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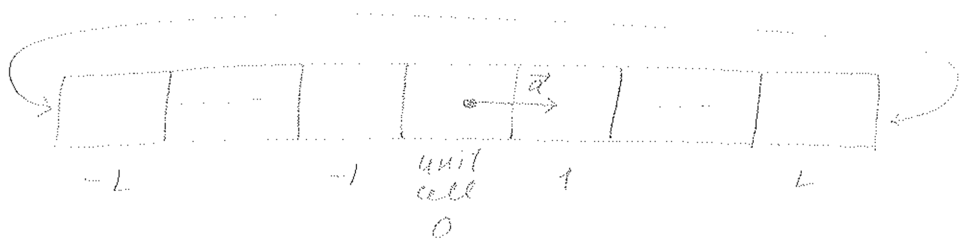
① Crystal orbital theory ≡ ab initio band theory

Periodic boundary condition



$(2L+1)$ cells in the whole chain

↳ n electrons

N nuclei

M basis functions

normalization $\left(\text{cf. particle in a box} : \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \right)$

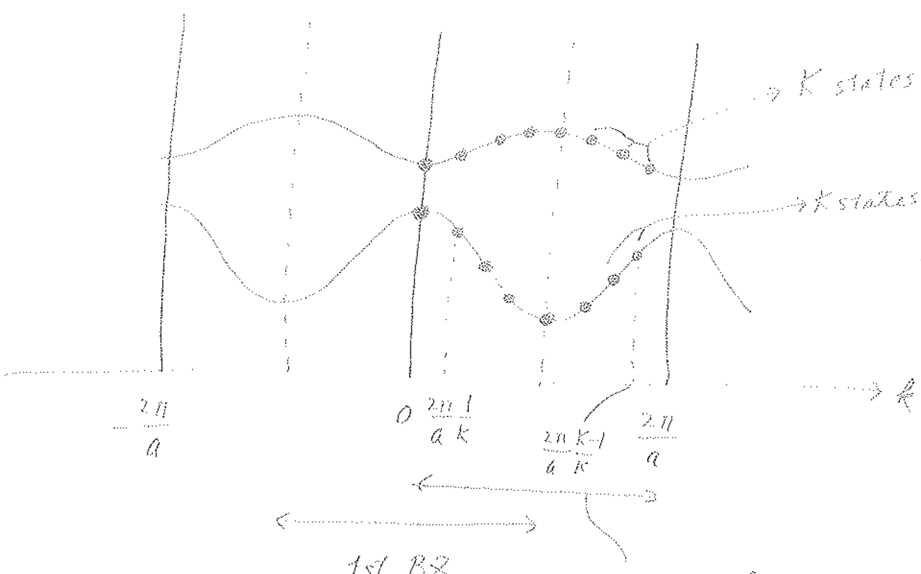
CO ; $\varphi_{pk_p}(\mathbf{r}) = \frac{1}{\sqrt{K}} \sum_{\mu}^{M} \sum_{m=-L}^{+L} \underbrace{C_{pk_p}^{\mu} \chi_{\mu}(\mathbf{r} - m\mathbf{a})}_{\text{intracell structure}} \underbrace{\exp(imk_p a)}_{\text{overall intercell phase}}$

MO ; $\varphi_p(\mathbf{r}) = \sum_{\mu}^{M} C_p^{\mu} \chi_{\mu}(\mathbf{r})$

$K = 2L+1$

$$k_p = \frac{2\pi}{a} \frac{n}{K}, \quad n = 0, 1, \cdots, K-1$$

$K = 2L+1$ (K ≡ volume or size of system)



M bands ($\frac{n}{2}$ of which occupied)

KM states from $(2L+1)M$ basis functions

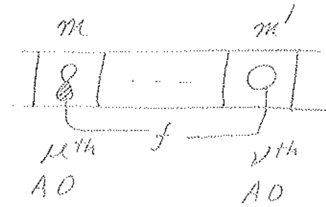
CO: $E_{HF} = \sum_{i}^{occ.} \sum_{k_i = \frac{2\pi}{a}\cdot\frac{0}{K}}^{\frac{2\pi}{a}\cdot\frac{K-1}{K}} \langle ik_i|\hat{f}|ik_i\rangle - \frac{1}{2}\sum_{i,j}^{occ.} \sum_{k_i,k_j} \langle ik_i, jk_j \| ik_i, jk_j\rangle$

