Quantum Mechanics of n-Electron Systems in terms of the Cumulants of the Reduced Density Matrices

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Introduction

$H\Psi = E\Psi$; **Don't search for** Ψ !

1.Ψ contains too much *irrelevant* information.

2.*Overlap* between exact and any approximative Ψ *decreases exponentially* with the particle number n.

3. Ψ is not an *extensive* (additively separable) quantity.

Formulate the **energy** $E = \langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle$ and the **stationarity condition** $\delta E = 0$ entirely in terms of **additively separable quantities**.

Good candidates: the **one-particle density matrix** $\boldsymbol{\gamma} = \boldsymbol{\gamma}_1$ and the k-particle density **cumulants** $\boldsymbol{\lambda}_k$.

Excitation operators and reduced density matrices.

Start from *orthonormal basis* $\{\psi_p\}$ of *spin orbitals*.

Creation and **annihilation operators** for the ψ_p:

$$a_p;\ a^q = a_q^\dagger \tag{1}$$

Excitation operators; W.K. JCP **77**, 3081 (1982)

$$\begin{aligned} a_q^p &= a^p a_q &(2)\\ a_{rs}^{pq} &= a^q a^p a_r a_s &(3)\\ a_{stu}^{pqr} &= a^r a^q a^p a_s a_t a_u;\ etc. &(4) \end{aligned}$$

(particle-number-conserving *normal products* of creation and annihilation operators).

Consider a state described by the wave function Ψ:

k-particle **density matrices**:

$$\boldsymbol{\gamma}_1 : \ \gamma^p_q = \langle \Psi | a^p_q | \Psi \rangle \quad (5)$$

$$\boldsymbol{\gamma}_2 : \ \gamma^{pq}_{rs} = \langle \Psi | a^{pq}_{rs} | \Psi \rangle \quad (6)$$

$$\boldsymbol{\gamma}_3 : \ \gamma^{pqr}_{stu} = \langle \Psi | a^{pqr}_{stu} | \Psi \rangle \quad (7)$$

Normalization

$$\mathrm{Tr}\boldsymbol{\gamma}_k = n!/(n-k)! \quad (8)$$

$$\mathrm{Tr}\boldsymbol{\gamma}_1 = n \quad (9)$$

$$\mathrm{Tr}\boldsymbol{\gamma}_2 = n(n-1) \quad (10)$$

Easily generalized to *ensemble states*.

Hamiltonian in *configuration space*:

$$H(1,2,3\ldots .n) = \sum_{k=1}^{n} h(k) + \sum_{k<l=1}^{n} \frac{1}{r_{kl}} \tag{11}$$

Fock space Hamiltonian:; (*Einstein summation convention*):

$$\begin{aligned} H &= h_q^p a_p^q + \frac{1}{2} g_{rs}^{pq} a_{pq}^{rs} && (12) \\ h_q^p &= \langle \psi_q | h | \psi_p \rangle && (13) \\ g_{rs}^{pq} &= \langle \psi_r(1)\psi_r(2) | \frac{1}{r_{12}} | \psi_p(1)\psi_q(2) \rangle && (14) \end{aligned}$$

Energy expectation value:

$$E = h_q^p \gamma_p^q + \frac{1}{2} g_{rs}^{pq} \gamma_{pq}^{rs} \tag{15}$$

One-particle density matrix: $\boldsymbol{\gamma} = \boldsymbol{\gamma}_1$; Natural orbital (NSO) basis: $\gamma_q^p = n_p \delta_q^p$
$0 \leq n_p \leq 1$: **occupation number** of the p^{th} NSO

Separability

$$H = H_A + H_B \tag{16}$$

A and B subsystems in exclusive (orthogonal) Hilbert spaces. States of H should be described in terms of additively separable quantities, like

$$X = X_A + X_B \tag{17}$$

The cluster amplitudes S in coupled-cluster theory have this property

$$\Psi = \exp(S)\Phi;\ S = S_A + S_B \tag{18}$$

if the reference function is multiplicatively separable

Block diagonalization of H by means of a similarity transformation

$$L = W^{-1}HW \tag{19}$$

Separability requires that $W = exp(S)$ with S additively separable

Coupled-cluster (CC) theory.

$$W = e^{S};\ S = S_1 + S_2 + S_3 + \ldots$$
$$S_1 = S_a^i a_i^a; S_2 = S_{ab}^{ij} a_{ij}^{ab}$$

In *intermediate normalization*, n-representability and separability.
No variation principle.

Unitary CC

$$W = e^{\sigma}; \sigma = T - T\dagger$$

Variation principle. Hausdorff expansion does not terminate. Probably less serious than often believed.

Nooijen conjecture

$$W = e^{S};\ S = S_q^p a_p^q + \frac{1}{2} S_{rs}^{pq} a_{pq}^{rs}$$

Reduced density matrices and cumulants

Reduced k-particle density matrices $\boldsymbol{\gamma}_k$

All information is in $\boldsymbol{\gamma}_2$.

Variational calculations in terms of $\boldsymbol{\gamma}_2$ failed.

n-representability problem.

Attempts to circumvent this problem:

Contracted k-particle Schrödiger equations and
k-particle Brillouin conditions. Hierarchy for the $\boldsymbol{\gamma}_k$

The $\boldsymbol{\gamma}_k$ are not additively separable. Use the cumulants $\boldsymbol{\lambda}_k$ instead.

Irreducible contracted k-particle Schrödiger equations and k-particle Brillouin conditions. Hierarchy for the $\boldsymbol{\lambda}_k$. Truncation possible.

Cumulants of the k-particle density matrices

The **cumulant** $\boldsymbol{\lambda}_2 = \{\lambda^{pq}_{rs}\}$ of the two-particle density matrix γ^{pq}_{rs} is the *difference* between γ^{pq}_{rs} and *what one expects for independent particles* - that obey Fermi statistics; $\boldsymbol{\lambda}_3 = \{\lambda^{pqr}_{stu}\}$ analogous

$$\lambda^{pq}_{rs} = \gamma^{pq}_{rs} - \gamma^p_r\gamma^q_s + \gamma^p_s\gamma^q_r \quad (20)$$

$$\begin{aligned} \lambda^{pqr}_{stu} &= \gamma^{pqr}_{stu} - \gamma^p_s\lambda^{qr}_{tu} - \gamma^q_t\lambda^{pr}_{su} - \gamma^r_u\lambda^{pq}_{st} + \gamma^p_t\lambda^{qr}_{su} \\ &+ \gamma^p_u\lambda^{qr}_{ts} + \gamma^q_s\lambda^{pr}_{tu} + \gamma^q_u\lambda^{pr}_{st} + \gamma^r_s\lambda^{pq}_{ut} + \gamma^r_t\lambda^{pq}_{su} \\ &- \gamma^p_s\gamma^q_t\gamma^r_u - \gamma^p_t\gamma^q_u\gamma^r_s - \gamma^p_u\gamma^q_s\gamma^r_t \\ &+ \gamma^p_s\gamma^q_u\gamma^r_t + \gamma^q_t\gamma^p_u\gamma^r_s + \gamma^p_t\gamma^q_s\gamma^r_u \end{aligned} \quad (21)$$

Cumulants of any *particle rank* be defined via a **generating function**.

