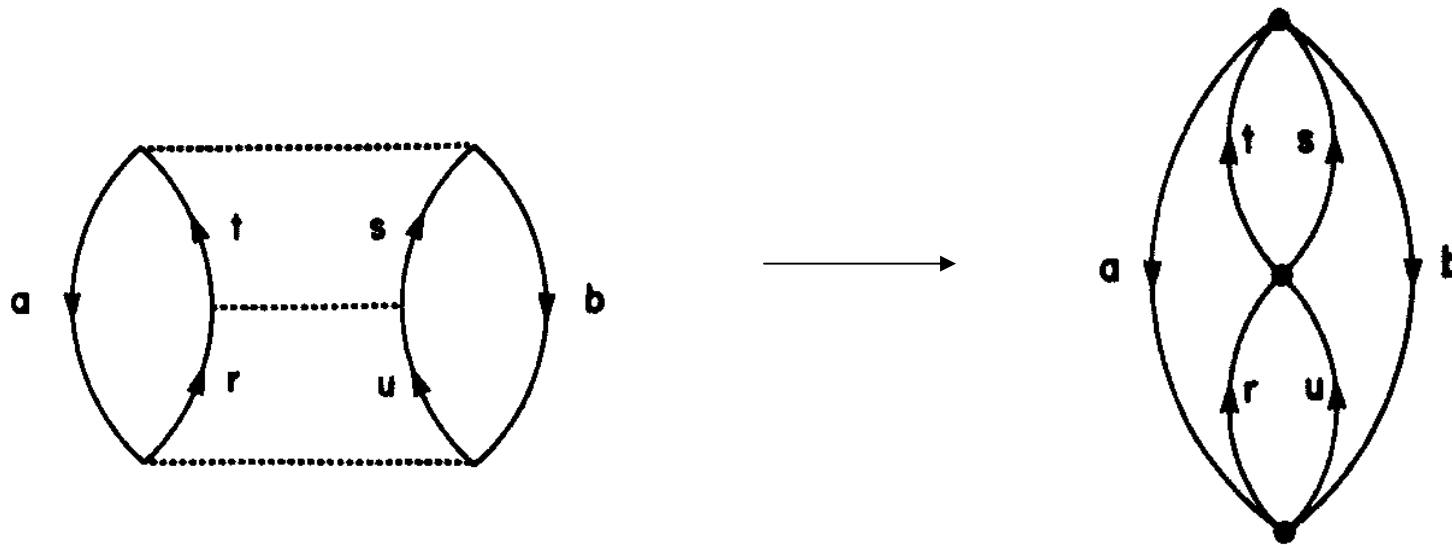
Push all third-order diagram in Table in similar way find which Goldstone diagram come to Hugenholtz. For above Hugenholtz diagram,verify that its mathematical value indeed the sum of the values of corresponding Goldstone diagrams.

Example: H$_2$

Two second order diagram

$$1 \leftrightarrow (2)^2(1/2) \frac{\langle 11|22 \rangle^2}{(2\varepsilon_1 - 2\varepsilon_2)} = \frac{K_{12}^2}{(\varepsilon_1 - \varepsilon_2)}$$

$$2 \leftrightarrow -(2)(1/2) \frac{\langle 11|22 \rangle^2}{(2\varepsilon_1 - 2\varepsilon_2)} = -\frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}$$

Third order diagram

$$1 \leftrightarrow (2)^2 \left(\frac{1}{2}\right) \frac{\langle 11|22 \rangle \langle 22|22 \rangle \langle 22|11 \rangle}{4(\varepsilon_1 - \varepsilon_2)^2} = \frac{K_{12}^2 J_{22}}{2(\varepsilon_1 - \varepsilon_2)^2}$$

$$2 \leftrightarrow (2)^2 \left(\frac{1}{2}\right) \frac{\langle 11|22 \rangle \langle 11|11 \rangle \langle 22|11 \rangle}{4(\varepsilon_1 - \varepsilon_2)^2} = \frac{K_{12}^2 J_{11}}{2(\varepsilon_1 - \varepsilon_2)^2}$$