MO: $E_{HF} = \sum_{i}^{occ.} \langle i|\hat{f}|i\rangle - \frac{1}{2}\sum_{i,j}^{occ.} \langle ij\|ij\rangle$

$$\langle pk_p|\hat{f}|qk_q\rangle = \frac{1}{K}\sum_{\mu,\nu}\sum_{m,m'} C_{pk_p}^{\mu *} C_{qk_q}^{\nu} \exp(-imk_p a + im'k_q a)$$

$$\times \underbrace{\int \chi_\mu^*(\mathbf{r}-m\mathbf{a})\,\hat{f}\,\chi_\nu(\mathbf{r}-m'\mathbf{a})\,d\mathbf{r}}_{\langle \mu^{(m)}|\hat{f}|\nu^{(m')}\rangle}$$

AO Fock integrals



Because of periodicity, $\langle \mu^{(m)}|\hat{o}|\nu^{(m')}\rangle = \langle \mu^{(0)}|\hat{o}|\nu^{(m'-m)}\rangle$

$$\langle pk_p|\hat{f}|qk_q\rangle = \frac{1}{K}\sum_{\mu,\nu}\sum_{m,m'} C_{pk_p}^{\mu *} C_{qk_q}^{\nu} \exp\{i(m'-m)k_q a\}$$

$$\times \exp\{im(k_q-k_p)a\}\langle \mu^{(0)}|\hat{f}|\nu^{(m'-m)}\rangle$$

In an infinite, periodic system, $\sum_{m=-\infty}^{+\infty}\sum_{m'=-\infty}^{+\infty} \equiv \sum_{m=-\infty}^{+\infty}\sum_{m'-m=-\infty}^{+\infty}$

Also $\sum_{m=-\infty}^{\infty} \exp\{im(k_p-k_q)a\} \approx \sum_{m=-L}^{+L} \exp\{im(k_p-k_q)a\}$

$\left(\text{cf. } \int_{-\infty}^{\infty} \exp(ikx)dx = 2\pi\delta(k)\right)$ $= \begin{cases} 2L+1 = K & \left(k_p-k_q = \frac{2\pi}{a}\times\text{integer}\right) \\ \text{constructive} & \\ 0 & (\text{otherwise}) \\ \text{destructive} & \end{cases}$

$$\langle p k_p | \hat{f} | q k_q \rangle = \begin{cases} \sum_{\mu,\nu} \sum_{m''} C_{pk_p}^{\mu *} C_{qk_q}^{\nu} \langle \mu^{(0)} | \hat{f} | \nu^{(m'')} \rangle \exp(i m'' k_q a) & (k_p - k_q = \frac{2\pi}{a} \times \text{integer}) \\ 0 & (\text{otherwise}) \end{cases}$$

$k_p - k_q = \frac{2\pi}{a} \times$ integer : momentum conservation

$$\langle p k_p, q k_q \| r k_r, s k_s \rangle = \frac{1}{K^2} \sum_{\kappa,\lambda,\mu,\nu} \sum_{m_1 m_2 m_3 m_4} C_{pk_p}^{\kappa *} C_{qk_q}^{\lambda *} C_{rk_r}^{\mu} C_{sk_s}^{\nu}$$

$$\times \langle \kappa^{(m_1)} \lambda^{(m_2)} \| \mu^{(m_3)} \nu^{(m_4)} \rangle$$

$$\times \exp(-i m_1 k_p a - i m_2 k_q a + i m_3 k_r a + i m_4 k_s a)$$

$$= \begin{cases} \frac{1}{K} \sum_{\kappa,\lambda,\mu,\nu} \sum_{m_1' m_2' m_3'} C_{pk_p}^{\kappa *} C_{qk_q}^{\lambda *} C_{rk_r}^{\mu} C_{sk_s}^{\nu} \\ \quad \times \langle \kappa^{(0)} \lambda^{(m_1')} \| \mu^{(m_2')} \nu^{(m_3')} \rangle \\ \quad \times \exp(-i m_1' k_q a + i m_1' k_r a + i m_3' k_s a) \\ \qquad (k_p + k_q - k_r - k_s = \frac{2\pi}{a} \times \text{integer : momentum conservation}) \\ 0 \qquad (\text{otherwise}) \end{cases}$$

