Reduced density matrices, their spectral resolutions, and the 

Kimball-Overhauser approach

P. Ziesche\textsuperscript{1,*} and F. Tasnádi\textsuperscript{2,†}

\textsuperscript{1}Max-Planck-Institut für Physik komplexer Systeme, 
Nöthnitzer Str. 38, D-01187 Dresden, Germany

\textsuperscript{2}Leibniz-Institut für Festkörper- und Werkstoffforschung, 
Helmholtzstr. 20, D-01069 Dresden, Germany, and 
University of Debrecen, Hungary

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Recently, it has been shown, that the pair density of the homogeneous electron gas 
can be parametrized in terms of 2-body wave functions (geminals), which are scattering 
solutions of an effective 2-body Schrödinger equation. For the corresponding 
scattering phase shifts, new sum rules are reported in this paper. These sum rules 
describe not only the normalization of the pair density (similar to the Friedel sum 
rule of solid state theory), but also the contraction of the 2-body reduced density 
matrix. This allows one to calculate also the momentum distribution, provided that 
the geminals are known from an appropriate screening of the Coulomb repulsion. 
An analysis is presented leading from the definitions and (contraction and spectral) 
properties of reduced density matrices to the Kimball-Overhauser approach and its 
generalizations. Thereby cumulants are used. Their size-extensivity is related to the 
thermodynamic limit.

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\textsuperscript{*}E-mail: pz@mpipks-dresden.mpg.de
\textsuperscript{†}E-mail: f.tasnadi@ifw-dresden.de

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Introduction

The description of an electronic many-body system in its ground-state (GS) by means of 1-body orbitals $\psi_\kappa(1)$ with the short-hand $1 \equiv (r_1, \sigma_1)$ is well-known and widely used. For example in the configuration-interaction (CI) method \[1, 2, 3\] these orbitals are used to build up the $N$-electron Slater determinants. The linearly combined Slater determinants form the GS-wave function $\Psi(1, \ldots, N)$ such that the electron density is given by $\rho(1) = \sum_\kappa \nu_\kappa |\psi_\kappa(1)|^2$ with a non-idempotent occupancy $\nu_\kappa$ being between 0 and 1 as a consequence of the Pauli principle, $\sum_\kappa \nu_\kappa = N$. In the Hartree-Fock approximation and in the Kohn-Sham treatment of the density-functional theory (DFT), cf. e.g. \[4\], the orbitals $\psi_\kappa(1)$ are solutions of effective 1-body Schrödinger equations and the occupancies are idempotent, $\nu_\kappa^2 = \nu_\kappa$, using thereby the aufbau principle. The DFT shows the ‘power and charm’ of the 1-body density $\rho(1)$ \[5\]. In the theory of reduced density matrices (RDMs) \[6, 7, 8, 9, 10, 11, 12\] and in the density matrix functional theory (DMFT) \[9, 13\] the $\psi_\kappa(1)$ diagonalize the 1-body reduced density matrix (1-matrix) so that $\gamma(1|1') = \sum_\kappa \psi_\kappa(1)\nu_\kappa\psi_\kappa^*(1')$ holds, what is called spectral resolution. The $\nu_\kappa$ are again non-idempotent as a consequence of the electron correlation phenomenon such that the non-idempotency of $\gamma$ or $\nu_\kappa$ can be used to measure the strength of correlation, $\nu_\kappa^2 < \nu_\kappa$, $\text{Tr} \gamma^2 < \text{Tr} \gamma$ \[14, 15, 16, 17\]. For crystalline solids the $\nu_\kappa$ describe the occupation band structure. The $\psi_\kappa(1)$ are the natural orbitals and the $\kappa$ are 1-body quantum numbers.