W.K. & D.M. JCP **107**, 4332 (1997); JCP **110**, 2800 (1999)

Generating function for the γ_k

$$\begin{aligned} A &= <\Phi| : \exp \hat{k} : |\Phi> = <\Phi| 1 + \hat{k} + : \hat{k}^2 : + ... |\Phi> \\ \hat{k} &= k^p_q a^q_p \end{aligned} \tag{22}$$

Double dots (: ... :) mean normal products with respect to the genuine vacuum, e. g. $: a^p_q a^r_s := a^{pr}_{qs}$

$$\begin{aligned} A &= 1 + k^p_q \gamma^q_p + \frac{1}{2} k^p_q k^r_s \gamma^{qs}_{pr} + ... \\ &= 1 + k^p_q \gamma^q_p + \sum_{p<r,q<s} (k^p_q k^r_s - k^p_s k^r_q) \gamma^{qs}_{pr} + ... \end{aligned} \tag{23}$$

γ^q_p is the coefficient of k^p_q , γ^{qs}_{pr} that of $(k^p_q k^r_s - k^p_s k^r_q)$

$$B = \ln_a A = k^p_q \lambda^q_p + \frac{1}{4} (k^p_q k^r_s - k^p_s k^r_q) \lambda^{qs}_{pr} + ... \tag{24}$$

$\ln_a$ is *antisymmetrized logarithm*
B : generating function for the $\boldsymbol{\lambda}_k$ in the same sense as A is for the $\boldsymbol{\gamma}_k$.

The cumulant is a **correlation increment**, which is preferable to the more common **correlation factor**

$$E = \frac{1}{2}(h_q^p + f_q^p)\gamma_p^q + \frac{1}{2}g_{rs}^{pq}\lambda_{pq}^{rs} \tag{25}$$

$$f_q^p = h_q^p + \bar{g}_{qs}^{pr}\gamma_r^s;\ \bar{g}_{qs}^{pr} = g_{qs}^{pr} - g_{sq}^{pr} \tag{26}$$

Decomposition of the electron interaction energy:

$$\begin{aligned}
Coulomb: \quad & \tfrac{1}{2}\gamma_r^p\gamma_s^q g_{pq}^{rs} &= \int \frac{\boldsymbol{\gamma}(1)\boldsymbol{\gamma}(2)}{2r_{12}}d\tau_1 d\tau_2 \\
-\ exchange: \quad & \tfrac{1}{2}\gamma_s^p\gamma_r^q g_{pq}^{rs} &= \int \frac{\boldsymbol{\gamma}(1,2)\boldsymbol{\gamma}(2,1)}{2r_{12}}d\tau_1 d\tau_2 \\
correlation: \quad & \tfrac{1}{2}\lambda_{rs}^{pq} g_{pq}^{rs} &= \int \frac{\boldsymbol{\lambda}(1,2)}{2r_{12}}d\tau_1 d\tau_2 \\
interaction: \quad & \tfrac{1}{2}\gamma_{rs}^{pq} g_{pq}^{rs} &= \int \frac{\boldsymbol{\gamma}(1,2)}{2r_{12}}d\tau_1 d\tau_2
\end{aligned} \tag{27}$$

This decomposition differs from all conventional ones.

Properties of density cumulants

Hermiticity: $\lambda^{pq}_{rs} = (\lambda^{rs}_{pq})^*$

Antisymmetry: $\lambda^{pq}_{rs} = -\lambda^{qp}_{rs} = -\lambda^{pq}_{sr} = \lambda^{qp}_{sr}$

Separability:
For $\Psi = \mathcal{A}\{\Psi_A(1,2,\ldots n_A)\Psi_B(n_A+1,\ldots n_A+n_B)\}$ with Ψ_A and Ψ_B *strongly orthogonal*, $\lambda^{pq}_{rs} = 0$, unless **all labels** refer either to subsystem A or B.

$$\lambda^{pq}_{rs} = (\lambda_A)^{pq}_{rs} + (\lambda_B)^{pq}_{rs} \tag{28}$$

$$\lambda^{pq}_{rs} = = 0, \text{ in NSO} - \text{basis if any } n_p = 0 \; or = 1 \tag{29}$$

Trace relations:

$$\begin{aligned}
\mathrm{Tr}(\boldsymbol{\gamma}_1) &= \Sigma_k n_k = n \\
\mathrm{Tr}(\boldsymbol{\lambda}_2) &= \mathrm{Tr}(\boldsymbol{\gamma}_1^2 - \boldsymbol{\gamma}_1) = \Sigma_k(n_k^2 - n_k) = O(n) \\
\mathrm{Tr}(\boldsymbol{\lambda}_3) &= \mathrm{Tr}(-4\boldsymbol{\gamma}_1^3 + \boldsymbol{\gamma}_1^2 - 2\boldsymbol{\gamma}_1) = 6\Sigma_k n_k(n_k - \frac{1}{2})(n_k - 1) = O(n)
\end{aligned}$$

Partial trace relations

$$\begin{aligned}
\lambda^{pr}_{qr} &= -\gamma^p_q + \gamma^p_r\gamma^r_q = (\boldsymbol{\gamma}^2 - \boldsymbol{\gamma})^p_q \qquad (30)\\
\lambda^{prt}_{qst} &= 2\lambda^{pr}_{qs} - \gamma^p_t\lambda^{rt}_{sq} - \gamma^r_t\lambda^{pt}_{qs} - \gamma^t_q\lambda^{pr}_{ts} - \gamma^t_s\lambda^{pr}_{qt}\\
\lambda^{prt}_{qrt} &= (-2\boldsymbol{\gamma}^3 + 4\boldsymbol{\gamma}^2 - 2\boldsymbol{\gamma})^p_q - \gamma^r_t\lambda^{tp}_{rq} - \gamma^t_r\lambda^{pr}_{qt}
\end{aligned}$$

Particle-hole symmetry/ *Hole density matrices*

$$\begin{aligned}
\eta^p_q &= < \Phi|a_q a^p|\Phi >= \delta^p_q - \gamma^p_q \qquad (31)\\
\eta^{pq}_{rs} &= < \Phi|a_s a_r a^p a^q|\Phi >\\
&= \delta^p_r\delta^q_s - \delta^p_s\delta^q_r - \delta^p_r\gamma^q_s - \gamma^p_r\delta^q_s + \delta^p_s\gamma^q_r + \gamma^p_s\delta^q_r\\
&+ \gamma^{pq}_{rs}; etc. \qquad (32)\\
\eta^p_q &= \delta^p_q(1 - n_p)\ in\ NSO - basis \qquad (33)
\end{aligned}$$

These $\boldsymbol{\eta}_m$ matrices have the *same cumulants* as the corresponding $\boldsymbol{\gamma}_m$ matrices, just with γ^p_q replaced by η^p_q and with some sign changes, e. g.

$$\eta^{pq}_{rs} = \lambda^{pq}_{rs} + \eta^p_r\eta^q_s - \eta^p_s\eta^q_r \qquad (34)$$

Inequalities

Three necessary n-representability conditions for $\boldsymbol{\gamma}_2$ or $\boldsymbol{\lambda}_2$.

The following matrices must be non-negative:

$$\boldsymbol{\gamma} \geq 0; \boldsymbol{\eta} \geq 0; \boldsymbol{\gamma}_2 \geq 0; \boldsymbol{\eta}_2 \geq 0; \boldsymbol{\beta}_2 \geq 0 \tag{35}$$

$$\gamma_p^p = \langle \Psi | a^p a_p | \Psi \rangle = \langle a_p \Psi | a_p \Psi \rangle \geq 0 \tag{36}$$

$$1 - \eta_p^p = \langle \Psi | a_p a^p | \Psi \rangle = \langle a^p \Psi | a^p \Psi \rangle \geq 0 \tag{37}$$

implies

$$0 \leq n_p \leq 1 \tag{38}$$

Conditions for diagonal elements

$$\begin{aligned}
\gamma^{pq}_{pq} &= \langle a_p a_q \Psi | a_p a_q \Psi \rangle \geq 0; \;\; (D) && (39)\\
\eta^{pq}_{pq} &= \langle a^p a^q \Psi | a^p a^q \Psi \rangle \geq 0; \;\; (Q) && (40)\\
\beta^{q,p}_{p,q} &= \langle a^p_q \Psi | a^p_q \Psi \rangle \geq 0; \qquad (G) && (41)
\end{aligned}$$

can be fomulated as inequalities for $\boldsymbol{\lambda}_2$. There are further Cauchy-Schwarz-type inequalities like

$$\gamma^{pq}_{rs}\gamma^{rs}_{pq} \leq \gamma^{pq}_{pq}\gamma^{rs}_{rs} \qquad (42)$$

which imply relations between λ^{pq}_{rs} and λ^{pq}_{pq}.