② Size consistency of HF

$$E_{HF} = \sum_i^{occ.} \underbrace{\left(\sum_{k_i}\right)}_{\propto K^1} \overbrace{\underbrace{\langle ik_i|\hat{f}|ik_i\rangle}_{\propto K^0}}^{\text{momentum conservation ok}} - \frac{1}{2}\sum_{i,j}^{occ.} \underbrace{\left(\sum_{k_i,k_j}\right)}_{\propto K^2} \overbrace{\underbrace{\langle ik_i, jk_j \| ik_i, jk_j\rangle}_{\propto K^{-1}}}^{\text{momentum conservation ok}}$$

$\propto K^1 = \text{size}$ E_{HF} is extensive (size consistent)

$\epsilon_{ik_i} = \langle ik_i|\hat{f}|ik_i\rangle \propto K^0 = $ independent of size

ϵ_{ik_i} (band, IP) is intensive (size consistent)

③ Hamiltonian

i) First quantized

$$\hat{H} = \sum_i -\frac{1}{2}\nabla_i^2 - \sum_i\sum_I \frac{Z_I}{r_{iI}} + \sum_{i<j}\frac{1}{r_{ij}} + \sum_{I<J}\frac{Z_I Z_J}{r_{IJ}}$$

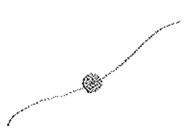
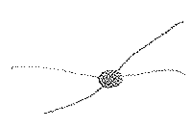
ii) Second quantized

$$\hat{H} = E_{nuc} + \sum_{p,q}\langle p|\hat{h}|q\rangle \hat{p}^\dagger\hat{q} + \frac{1}{4}\sum_{p,q,r,s}\langle pq\|rs\rangle \hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}$$

iii) Normal ordered

$$\hat{H} = \underbrace{E_{HF}}_{K^1} + \sum_{p,q}\underbrace{\langle p|\hat{f}|q\rangle}_{K^0}\{\hat{p}^\dagger\hat{q}\} + \frac{1}{4}\sum_{p,q,r,s}\underbrace{\langle pq\|rs\rangle}_{K^{-1}}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}$$

iv) Diagrammatic

$\hat{H} = \underbrace{E_{HF}}_{K^1} +$  $+$ 

K^0 K^{-1}

④ Size consistency of MP2

CO : $$E_{MP2} = \frac{1}{4} \sum_{i,j,a,b} \sum_{k_i, k_j, k_a, k_b} \frac{\langle a k_a, b k_b \| i k_i\, j k_j \rangle \langle i k_i, j k_j \| a k_a, b k_b \rangle}{\epsilon_{i k_i} + \epsilon_{j k_j} - \epsilon_{a k_a} - \epsilon_{b k_b}}$$

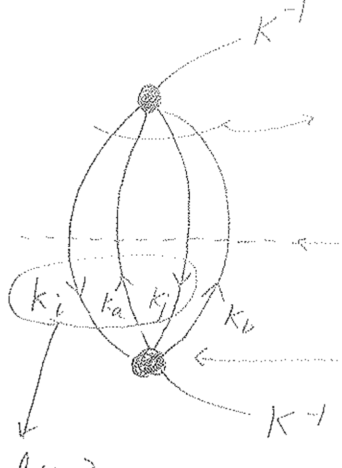
$$= \frac{1}{4} \sum_{i,j,a,b} \sum_{k_i, k_j, k_a} \frac{''}{''}$$

because only k_b's that satisfy $k_i + k_j - k_a - k_b = \frac{2\pi}{a} \times \text{int}$, will yield $\langle \cdot\cdot \| \cdot\cdot \rangle$ that are nonzero.

MO : $$E_{MP2} = \frac{1}{4} \sum_{i,j,a,b} \frac{\langle ab \| ij \rangle \langle ij \| ab \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

$$E_{MP2} = \frac{1}{4} \sum_{i,j,a,b} \overbrace{\sum_{k_i, k_j, k_a}}^{K^3} \frac{\overbrace{\langle a k_a \cdots \rangle}^{K^{-1}} \overbrace{\langle i k_i \cdots \rangle}^{K^{-1}}}{\underbrace{\epsilon_{i k_i}}_{K^0} \cdots}$$

$\propto K^1 = \text{size} \longrightarrow E_{MP2}$ is extensive (size consistent)