The 1-matrix $\gamma(1|1')$ is a 2-point function, not to be confused with another important 2-point function, the pair density (PD) $\rho_2(1, 2)$. This PD shows its power and charm in the Fermi hole for parallel-spin pairs (due to the Pauli ‘repulsion’ and modified by the Coulomb repulsion), in the Coulomb hole for antiparallel-spin pairs (due to the Coulomb repulsion), in the coalescing (or on-top) cusp and curvature properties, and in the possibility to calculate and discuss particle number fluctuations in partial regions of the system (e.g. Daudel loges or "stockholder" loges or Bader basins or Wigner-Seitz cells or \cdots) as another (more sensitive) measure of the correlation strength with the conclusion ‘(strong) correlations (strongly) suppress such fluctuations’, cf. \[1\], p. 157, and \[17, 18\]. Strong electron correlation thus
localizes electrons. Examples are the Wigner crystallization of the low-density HEG, the Wigner-like charge ordering in Yb$_4$As$_3$ [19], and the insulating GS of CoO (where DFT predicts a metal).

Related to the PD is the less known and less worked out use of 2-body wave functions (geminals) $\psi_K(1,2)$ for the description of an electronic many-body system [21]. The $K$ are 2-body quantum numbers. Recently, in an eventually possible pair density functional theory (PDFT) [22] and in the Kimball-Overhauser approach of the homogenous electron gas (HEG) [23, 24, 25, 26, 27, 28, 29] such geminals are discussed as solutions of an effective 2-body Schrödinger equation and used to parametrize the pair density (PD) $\rho_2(1,2) = \sum_K \mu_K |\psi_K(1,2)|^2$. More general, the so-called natural geminals diagonalize the 2-body RDM (2-matrix) $\gamma_2(1|1',2|2') = \sum_K \psi_K(1,2) \mu_K \psi_K^*(1',2')$. It is quite natural to CI expand the $\psi_K(1,2)$ in terms of the $\psi_n(1)$. In Ref. [30] it is suggested to generalize the Kimball-Overhauser approach by using its PD geminals as natural geminals in the spectral resolution of $\gamma_2$. This generalization has the advantage that from the natural geminals not only follows the PD, but also the 1-matrix $\gamma$ using thereby the contraction properties of $\gamma_2$. - Geminals appear also in "the antisymmetrized power (AGP) function as a flexible ansatz for fermion systems with arbitrary $N$" [10] and they appear in a generalized DFT in 2-particle space, cf. [20], p. 325 and refs. therein. Besides, there are links between DMFT and geminal theory [31]. Finally, a general remark of Davidson is "scientists have not yet learned to think in terms of $(N\choose2)$ geminals rather than in $N$ orbitals" [6], p. 97.

In the following, the Kimball-Overhauser approach is summarized from an RDM point of view and possible generalizations are presented.

**Basic notation**

The GS energy $E$ of a non-relativistic $N$-electron system in Born-Oppenheimer approximation is partitioned as $E = T[\gamma] + V_{\text{ext}}[\rho] + V_{\text{int}}[\rho_2]$, where the well-known linear functionals...
(using the short-hand notation $\int d1 \equiv \sum_{\sigma_1} \int d^3 r_1$)

$$T[\gamma] = \int d1 \; t(r_1) \gamma(1|1')|_{r'=1}, \quad t(r_1) = -\frac{\hbar^2}{2m} \left( \frac{\partial}{\partial r_1} \right)^2,$$

$$V_{\text{ext}}[\rho] = \int d1 \; \rho(1) v_{\text{ext}}(r_1), \quad V_{\text{int}}[\rho_2] = \int \frac{d1 d2}{2!} \rho_2(1, 2) \frac{e^2}{r_{12}}, \quad e^2 = \frac{e^2}{4\pi \varepsilon_0} \quad (1)$$

appear. $v_{\text{ext}}(r)$ is the potential of the nuclei (or the jellium background) binding the electrons. The 1-matrix $\gamma(1|1')$, the electron density $\rho(1) \geq 0$ and the PD $\rho_2(1, 2) \geq 0$ are functionals of the GS wave function $\Psi(1, \ldots, N)$ arising from $\Psi(1, \ldots, N)\Psi^*(1', \ldots, N')$ by appropriate contractions, which means the operations $i' = i$ and $\int di$. (In the many-body perturbation theory this term has another meaning.) $\gamma$, $\rho$ and $\rho_2$ follow from the 2-matrix (which is defined by the $N-2$ contraction of $\Psi(1, \ldots, N)\Psi^*(1', \ldots, N')$),