$$3 \leftrightarrow -(2)^2 \frac{\langle 11|22 \rangle \langle 21|21 \rangle \langle 22|11 \rangle}{4(\varepsilon_1 - \varepsilon_2)^2} = -\frac{K_{12}^2 J_{12}}{(\varepsilon_1 - \varepsilon_2)^2}$$

$$4 \leftrightarrow -(2)^2 \frac{\langle 11|22 \rangle \langle 21|21 \rangle \langle 22|11 \rangle}{4(\varepsilon_1 - \varepsilon_2)^2} = -\frac{K_{12}^2 J_{12}}{(\varepsilon_1 - \varepsilon_2)^2}$$

$$5 \leftrightarrow (2)^3 \frac{\langle 11|22\rangle\langle 12|21\rangle\langle 22|11\rangle}{4(\varepsilon_1 - \varepsilon_2)^2} = 2\frac{K_{12}^2 K_{12}}{(\varepsilon_1 - \varepsilon_2)^2}$$

$$6 \leftrightarrow (2) \frac{\langle 11|22\rangle\langle 12|21\rangle\langle 22|11\rangle}{4(\varepsilon_1 - \varepsilon_2)^2} = \frac{K_{12}^2 K_{12}}{2(\varepsilon_1 - \varepsilon_2)^2}$$

$$7 \leftrightarrow -(2)\left(\frac{1}{2}\right) \frac{\langle 11|22\rangle\langle 11|11\rangle\langle 11|22\rangle}{4(\varepsilon_1 - \varepsilon_2)^2} = -\frac{K_{12}^2 J_{11}}{4(\varepsilon_1 - \varepsilon_2)^2}$$

$$8 \leftrightarrow -(2)\left(\frac{1}{2}\right) \frac{\langle 11|22\rangle\langle 22|22\rangle\langle 11|22\rangle}{4(\varepsilon_1 - \varepsilon_2)^2} = -\frac{K_{12}^2 J_{22}}{4(\varepsilon_1 - \varepsilon_2)^2}$$

$$9 \leftrightarrow (2) \frac{\langle 11|22\rangle\langle 12|12\rangle\langle 11|22\rangle}{4(\varepsilon_1 - \varepsilon_2)^2} = \frac{K_{12}^2 J_{12}}{2(\varepsilon_1 - \varepsilon_2)^2}$$

$$10 \leftrightarrow (2) \frac{\langle 11|22\rangle\langle 21|21\rangle\langle 11|22\rangle}{4(\varepsilon_1 - \varepsilon_2)^2} = \frac{K_{12}^2 J_{12}}{2(\varepsilon_1 - \varepsilon_2)^2}$$

$$11 \leftrightarrow -(2)^2 \frac{\langle 11|22\rangle\langle 21|12\rangle\langle 11|22\rangle}{4(\varepsilon_1 - \varepsilon_2)^2} = -\frac{K_{12}^2 K_{12}}{(\varepsilon_1 - \varepsilon_2)^2}$$

$$12 \leftrightarrow -(2)^2 \frac{\langle 11|22\rangle\langle 12|21\rangle\langle 22|11\rangle}{4(\varepsilon_1 - \varepsilon_2)^2} = -\frac{K_{12}^2 K_{12}}{(\varepsilon_1 - \varepsilon_2)^2}$$