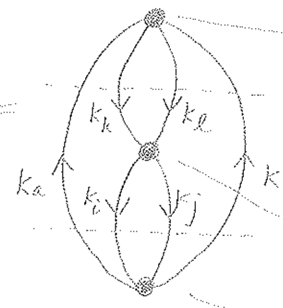


momentum conservation here is automatically satisfied if it is satisfied here

$$\frac{1}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \propto K^0$$

only 3 are linearly independent because the last one is determined by momentum conservation

(5) Size consistency of MP3

$E_{MP3} =$ 

$k_a + k_b = k_k + k_l \ (+ \frac{2\pi}{a} \cdot \text{int.})$ + 2 other diagrams

implies

$\underbrace{k_i + k_j}_{\text{independent}} = k_k + k_l \ (+ \frac{2\pi}{a} \cdot \text{int})$

$\underbrace{k_a + k_b}_{\text{independent}} = k_i + k_j \ (+ \frac{2\pi}{a} \cdot \text{int})$

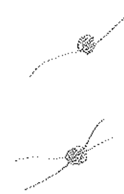
$$= \frac{1}{8} \sum_{i,j,k,l,a,b} \underbrace{\left(\sum_{k_i, k_j, k_k, k_b} \right)}_{K^4} \frac{\overbrace{\langle i k_i j k_j || a k_a b k_b \rangle}^{K^{-1}} \overbrace{\langle k k_k l k_l || i k_i j k_j \rangle}^{K^{-1}} \overbrace{\langle a k_a b k_b || k k_k l k_l \rangle}^{K^{-1}}}{\underbrace{(\epsilon_{ik_i} + \epsilon_{jk_j} - \epsilon_{ak_a} - \epsilon_{bk_b})}_{K^0} (\epsilon_{kk_k} + \epsilon_{lk_l} - \epsilon_{ak_a} - \epsilon_{bk_b})}$$

$\propto K^1$ (extensive)

(6) Extensive diagram theorem

i) Generally, an extensive vertex with "n" edges scales as

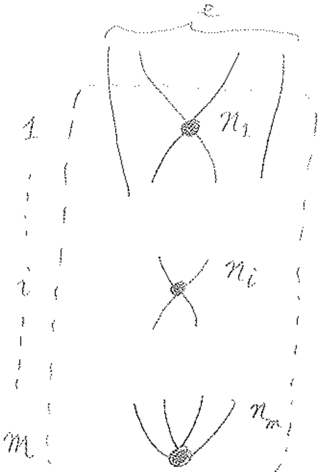
$$K^{1-n/2}$$



$n = 2 \quad K^0$

$n = 4 \quad K^{-1}$

ii) A diagram with "e" external edges made of "m" vertexes with "$n_1, \cdots n_m$" edges.



The total number of internal edges

$$= \left(\sum_i n_i - e \right) / 2$$

because each internal edge is shared by two vertexes

iii) In a <u>connected</u> diagram, there are "$m-1$" momentum conservation conditions, each of which from a vertex and removes one k vector from summation indexes.
The m^{th} momentum conservation condition is automatically satisfied when the other $m-1$ conditions are in a <u>connected</u> diagram

The number of k's summed (or the independent internal edges)

$$= \left(\sum_i n_i - e\right)/2 - (m-1)$$

$$\underbrace{\prod_{i=1}^{m} K^{1-n_i/2}}_{\substack{m \text{ vertexes} \\ \text{with } n_1 \cdots n_m \\ \text{edges}}} \cdot \underbrace{K^{(\sum_i n_i - e)/2-(m-1)}}_{\text{summation over } k} = K^{1-e/2}$$

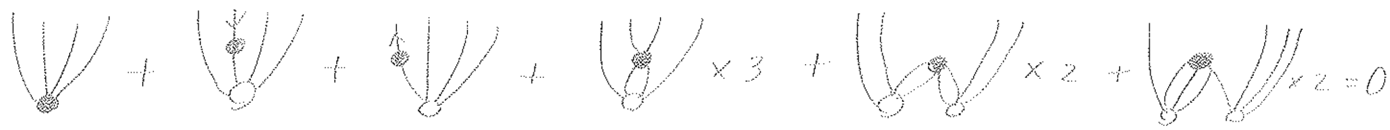
A connected diagram with "e" external edges scales as $K^{1-e/2}$ (consistent with (i) above)