Density cumulants for degenerate states

Spin-degeneracy: (2S+1) different M_S-values for one S.

$\rho(M_S) = |\Psi_{M_S}\rangle\langle\Psi_{M_S}|$ is **not** *irr.rep.* of SU_2.

All $\rho(M_S, M'_S) = |\Psi_{M_S}\rangle\langle\Psi_{M'_S}|$ span a $(2S+1)^2$-dimensional *reducible representation* of SU_2.

Irreducible tensor components ρ_σ with $\sigma = (0, 1, \ldots, 2S)$.

$$\rho_0 = (2S+1)^{-\frac{1}{2}} \sum_{M_S=-S}^{S} |\Psi_{M_S}\rangle\langle\Psi_{M_S}| \tag{43}$$

Spin-averaged ensemble state

Spinfree density matrices:

$$\Gamma^{P}_{Q} = \gamma^{P\alpha}_{Q\alpha} + \gamma^{P\beta}_{Q\beta} =< \Phi|E^{P}_{Q}|\Phi > \tag{44}$$

$$\Gamma^{PQ}_{RS} = \sum_{\eta,\xi=\alpha}^{\beta} \gamma^{P\eta Q\xi}_{Q\eta R\xi} =< \Phi|E^{PQ}_{RS}|\Phi >; \; etc. \tag{45}$$

One-particle spin-density matrix

$$\begin{aligned} (D^{0})^{P}_{S} &= 1/(\sqrt{2}) \; < \Psi|a^{P\alpha}_{S\alpha} - a^{P\beta}_{S\beta}|\Psi > \\ (D^{+})^{P}_{S} &= < \Psi|a^{P\alpha}_{S\beta}|\Psi > \\ (D^{-})^{P}_{S} &= < \Psi|a^{P\beta}_{S\alpha}|\Psi > \end{aligned} \tag{46}$$

Spinfree cumulants:

$$\Lambda^{PQ}_{RS} = \Gamma^{PQ}_{RS} - \Gamma^{P}_{R}\Gamma^{Q}_{S}\Gamma^{PQ}_{RS} + \frac{1}{2}\Gamma^{P}_{S}\Gamma^{Q}_{R}; \; etc. \tag{47}$$

k-particle Brillouin conditions

Unitary variations

$$\Psi \to e^{Z}\Psi;\ Z = -Z^{\dagger} \tag{48}$$

$$\{Z\} = \{a^{p}_{q}, a^{pq}_{rs}, a^{pqr}_{stu}, ...\} \tag{49}$$

Stationarity conditions

$$\langle\Psi|[H, Z]|\Psi\rangle = 0 \tag{50}$$

$$\langle\Psi|[H, a^{p}_{q}]|\Psi\rangle = 0 \tag{51}$$

$$\langle\Psi|[H, a^{pq}_{rs}]|\Psi\rangle = 0 \text{ etc.} \tag{52}$$

(51) : (one-particle) Brillouin condition BC_1,
(52) : **two-particle Brillouin condition** BC_2.

W.K. CPL **64**, 383 (1979); precursor: Thouless 1961

The BC_1 (51) and BC_2 (52) are explicitly

$$h^p_s \gamma^s_q - \gamma^p_r h^r_q + \frac{1}{2}\bar{g}^{pr}_{tu}\gamma^{tu}_{qr} - \frac{1}{2}\gamma^{pu}_{rs}\bar{g}^{rs}_{qu} = 0 \qquad (53)$$

$$\begin{aligned} h^p_u \gamma^{uq}_{rs} + h^q_u \gamma^{pu}_{rs} - \gamma^{pq}_{ts} h^t_r - \gamma^{pq}_{rt} h^t_s &\quad + \\ \frac{1}{2}\bar{g}^{pq}_{vw}\gamma^{vw}_{rs} - \frac{1}{2}\gamma^{pq}_{tu}\bar{g}^{tu}_{rs} + \frac{1}{2}\bar{g}^{pt}_{vw}\gamma^{vwq}_{rts} &\quad + \\ \frac{1}{2}\bar{g}^{qu}_{vw}\gamma^{vwp}_{sur} - \frac{1}{2}\bar{g}^{tu}_{rw}\gamma^{wpq}_{uts} - \frac{1}{2}\bar{g}^{tu}_{rs}\gamma^{vpq}_{tru} &= 0 \end{aligned} \qquad (54)$$

with $\bar{g}$ the antisymmetrized electron interaction (**??**).

No obvious truncation of the hierarchy of k-particle equations.

The BC_2 implies the BC_1 etc.
$\boldsymbol{\gamma}_1$ depends on $\boldsymbol{\gamma}_2$; $\boldsymbol{\gamma}_2$ depends on $\boldsymbol{\gamma}_3$ etc.

k-particle contracted Schrödinger equations

Alternatively stationarity with respect to *arbitrary* (not norm-conserving) *variations* of Ψ, with Lagrange multiplier E

$$\Psi \rightarrow (1+Z)\Psi \tag{55}$$

$$\langle\Psi|Z(H-E)|\Psi\rangle = 0 \tag{56}$$

According to the particle rank k of Z in (56) we get the k-particle *contracted Schrödinger equations* CSE$_k$

Nakatsuji PRA 1976, Cohen-Freshberg PRA 1976.

$$\langle\Psi|a^p_q(H-E)|\Psi\rangle = 0 \tag{57}$$

$$\langle\Psi|a^{pq}_{rs}(H-E)|\Psi\rangle = 0 \text{ etc.} \tag{58}$$

The explicit form of (57) is e.g.

$$h_s^r \gamma_{pr}^{qs} + h_p^r \gamma_r^q + \frac{1}{2} \bar{g}_{pt}^{rs} \gamma_{rs}^{qt} + \frac{1}{2} \bar{g}_{tu}^{rs} \gamma_{prs}^{qtu} = 0 \quad (59)$$

γ_1 expressed through γ_2 and γ_3 , γ_2 through γ_3 and γ_4

Again no obvious truncation of the k-particle hierarchy.

'Reconstruction' after Valdemoro (PRA 1985) and Nakatsuji/Yasuda (PRL 1996), analyzed by Mazziotti (CPL 1998):

Find approximation for γ_3 and γ_4 in terms of γ_1 and γ_2, then solve for γ_2.

Method of 'Contracted Schrödinger equations' (Valdemoro, Mazziotti), 'density equation' (Nakatsuji), 'VNM-method' (Coleman).