Sum over 12 expresions $\longrightarrow$ $E_0^{(3)}$

Summation of diagrams
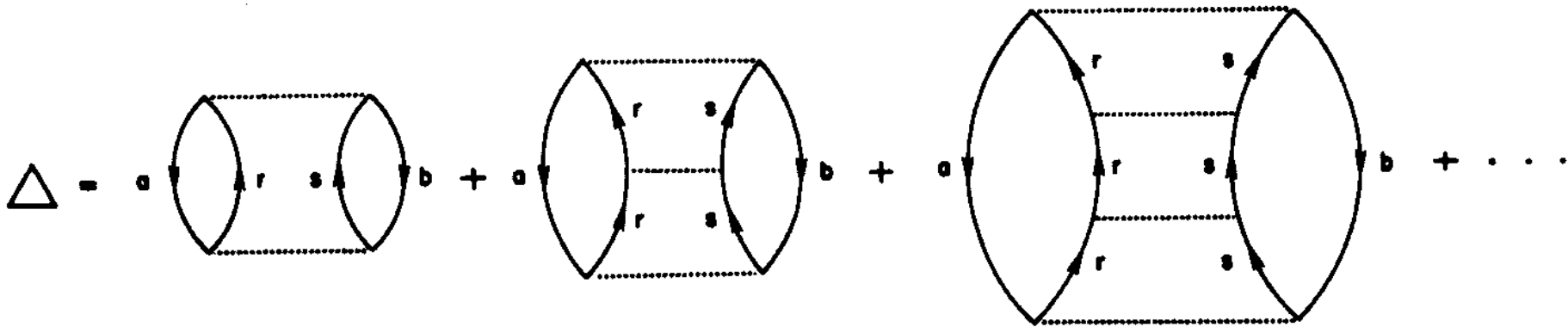
Transforming to second order diagrams; adding interaction lines, (labels below and above interaction line is same)

All have weight factor ½, same number of holes and particles – same sign

$$\Delta = \frac{1}{2} \frac{|\langle rs|ab \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \left[1 + \frac{\langle rs|rs \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} + \left(\frac{\langle rs|rs \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \right)^2 + \cdots \right]$$

$$= \frac{1}{2} \frac{|\langle rs|ab \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s - \langle rs|rs \rangle}$$

Shifted energy denominator

Sum over all diagrams $\longrightarrow$ $E_{\text{corr}}(\text{EN}) = -\dfrac{1}{4}\sum_{abrs}\dfrac{|\langle ab||rs\rangle|^2}{\langle\Psi_{ab}^{rs}|\mathscr{H}-E_0|\Psi_{ab}^{rs}\rangle}$

Similar as Epstein-Nesbet pair energy

If we sum over all double excitation diagrams (imaginary line cross only two holes and two particles line) $\longrightarrow$ double excited MBPT (D-MBPT) of Bartlett and co. Tis is equivalent to linear CCA.

$$E_{\text{corr}}(\text{D-MBPT}(\infty)) = -\mathbf{B}^\dagger(\mathbf{D})^{-1}\mathbf{B}$$

$$(\mathbf{B}^\dagger)_{rasb} = \langle\Psi_0|\mathscr{H}|\Psi_{ab}^{rs}\rangle$$

$$(\mathbf{D})_{rasb,tcud} = \langle\Psi_{ab}^{rs}|\mathscr{H}-E_0|\Psi_{cd}^{tu}\rangle \qquad \text{If D only diagonal} \longrightarrow \text{EN}$$

D-MBPT is exact third order of PT

Linked cluster theorem

Algebraic term proportional to N^2 can be represented by diagram with separate pieces (*unlinked diagrams*). But such diagrams never appear in final result of the nth-order of energy.
So:

Nth order can be written only with *linked* diagrams.

Ex.Calculate $E_0^{(3)}$ for supermolecule consist of N noninteracting minimal basis H_2 molecules evaluating the Goldstone diagrams in Table. Compare your result with

$$E_0^{(3)} = A_0^{(3)} + B_0^{(3)} = \frac{NK_{12}^2(J_{11} + J_{22} - 4J_{12} + 2K_{12})}{4(\varepsilon_1 - \varepsilon_2)^2}$$

which was obtained algebraically explicitly cancelling term proportional to N^2

Hint: Simply show that value of each Goldstone diagram for the supermolecule is N times the result for a single molecule.

Calculations

Table 6.3 Correlation energy (a.u.) of H_2 at $R = 1.4$

Basis	$E_0^{(2)}$	Percent of full CI	$E_0^{(2)} + E_0^{(3)}$	Percent of full CI	Full CI
STO-3G	−0.0132	64	−0.0180	87	−0.0206
4-31G	−0.0174	70	−0.0226	91	−0.0249
6-31G**	−0.0263	78	−0.0319	94	−0.0339
$(10s, 5p, 1d)^a$	−0.0321	81	−0.0376	95	−0.0397
Exact[b]			−0.0409		

inc

Table 6.4 Equilibrium bond length (a.u.) for H_2

Basis set	SCF	$E_0^{(2)}$	Full CI
STO-3G	1.346	1.368	1.389
4-31G	1.380	1.394	1.410
6-31G**	1.385	1.387	1.396
Exact[a]		1.401	

SCF/6-31G** differ 0.011 a.u.