A closed, connected diagram scales as K^1 (extensive)

$$\boxed{\text{extensive diagram theorem}}$$

(part of linked diagram theorem by Goldstone)

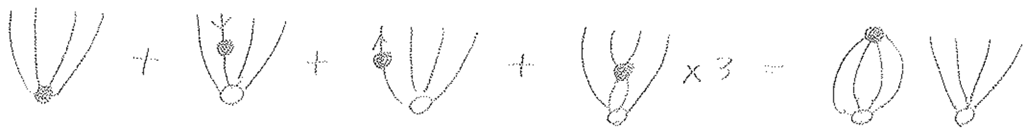
(7) CCD versus CID

CCD 

K^{-1} K^{-1} K^{-1} K^{-1} K^{-1} K^{-1}

consistent size dependence

$E_{CCD}^{corr} =$  K^{1} extensive correlation energy

CID 

K^{-1} K^{-1} K^{-1} K^{-1} $\underbrace{K^{1} \quad K^{-1}}_{K^{0}}$

inconsistent size dependence

$E_{CID}^{corr} =$  K^{1} "formally" extensive correlation energy

but see

⑧ Intensive diagram theorem

extensive operator/vertex —— $\hat{H}$, $\hat{T}$ (in CC) subject to intermediate normalization

intensive operator/vertex —— $\hat{C}$ (in CIS, EOM-CC) subject to standard normalization

i) Intermediate normalization leads to

$$t_{ij}^{ab} \approx \frac{\langle ab||ij\rangle}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b} \quad (\text{MP2, CCD, } \cdots)$$

n-edge "extensive" vertex scales as $K^{1-n/2}$

ii) Normalization means

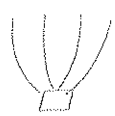
 $= 1$

$$\sum_{i,a}\sum_{k_i}\left|c_{ik_i}^{ak_a}\right|^2 = 1 \quad \left(k_a = k_i + \frac{2\pi}{a}\times\text{int}\right)$$

 $\propto K^{-1/2}$

 $= 1$

$$\sum_{i,j,a,b}\sum_{k_i,k_j,k_a}\left|c_{ik_ijk_j}^{ak_abk_b}\right|^2 = 1 \quad \left(k_a+k_b = k_i+k_j+\frac{2\pi}{a}\times\text{int}\right)$$

 $\propto K^{-3/2}$

n-edge "intensive" vertex scales as $K^{1/2-n/2}$

A connected diagram with "e" external edges and "m" intensive vertexes scale as

$$K^{1-e/2-m/2}$$

Intensive diagram theorem

Amplitude eq = connected diagram with one intensive vertex

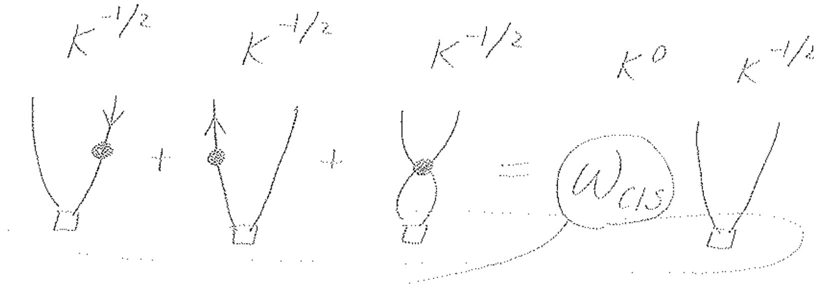
or

disconnected diagram with one open, connected subdiagram with one intensive vertex plus any number of closed connected subdiagrams with two intensive vertexes

Energy eq = Closed, connected diagram with two intensive vertexes.

⑨ CIS

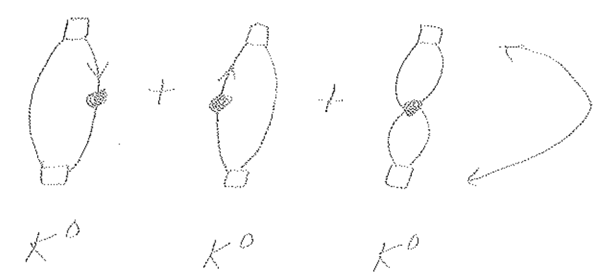
Amp. eq



intensive one vertex

Ene. eq

W_{CIS} =



two intensive vertexes