Generalized *normal ordering* theorem for an arbitrary reference function Ψ

W.K & D.M., JCP **107**, 432 (1997)

Excitation operators in normal order
with respect to Ψ:

$$\tilde{a}^p_q,\ \tilde{a}^{pq}_{rs},\ etc. \tag{60}$$

1. The $\tilde{a}^p_q$, $\tilde{a}^{pq}_{rs}$, *etc.* are *expressible* through the standard excitation operators a^p_q, a^{pq}_{rs}, *etc.*, e.g.

$$\tilde{a}^{pq}_{rs} = a^{pq}_{rs} - \gamma^p_r \tilde{a}^q_s - \gamma^q_s \tilde{a}^p_r + \gamma^p_s \tilde{a}^q_r + \gamma^q_r \tilde{a}^p_s - \gamma^{pq}_{rs} \tag{61}$$

2. The *expectation values* with respect to Ψ *vanish*:

$$\langle\Psi|\tilde{a}^p_q|\Psi\rangle = 0,\ \langle\Psi|\tilde{a}^{pq}_{rs}|\Psi\rangle = 0 \tag{62}$$

3. Products of $\tilde{a}$-operators are equal to the *normal product plus all contractions*.

The contractions involve $\boldsymbol{\gamma}$, $\boldsymbol{\eta}$, and the $\boldsymbol{\lambda}_k$. E.g.

$$\tilde{a}_q^p \tilde{a}_s^r = \tilde{a}_{qs}^{pr} + \eta_q^r \tilde{a}_s^p - \gamma_s^p \tilde{a}_q^r + \gamma_s^p \eta_q^r + \lambda_{qs}^{pr} \tag{63}$$

4. The expectation value of a product of operators is the *sum of all full contractions*. E.g.

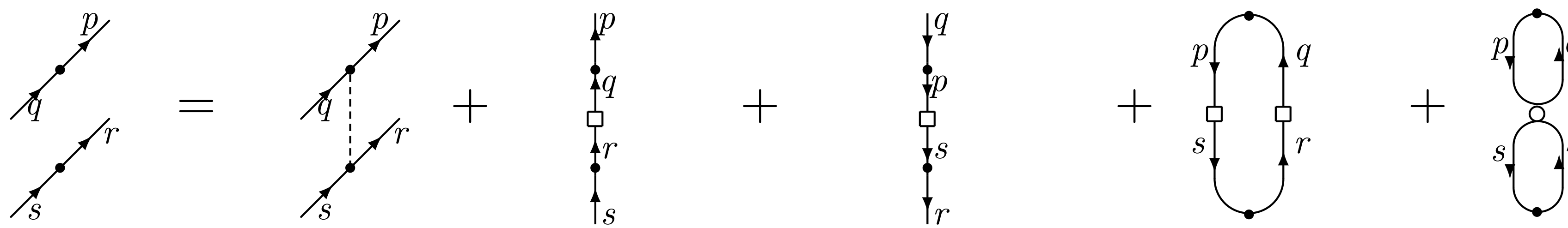
$$\langle \Psi | \tilde{a}_s^r \tilde{a}_q^p | \Psi \rangle = \lambda_{sq}^{rp} + \eta_s^p \gamma_q^r \tag{64}$$

5. Graphical representation of the generalized Wick theorem with *contraction rules*.

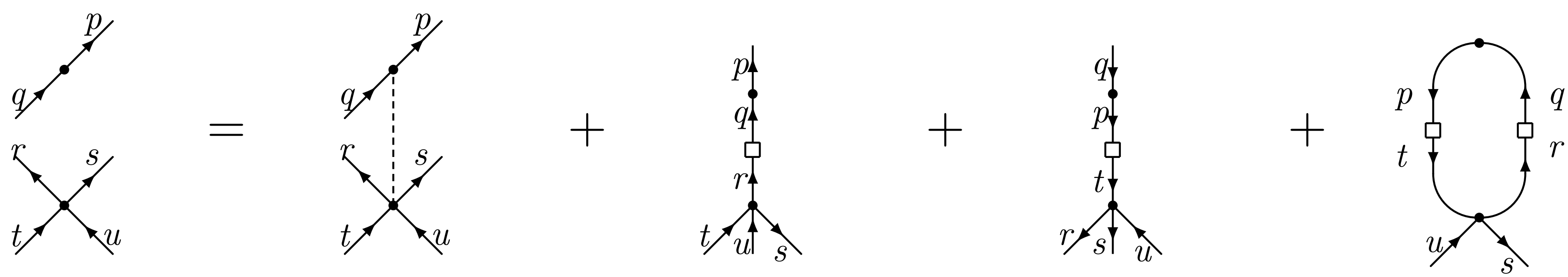
6. For a closed-shell Slater determinant reference all cumulants vanish, and there are only *particle-* and *hole-contractions.*

7. *Simplification* in NSO-basis:

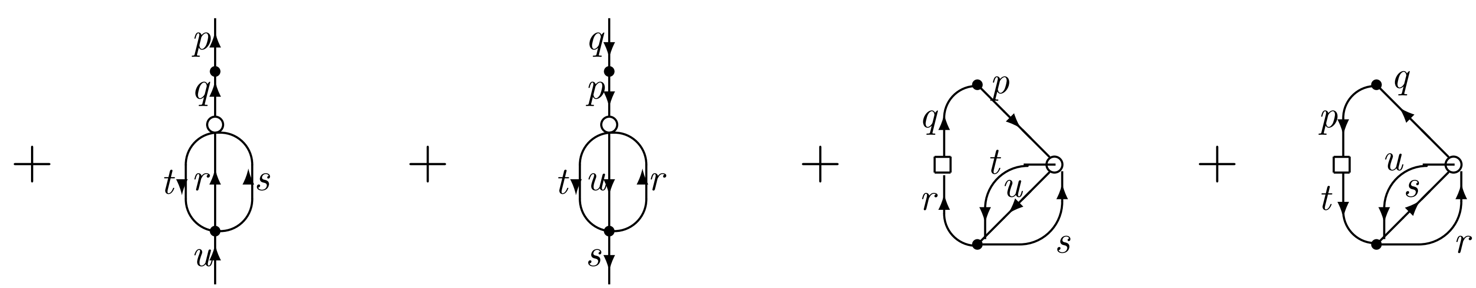
$$\gamma_q^p = n_p \delta_q^p; \;\; \eta_q^p = (1 - n_p)\delta_q^p \tag{65}$$



$$\tilde{a}^{p}_{q}\tilde{a}^{r}_{s} \qquad \tilde{a}^{pr}_{qs} \qquad \eta^{r}_{q}\tilde{a}^{p}_{s} \qquad -\gamma^{p}_{s}\tilde{a}^{r}_{q} \qquad \eta^{r}_{q}\gamma^{p}_{s} \qquad \lambda^{pr}_{qs}$$



$$\tilde{a}^{p}_{q}\tilde{a}^{rs}_{tu} = \tilde{a}^{prs}_{qtu} + \eta^{r}_{q}\tilde{a}^{ps}_{tu} - \gamma^{p}_{t}\tilde{a}^{rs}_{qu} + \eta^{r}_{q}\gamma^{p}_{t}\tilde{a}^{s}_{u}$$



$$+ \left(-\lambda^{rs}_{tq}\tilde{a}^{p}_{u}\right) + \left(-\lambda^{pr}_{ut}\tilde{a}^{s}_{q}\right) + \eta^{r}_{q}\lambda^{ps}_{tu} + \left(-\gamma^{p}_{t}\lambda^{rs}_{qu}\right)$$

Irreducible k-particle Brillouin conditions

W.K & D.M., CPL **317**, 567 (2000), JCP **114**, 2047 (2001)

Hamiltonian H in **generalized normal order**:

$$H = E + f_q^p \tilde{a}_p^q + \frac{1}{2} g_{rs}^{pq} \tilde{a}_{pq}^{rs} \tag{66}$$

The generalized Fock operator f_q^p (26) arises naturally.