Equilibrium bond length(a.u) for ten-electron series

	STO-3G	4-31G	6-31G*	6-31G**	Experiment
CH_4					
SCF	2.047	2.043	2.048	2.048	2.050
$E_0^{(2)}$	2.077	2.065	2.060	2.048	
NH_3					
SCF	1.952	1.873	1.897	1.897	1.913
$E_0^{(2)}$	1.997	1.907	1.922	1.912	
H_2O					
SCF	1.871	1.797	1.791	1.782	1.809
$E_0^{(2)}$	1.916	1.842	1.831	1.816	
FH					
SCF	1.812	1.742	1.722	1.703	1.733
$E_0^{(2)}$	1.842	1.790	1.765	1.740	

SCF largest diff. to exp. is 0.03
MP2 below 0.01 a.u.

Table 6.6 Equilibrium bond angles for NH_3 and H_2O

	STO-3G	4-31G	6-31G*	6-31G**	Experiment
NH_3					
SCF	104.2	115.8	107.5	107.6	106.7
$E_0^{(2)}$	100.9	113.9	106.3	106.1	
H_2O					
SCF	100.0	111.2	105.5	106.0	104.5
$E_0^{(2)}$	97.2	108.8	104.0	103.9	

MP2 reduce SCF error to half

Problems with multiple bonds

Table 6.7 Equilibrium bond lengths (a.u.) of N_2 and CO

Basis set	N_2			CO		
	SCF	$E_0^{(2)}$	$E_0^{(2)} + E_0^{(3)}$	SCF	$E_0^{(2)}$	$E_0^{(2)} + E_0^{(3)}$
STO-3G	2.143	2.322	2.222	2.166	2.264	2.216
4-31G	2.050	2.171	2.098	2.132	2.216	2.169
6-31G*	2.039	2.133	2.109	2.105	2.175	2.145
Experiment		2.074			2.132	

Error SCF 0.03 a.u.

MP2 overestimates correction

Table 6.8 Correlation energies (a.u.) of H_2O at the experimental geometry calculated with the 39-STO basis described in Chapter 4[a]

	E_{corr}
$E_0^{(2)}$	-0.2818
$E_0^{(2)} + E_0^{(3)}$	-0.2850
$E_0^{(2)} + E_0^{(3)} + E_0^{(4)}$	-0.2960
SDCI	-0.2756
IEPA	-0.3274
L-CCA	-0.2908
CCA	-0.2862
Estimated full CI	-0.296 ± 0.001
Exact	-0.37

Base is near HF limit
MP2 better than SDCI

PT poor convergence, non monotonic

Table 6.9 Equilibrium geometry and some force constants of H_2O calculated with the 39-STO base described in Chapter 4[a]

	R_e (a.u.)	θ_e	f_{RR}^b	$f_{\theta\theta}^b$
SCF	1.776	106.1	9.79	0.88
$E_0^{(2)}$	1.811	104.4	8.55	0.78
$E_0^{(2)} + E_0^{(3)}$	1.803	104.8	8.80	0.81
$E_0^{(2)} + E_0^{(3)} + E_0^{(4)}$	1.813	104.4	8.42	0.79
SDCI	1.800	104.9	8.88	0.81
L-CCA	1.810	104.6	8.51	0.80
CCA	1.806	104.7	8.67	0.80
Experiment	1.809	104.5	8.45	0.76

H_2 r $\longrightarrow$ infinity

SCF dissociation into 2 H

$$\lim_{R \to \infty} E_0(R) = 2E(\mathrm{H}) + \tfrac{1}{2}(\phi\phi|\phi\phi)$$

CI

$$E_0^{(2)} = \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)} \longrightarrow \text{infinity}$$