Irreducible Brillouin conditions IBC_k

$$\begin{aligned} \langle\Psi|[H, \tilde{a}_q^p]|\Psi\rangle &= 0 && (67) \\ \langle\Psi|[H, \tilde{a}_{rs}^{pq}]|\Psi\rangle &= 0 \text{ etc.} && (68) \end{aligned}$$

IBC_1 in an NSO basis:

$$f_q^p(n_q - n_p) + \frac{1}{2}\bar{g}_{r_1 r_2}^{p\,s_1}\lambda_{q\,s_1}^{r_1 r_2} - \frac{1}{2}\lambda_{s_1 s_2}^{r_1 p}\bar{g}_{r_1 q}^{s_1 s_2} = 0 \tag{69}$$

IBC$_2$ in an NSO basis:

$$
\begin{aligned}
& f^{p_2}_{r}\lambda^{p_1 r}_{q_1 q_2} + f^{p_1}_{r}\lambda^{r\ p_2}_{q_1 q_2} - \lambda^{p_1 p_2}_{s\ q_2} f^{s}_{q_1} - \lambda^{p_1 p_2}_{q_1 s} f^{s}_{q_2} \\
+ \quad & \bar{g}^{p_1 p_2}_{q_1 q_2}\Big\{ (1-n_{p_1})(1-n_{p_2}) n_{q_1} n_{q_2} \\
& \quad - \quad (1-n_{q_1})(1-n_{q_2}) n_{p_1} n_{p_2} \Big\} \\
+ \quad & \frac{1}{2}\bar{g}^{p_1 p_2}_{r_1 r_2}\lambda^{r_1 r_2}_{q_1 q_2}(1 - n_{p_1} - n_{p_2}) \\
- \quad & \frac{1}{2}\bar{g}^{s_1 s_2}_{q_1 q_2}\lambda^{p_1 p_2}_{s_1 s_2}(1 - n_{q_1} - n_{q_2}) \\
+ \quad & (n_{p_2} - n_{q_1})\bar{g}^{p_2 s_1}_{r_1 q_1}\lambda^{p_1 r_1}_{s_1 q_2} - (n_{p_2} - n_{q_2})\bar{g}^{p_2 s_1}_{r_1 q_2}\lambda^{p_1 r_1}_{s_1 q_1} \\
- \quad & (n_{p_1} - n_{q_1})\bar{g}^{p_1 s_1}_{r_1 q_1}\lambda^{p_2 r_1}_{s_1 q_2} + (n_{p_1} - n_{q_2})\bar{g}^{p_1 s_1}_{r_1 q_2}\lambda^{p_2 r_1}_{s_1 q_1} \\
+ \quad & \frac{1}{2}\bar{g}^{p_2 s_2}_{r_1 r_2}\lambda^{r_1 r_2 p_1}_{q_2 s_2 q_1} + \frac{1}{2}\bar{g}^{p_1 s_2}_{r_1 r_2}\lambda^{r_1 r_2 p_2}_{q_1 s_2 q_2} \\
- \quad & \frac{1}{2}\bar{g}^{s_1 s_2}_{r_1 q_1}\lambda^{p_1 p_2 r_1}_{s_2 q_2 s_1} - \frac{1}{2}\bar{g}^{s_1 s_2}_{r_1 q_2}\lambda^{p_1 p_2 r_1}_{q_1 s_2 s_1} = 0
\end{aligned}
\tag{70}
$$

Now a **truncation** at particle rank k **is possible**.

The original BC_k are *not independent* of each other. In fact BC_2 implies BC_1, BC_3 implies BC_2 etc.

The IBC_k, are *independent.* So **all** k up to a certain k_{max} must be considered

At variance with the BC_k, the IBC_k are **separable**.

There is an **infinity of solutions**. Specify the desired one (e.g. by the choice of the starting approximation) and care for n-representability

A hierarchy of k-particle approximations.

One-particle-approximation: Hartree-Fock
Two-particle-approximation: CEPA-0-like

The one-electron approximation

Take the IBC_1:

$$f_r^p \gamma_q^r - \gamma_r^p f_q^r + \frac{1}{2}\bar{g}^{p\ \ s_1}_{r_1 r_2}\lambda^{r_1 r_2}_{q\ \ s_1} - \frac{1}{2}\lambda^{r_1 p}_{s_1 s_2}\bar{g}^{s_1 s_2}_{r_1 q} = 0 \tag{71}$$

$$f_r^p = h_r^p + \bar{g}^{ps}_{rt}\gamma_s^r \tag{72}$$

and neglect $\boldsymbol{\lambda}_2$:

$$f_r^p \gamma_q^r - \gamma_r^p f_q^r = [\mathbf{f}, \boldsymbol{\gamma}]_q^p = 0 \tag{73}$$

A *Liouville*-like equation (Hartree-Fock).
$\boldsymbol{\gamma}$ is diagonal in the basis of eigenstates of $\mathbf{f}$.
No information on the *diagonal* elements of $\boldsymbol{\gamma}$.

$\boldsymbol{\lambda}_2 = 0$ only compatible with $\boldsymbol{\gamma}^2 = \boldsymbol{\gamma}$, hence choose the diagonal elements $\gamma_p^p = n_p$ equal to 0 or 1.
So one satisfies *n-representability.*

Stationarity determines the *non-diagonal* elements,
n-**representability** the *diagonal* elements.

Irreducible k-particle contracted Schrödinger equations

Generally the irreducible counterparts ICSE$_k$ of the CSE$_k$ are (consider also the hermitean conjugates!)

$$\langle\Psi|\tilde{a}^{p}_{q}(H-E)|\Psi\rangle = 0 \tag{74}$$

$$\langle\Psi|\tilde{a}^{pq}_{rs}(H-E)|\Psi\rangle = 0 \text{ etc.} \tag{75}$$

The Lagrange multiplier E cancels with the constant part of H in (66) such that the ICSE$_1$(74) becomes e.g.

$$\begin{aligned} 0 &= f^{s}_{r}\langle\Psi|\tilde{a}^{p}_{q}\tilde{a}^{r}_{s}|\Psi\rangle + \frac{1}{2}g^{s_1s_2}_{r_1r_2}\langle\Psi|\tilde{a}^{p}_{q}\tilde{a}^{r_1r_2}_{s_1s_2}|\Psi\rangle \\ &= f^{s}_{r}\left\{\lambda^{pr}_{qs} + \gamma^{p}_{s}\eta^{r}_{q}\right\} \\ &+ \frac{1}{2}\bar{g}^{s_1s_2}_{r_1r_2}\left\{\frac{1}{2}\lambda^{pr_1r_2}_{qs_1s_2} - \gamma^{p}_{s_1}\lambda^{r_1r_2}_{q\ s_2} + \eta^{r_1}_{q}\lambda^{p\ r_2}_{s_1s_2}\right\} \end{aligned} \tag{76}$$

The result in an NSO basis is

$$
\begin{aligned}
0 &= f^s_r \lambda^{pr}_{qs} + f^p_q (1-n_q) n_p + \frac{1}{4} \bar{g}^{s_1 s_2}_{r_1 r_2} \lambda^{q s_1 s_2}_{p r_1 r_2} \\
&\quad - \frac{1}{2} n_p \bar{g}^{s_1 p}_{r_1 r_2} \lambda^{r_1 r_2}_{s_1 q} + \frac{1}{2} (1-n_q) \bar{g}^{s_1 s_2}_{r_1 q} \lambda^{r_1 p}_{s_1 s_2}
\end{aligned}
\tag{77}
$$

To get $\boldsymbol{\gamma} = \boldsymbol{\gamma}_1$, one needs $\boldsymbol{\lambda}_2$ and $\boldsymbol{\lambda}_3$.

Neglect of $\boldsymbol{\lambda}_2$ and $\boldsymbol{\lambda}_3$ (one-particle approximation) consistent with idempotency of $\boldsymbol{\gamma}$.

Same result as from IBC_1.

$IBC_2 \to \boldsymbol{\lambda}_2$

The ICSE$_k$ imply the IBC$_k$. The latter are much simpler. Which are better?

$\mathbf{IBC}_k$ and $\mathbf{ICSE}_k$ vs. $\mathbf{BC}_k$ and $\mathbf{CSE}_k$

What have we gained?

1. Obvious truncation scheme.

2. A posteriori justification of the *reconstruction.*

3. Theory entirely in terms of *additively separable quantities.*

See also Nooijen, Herman and Harriman

4. We can refine the theory beyond the *obvious truncation* and discover so far undetected problems.

Unexpected problems

1. Stationarity of the energy determines the non-diagonal elements of γ and the $\boldsymbol{\lambda}_k$, while the diagonal elements are determined by n-representability.

More precisely: The IBC$_k$ don't determine the diagonal elements at all. The ICSE$_k$ give an access to the diagonal elements, but this is indirect, ineffective, and expensive.

The conjecture that a CSE$_k$-based theory circumvents the n-representability problem *is false*.

2. In order to get the energy correct to second-order in PT one needs to solve the ICSE$_3$, unless one explicitly takes care of n-representability.

3. There is a hierarchy with respect to particle number only for the non-diagonal elements, not for the diagonal ones.

4. Unlike the $\boldsymbol{\gamma}_k$, the $\boldsymbol{\lambda}_k$ do not terminate at $k{=}n$. The price to pay for strict extensivity is the presence of *EPV cumulants*. These are not easily truncated.

5. Even for a two-particle system the two-particle approximation is not exact.

6. Our formal analysis confirms pessimistic results of numerical studies by Noga, Nooijen, and others, but appears to be in conflict with encouraging numerical results of Valdemoro, Nakatsuji and Mazziotti. (Compensation of errors?)

Solution of the IBC$_k$ and ICSE$_k$ by perturbation theory

$$
\begin{aligned}
H(\mu) &= E + f^p_q \tilde{a}^q_p + \mu \frac{1}{2} g^{pq}_{rs} \tilde{a}^{rs}_{pq} = H_0 + \mu V && (78)\\
f^p_q &= h^p_q + \bar{g}^{pr}_{qs} \gamma^s_r && (79)
\end{aligned}
$$

$$
\begin{aligned}
A_k &= \langle \Psi | [H_0, \tilde{X}_k] | \Psi \rangle && (80)\\
B_k &= \langle \Psi | [V, \tilde{X}_k] | \Psi \rangle && (81)\\
C_k &= \langle \Psi | \tilde{X}_k (H_0 - E) | \Psi \rangle && (82)\\
D_k &= \langle \Psi | \tilde{X}_k V | \Psi \rangle && (83)\\
0 &= A_k + \mu B_k = 0;\ \mathrm{IBC}_k && (84)\\
0 &= C_k + \mu D_k = 0;\ \mathrm{ICSE}_k && (85)
\end{aligned}
$$

$\tilde{X}_k$: k-particle excitation operator in generalized normal order with respect to Ψ

Expand in powers of μ (via $\boldsymbol{\gamma}$ and the $\boldsymbol{\lambda}_k$)!
To zeroth order in μ we have to satisfy the IBC$_k^{(0)}$

$$\begin{aligned}\mathrm{IBC}_1^{(0)}:\ (A_0)_q^p &= (f_0)_s^p(\gamma_0)_q^s - (f_0)_q^r(\gamma_0)_r^p = 0 \\ (f_0)_q^p &= (f_0)_q^p + \bar{g}_{qs}^{pr}(\gamma_0)_r^s \end{aligned} \tag{86}$$

Hartree-Fock

The other IBC$_k^{(0)}$ are satisfied, if all $\boldsymbol{\lambda}_k^{(0)}$ *vanish*.

Use Hartree-Fock orbitals as one-electron basis. Eigenvalues $\varepsilon_p^{(0)}$ of $\mathbf{f^{(0)}}$ and $n_p^{(0)}$ of $\boldsymbol{\gamma}^{(0)}$.

The occupation numbers $n_p^{(0)}$ are **undetermined** by the stationarity condition (86).

They are determined by the state to be studied, and by the n-representability condition!

First-order corrections:

Get $\boldsymbol{\gamma}^{(1)}$ and $\boldsymbol{\lambda}_k^{(1)}$ (their non-diagonal elements) from

$$\mathrm{IBC}_1^{(1)}; \qquad (A_1)^p_q + (B_0)^p_q = 0 \tag{87}$$

$$\mathrm{IBC}_2^{(1)}; \qquad (A_1)^{pq}_{rs} + (B_0)^{pq}_{rs} = 0 \tag{88}$$

$$(A_1)^{pq}_{rs} = \{\varepsilon_p^{(0)} + \varepsilon_q^{(0)} - \varepsilon_r^{(0)} - \varepsilon_s^{(0)}\}(\lambda_1)^{pq}_{rs} \tag{89}$$

$$\begin{aligned}(B_0)^{pq}_{rs} &= \bar{g}^{pq}_{rs}\{(1-n_p^{(0)})(1-n_q^{(0)})n_r^{(0)}n_s^{(0)} \\ &- (1-n_r^{(0)})(1-n_s^{(0)})n_p^{(0)}n_q^{(0)}\}\end{aligned} \tag{90}$$

$\boldsymbol{\gamma}^{(1)}$ and the $\boldsymbol{\lambda}_k^{(1)}$ with $k > 2$ vanish.

Labels $i, j, k, \ldots$ for Hartree-Fock spin orbitals with $n_i^{(0)}$=1, and $a, b, c, \ldots$ for those with $n_a^{(0)}$=0.

Only nonvanishing elements of $\boldsymbol{\lambda}_2^{(1)}$:

$$(\lambda_1)_{ab}^{ij} = \{\varepsilon_i^{(0)} + \varepsilon_j^{(0)} - \varepsilon_a^{(0)} - \varepsilon_b^{(0)}\}^{-1} \bar{g}_{ab}^{ij} \tag{91}$$

$$(\lambda_1)_{ij}^{ab} = \{\varepsilon_i^{(0)} + \varepsilon_j^{(0)} - \varepsilon_a^{(0)} - \varepsilon_b^{(0)}\}^{-1} \bar{g}_{ij}^{ab} \tag{92}$$

Second-order corrections

$$E_2 = \varepsilon_p^{(0)} (\gamma_2)_p^p + \frac{1}{4} \bar{g}_{rs}^{pq} (\lambda_1)_{pq}^{rs} \tag{93}$$

The *second term* in (93) is easily evaluated as

$$\frac{1}{2} g_{rs}^{pq} (\lambda_1)_{pq}^{rs} = \frac{1}{4} \{\varepsilon_i^{(0)} + \varepsilon_j^{(0)} - \varepsilon_a^{(0)} - \varepsilon_b^{(0)}\}^{-1} \bar{g}_{ab}^{ij} \bar{g}_{ij}^{ab} \tag{94}$$

For the *first term* in (93), we need the diagonal elements of $\boldsymbol{\gamma}^{(2)}$, the 2^{nd} order correction to $\boldsymbol{\gamma}$.

No information from IBC_1, try ICSE_1 :

$$
\begin{aligned}
0 &= (C_2)_p^p + (D_1)_p^p \qquad (95) \\
(C_2)_p^p &= \varepsilon_r^{(0)}(\lambda_2)_{pr}^{pr} + \varepsilon_p^{(0)}(\gamma_2)_p^p\{1 - 2n_p^{(0)}\} \\
&+ n_p^{(0)}\{1 - n_p^{(0)}\}\varepsilon_p^{(2)} \\
(D_1)_p^p &= \frac{1}{2}(1 - n_p^{(0)})\bar{g}_{tq}^{rs}(\lambda_1)_{rs}^{pq} - \frac{1}{2}n_p^{(0)}\bar{g}_{rs}^{pq}(\lambda_1)_{tq}^{rs} \\
&+ \frac{1}{4}\bar{g}_{r_1r_2}^{s_1s_2}(\lambda_1)_{ps_1s_2}^{pr_1r_2}
\end{aligned}
$$

$(C_2)_p^p$ contains the *diagonal elements* $(\lambda_2)_{pr}^{pr}$.

In order to get these we have to solve the $\mathsf{ICSE}_2^{(0)}$,which contain the $(\lambda_2)_{pqr}^{pqr}$ to be obtained from the the $\mathsf{ICSE}_3^{(2)}$. Fortunately, the $(\lambda_2)_{pqrs}^{pqrs}$ and cumulants of higher particle rank vanish.

After some tedious manipulations, solving the ICSE$_3^{(2)}$, ignoring $\boldsymbol{\lambda}_4^{(2)}$ and $\boldsymbol{\lambda}_5^{(2)}$, then the ICSE$_2^{(2)}$, and finally the ICSE$_1^{(2)}$, we arrive at

$$(\gamma_2)_i^i = -\frac{1}{2}(\lambda_1)_{ab}^{ij}(\lambda_1)_{ij}^{ab} \tag{96}$$

$$(\gamma_2)_a^a = +\frac{1}{2}(\lambda_1)_{ac}^{ij}(\lambda_1)_{ij}^{ac} \tag{97}$$

and at the correct result for E_2.

The two-particle approximation is not even correct to O(μ^2)

Use of n-representability

The n-particle density matrix of an n-particle state is *pure-state n-representable* if – for unit trace – it is idempotent. Since we normalize $\boldsymbol{\gamma}_n$ as

$$\mathrm{Tr}(\boldsymbol{\gamma}_n) = n! \tag{98}$$

the pure-state n-representability condition is

$$(\boldsymbol{\gamma}_n)^2 = n!\boldsymbol{\gamma}_n \tag{99}$$

For the perturbation expansion in powers of μ we get:

$$(\boldsymbol{\gamma}_n^{(0)})^2 = n!\boldsymbol{\gamma}_n^{(0)} \tag{100}$$

$$\boldsymbol{\gamma}_n^{(0)}\boldsymbol{\gamma}_n^{(1)} + \boldsymbol{\gamma}_n^{(1)}\boldsymbol{\gamma}_n^{(0)} - n!\boldsymbol{\gamma}_n^{(1)} = 0 \tag{101}$$

$$\boldsymbol{\gamma}_n^{(0)}\boldsymbol{\gamma}_n^{(2)} + \boldsymbol{\gamma}_n^{(2)}\boldsymbol{\gamma}_n^{(0)} - n!\boldsymbol{\gamma}_n^{(2)} = -(\boldsymbol{\gamma}_n^{(1)})^2 \tag{102}$$

After some elementary manipulations we find that the only non-vanishing elements of $\boldsymbol{\gamma}_n^{(2)}$ (except for a permutation of indices) of are:

$$(\gamma_2)^{abi_3....i_n}_{abi_3....i_n} = \frac{1}{2}\sum_{i_1 i_2}(\lambda_1)^{ab}_{i_1 i_2}(\lambda_1)^{i_1 i_2}_{ab} \tag{103}$$

$$(\gamma_2)^{i_1 i_2 i_3....i_n}_{i_1 i_2 i_3....i_n} = -\frac{1}{2}\sum_{i_k i_l}\sum_{ab}(\lambda_1)^{i_k i_l}_{ab}(\lambda_1)^{ab}_{i_k i_l} \tag{104}$$

From this we get:

$$(\gamma_2)^{i_1}_{i_1} = -\frac{1}{2}\sum_{i_2}\sum_{a,b}(\lambda_1)^{i_1 i_2}_{a\ b}(\lambda_1)^{a\ b}_{i_1 i_2} \tag{105}$$

$$(\gamma_2)^{a}_{a} = \frac{1}{2}\sum_{i_1 i_2}\sum_{b}(\lambda_1)^{i_1 i_2}_{a\ b}(\lambda_1)^{a\ b}_{i_1 i_2} \tag{106}$$

without any need to consider the ICSE$_1^{(2)}$, ICSE$_2^{(2)}$, ICSE$_3^{(2)}$

Use of a unitary transformation

Φ = reference function; Ψ = exact function

$$\Psi = e^{\boldsymbol{\sigma}}\Phi \quad (107)$$

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2 + ... = \sigma^p_q \tilde{a}^q_p + \frac{1}{2}\sigma^{pq}_{rs}\tilde{a}^{rs}_{pq} + ... \quad (108)$$

Now *normal ordering with respect to* Φ.
Energy E and Brillouin conditions BC$_k$:

$$\begin{aligned} E &= \langle\Phi|e^{-\boldsymbol{\sigma}}He^{\boldsymbol{\sigma}}|\Phi\rangle \\ &= \langle\Phi|H + [H,\boldsymbol{\sigma}] + \frac{1}{2}[[H,\boldsymbol{\sigma}],\boldsymbol{\sigma}] + \ldots|\Phi\rangle \\ 0 &= \langle\Phi|e^{-\boldsymbol{\sigma}}[H,X]e^{\boldsymbol{\sigma}}|\Phi\rangle \\ &= \langle\Phi|[H,X] + [[H,X],\boldsymbol{\sigma}] + \frac{1}{2}[[[H,X],\boldsymbol{\sigma}],\boldsymbol{\sigma}] + \ldots|\Phi\rangle \quad (109) \end{aligned}$$

In principle, exact.
The unitary transformation *preserves the n-representabilty.*

Perturbation expansion is feasible to any desired order.

$\boldsymbol{\sigma}^{(1)}$ consists only of $\boldsymbol{\sigma}_2^{(1)}$. We obtain it from

$$\langle\Phi|[[H_0, \boldsymbol{\sigma}_2^{(1)}], X]\Phi\rangle = -\langle\Phi|[V, X]|\Phi\rangle \tag{110}$$

The only nonvanishing elements are:

$$(\sigma_1)_{ab}^{ij} = (\varepsilon_i^{(0)} + \varepsilon_j^{(0)} - \varepsilon_a^{(0)} - \varepsilon_b^{(0)})^{-1}\bar{g}_{ab}^{ij} \tag{111}$$

$$(\sigma_1)_{ij}^{ab} = -(\varepsilon_i^{(0)} + \varepsilon_j^{(0)} - \varepsilon_a^{(0)} - \varepsilon_b^{(0)})^{-1}\bar{g}_{ij}^{ab} \tag{112}$$

The equation (110) only determines the $non\text{-}diagonal$ elements of $\boldsymbol{\sigma}_2^{(1)}$.

Unlike for the $\boldsymbol{\lambda}_2^{(1)}$, **no loss of generality** to impose that the **diagonal elements** of $\boldsymbol{\sigma}_2^{(1)}$ **vanish**.

Knowing $\boldsymbol{\sigma}_2^{(1)}$ we can easily construct the nonvanishing elements of $\boldsymbol{\lambda}_2^{(1)}$ and of the diagonal part of $\boldsymbol{\gamma}^{(2)}$ that we need for the evaluation of E_2.

$$(\lambda_1)^{ij}_{ab} = = (\sigma_1)^{ij}_{ab}\langle\Phi|[\tilde{a}^{ij}_{ab}, \tilde{a}^{ab}_{ij}]|\Phi\rangle = -(\sigma_1)^{ij}_{ab} \tag{113}$$

$$(\lambda_1)^{ab}_{ij} = = (\sigma_1)^{ij}_{ab}\langle\Phi|[\tilde{a}^{ab}_{ij}, \tilde{a}^{ij}_{ab}]|\Phi\rangle = \quad (\sigma_1)^{ab}_{ij} \tag{114}$$

$$(\gamma_2)^i_i = \frac{1}{2}\langle\Phi|[[\tilde{a}^i_i, \sigma_2^{(1)}], \sigma_2^{(1)}]|\Phi\rangle = -\frac{1}{2}(\sigma_1)^{ij}_{ab}(\sigma_1)^{ab}_{ij} \tag{115}$$

$$(\gamma_2)^a_a = \frac{1}{2}\langle\Phi|[[\tilde{a}^a_a, \sigma_2^{(1)}], \sigma_2^{(1)}]|\Phi\rangle = \quad \frac{1}{2}(\sigma_1)^{ij}_{ab}(\sigma_1)^{ab}_{ij} \tag{116}$$

In terms of the $\boldsymbol{\sigma}_k$ the *two-particle approximation* (i.e. the truncation at $k = 2$) appears to work better than in terms of $\boldsymbol{\lambda}_k$

A quadratically convergent theory

1. Construction of cumulants by satisfying the IBC$_k$ or ICSE$_k$ can be regarded as a generalization of Hartree-Fock theory, (where one only satisfies the IBC$_1$ – or ICSE$_1$).One cares for vanishing of the first derivatives of the energy with respect to k*-particle excitations*.

2. Any theory based on the IBC$_k$ or the ICSE$_k$ is a *first-order theory* that can, at best, converge *linearly*.

3. An **alternative** is a *quadratically* convergent scheme, in which, in addition to the first derivatives F_p (vanishing of which imply the IBC$_k$), one also considers the second derivatives of the energy with respect to orbital rotations or their generalization, i.e. where one makes explicit use of the Hessean $\mathcal{H}_{pq}$

$$F_p = \langle\Psi|[H, X_p]|\Psi\rangle; \; \mathcal{H}_{pq} = \langle\Psi|[[H, X_p], X_q]|\Psi\rangle \tag{117}$$

for X_p all possible (antihermitean) excitation operators.

Of course, the elements of F_p and the Hessean are expressible in terms of the density cumulants related to Ψ, provided that the operators X_p are in normal order with respect to Ψ.

4. In a second-order theory n-representability is easily imposed. A unitary transformation in Fock space starting from a zeroth-order n-representable state preserves n-representability.

5. Should one use the ICSE$_k$ or the IBC$_k$? Nakatsuji theorem.

6. Nothing is free. One is now faced to the problem that the Hausdorff expansion does not terminate. However, it is likely to converge fast.

Minimization of the energy with respect to γ_2

The energy is a known functional of $\boldsymbol{\gamma}_2$

$$E = \bar{H}^{pq}_{rs}\gamma^{rs}_{pq};\ 2\bar{H}^{pq}_{rs} = (\delta^p_r h^q_s + \delta^q_s h^r_p)/(n-1) + g^{pq}_{rs} \tag{118}$$

with $\bar{H}^{pq}_{rs}$ a matrix element of the *reduced Hamiltonian*. Early attempts to make the energy stationary with respect to variations of $\boldsymbol{\gamma}_2$ failed. Surprisingly good results if one imposes all known *necessary* n-representability conditions (Garrod, Nakatsuji, Mazziotti).

Neither $\boldsymbol{\gamma}_2$ nor $\bar{H}$ are *separable* quantities. Start better from

$$E = \frac{1}{2}(f^p_q + h^p_q)\gamma^q_p + \frac{1}{2}g^{pq}_{rs}\lambda^{rs}_{pq} \tag{119}$$

and try to impose the known *necessary* n-representability conditions for $\boldsymbol{\gamma}$ and $\boldsymbol{\lambda}_2$. They are not independent. The partial trace relation relates the diagonal elements of $\boldsymbol{\lambda}_2$ to the deviation of $\boldsymbol{\gamma}$ from idempotency. We further need a relation between diagonal and non-diagonal elements of $\boldsymbol{\lambda}_2$.

Use of approximate n-representability conditions

In Møller-Plesset perturbation theory one gets

$$\lambda_{ij}^{ij} = -\frac{1}{2}\lambda_{ij}^{ab}\lambda_{ab}^{ij} + O(\mu^3) \quad (120)$$

$$\lambda_{ab}^{ab} = +\frac{1}{2}\lambda_{ab}^{ij}\lambda_{ij}^{ab} + O(\mu^3) \quad (121)$$

The non-negativity conditions lead to similar, but much weaker relations.

Systematic studies of the use of approximate n-representability conditions are recommended.

Alternatively one can start from an n-representable ansatz and use a transformation that preserves n-representability, at least approximatively. One uses $\boldsymbol{\sigma}$ to construct $\boldsymbol{\lambda}$.

Relation to density matrix functional theory

Consider a family of Hamiltonians in a matrix representation with different potential matrices $\mathbf{V}$. Then the ground state energy E is a concave functional of $\mathbf{V}$. The one-particle density matrix is the functional derivative of E with respect to $\mathbf{V}$.

$$\boldsymbol{\gamma} = \frac{\delta E}{\delta \mathbf{V}} \tag{122}$$

One can perform a Legendre transformation

$$F(\boldsymbol{\gamma}) = E(\boldsymbol{\gamma}) - \mathrm{Tr}(\mathbf{V}\boldsymbol{\gamma}); \ \frac{\delta F}{\delta \mathbf{V}} = 0 \tag{123}$$

to define the unknown 'universal' ($\mathbf{V}$-independent) functional $F(\boldsymbol{\gamma})$ for the sum of kinetic energy and electron interaction energy. Since the kinetic energy as well as the Coulomb- and exchange parts of the interaction energy are expressible through $\boldsymbol{\gamma}$, only the correlation part of $F(\boldsymbol{\gamma})$ is unknown. In DMFT this is usually parametrized by a guessed functional of $\boldsymbol{\gamma}$. This unknown part is, however, equal to a known functional of the unknown $\boldsymbol{\lambda}_2$.

Conclusions

1. For a state describable to zeroth order by a *single Slater determinant* one obtains from the IBC_2 or the $ICSE_2$ the *nondiagonal part of the first-order correction* $\boldsymbol{\lambda}_2^{(1)}$ to $\boldsymbol{\lambda}_2$, which is necessary for the construction of E_2. For this it is easier to use the IBC_2 than the $ICSE_2$.

2. The IBC_k do not give information on the *diagonal part* of the second order correction $\boldsymbol{\gamma}^{(2)}$ to the one-particle density matrix $\boldsymbol{\gamma}$, which is also needed for the construction of E_2. This information can be obtained from the $ICSE_2$, but requires $k = 1, 2, 3$, i.e. the *three-particle approximation*, in order to get E_2 correctly.

3. The *non-diagonal* elements of $\boldsymbol{\lambda}_2$ start with $O(\mu)$, i.e. with $\boldsymbol{\lambda}_2^{(1)}$, the *diagonal elements* of $\boldsymbol{\lambda}_2$ start with $O(\mu^2)$, as do the *diagonal elements* of $\boldsymbol{\gamma}$ and both diagonal and non-diagonal elements of $\boldsymbol{\lambda}_3$, while $\boldsymbol{\lambda}_4$ starts with $O(\mu^3)$.

4. A much simpler access to the low-order perturbation contributions to $\boldsymbol{\gamma}$ and the $\boldsymbol{\lambda}_k$ than via the solution of the IBC_k and the $ICSE_k$ is by means of the *unitary transformation* mediated by σ, or by the direct use of the *n-representability* condition. The first order term $\sigma_2^{(1)}$ of the two-particle transformation induced by σ_2 is sufficient to construct E up to E_3.