$$\gamma_2(1|1', 2|2') = \int \frac{d3 \ldots dN}{(N-2)!} \Psi(1, 2, 3, \ldots)\Psi^*(1', 2', 3, \ldots), \quad \text{Tr} \gamma_2 = N(N-1), \quad (2)$$

where the wave-function normalization

$$\int \frac{d1 \ldots dN}{N!} |\Psi(1, \ldots, N)|^2 = 1 \quad (3)$$

is used (each particle configuration is naturally counted only once).

**Contraction sum rules, cumulant expansions, spin structures, and pair densities**

The contraction of the 2-matrix yields

$$\gamma(1|1') = \frac{1}{N-1} \int d2 \; \gamma_2(1|1', 2|2), \quad \rho(1) = D\gamma(1|1') = \gamma(1|1). \quad (4)$$

$D$ projects out the off-diagonal elements $i' \neq i$. The contraction of $\rho_2 = D\gamma_2$ yields

$$\rho(1) = \frac{1}{N-1} \int d2 \; \rho_2(1, 2). \quad (5)$$

$\text{Tr} \gamma = N$ follows from $\text{Tr} \gamma_2 = N(N-1)$. $\rho$ is needed for the expectation value of the external (the electrons confining) potential, whereas $\gamma$ and $\rho_2$ are the quantities to calculate the kinetic and the interaction energy, respectively, cf. Eq. \( \Box \).
A fairly natural partitioning of $\gamma_2$ is its cumulant expansion

$$
\gamma_2(1|1',2|2') = \gamma_2^{HF}(1|1',2|2') - \chi(1|1',2|2'),
$$

$$
\gamma_2^{HF}(1|1',2|2') = A\gamma(1|1')\gamma(2|2') = \gamma(1|1')\gamma(2|2') - \gamma(1|2')\gamma(2|1').
$$

(6)

The index HF means generalized (with non-idempotent occupancies) Hartree-Fock part of $\gamma_2$. $A$ is the antisymmetrizer. $\chi$ is the so-called cumulant 2-matrix. (For cumulants, cf. e.g. Ref. 32.) For the diagonal elements, Eq.(6) is read as

$$
\rho_2(1,2) = \rho(1)\rho(2) - \gamma(1|2)\gamma(2|1) - u(1,2)
$$

(7)

with the cumulant PD $u = D\chi$. For $\chi$ the contraction sum rule (SR) is written as

$$
\int d2 \chi(1|1',2|2) = \sum_\kappa \psi_\kappa(1)\nu_\kappa(1 - \nu_\kappa)\psi^*_\kappa(1').
$$

(8)

This contraction SR contains the normalization SR

$$
\int d1d2 u(1,2) = \text{Tr}\chi = \text{Tr}\gamma(1 - \gamma) = \sum_\kappa \nu_\kappa(1 - \nu_\kappa) = Nc.
$$

(9)

It defines a quantity $c < 1$, which is the cumulant PD normalization per particle. This quantity is referred to as Löwdin parameter (because Löwdin has asked for the meaning of $\text{Tr}\gamma^2$). It vanishes for idempotent occupancies and increases with increasing correlation induced non-idempotency [14, 15, 16, 17]. Note that Eqs. (8) and (9) are invariant under the exchange $\nu_\kappa \leftrightarrow (1 - \nu_\kappa)$, what is called particle-hole symmetry [34].

The spin structure of $\gamma$ is simply

$$
\gamma(1|1') = \frac{1}{2} \delta_{\sigma_1,\sigma'_1}\gamma(r_1|r'_1),
$$

$$
\gamma(r_1|r'_1) = \rho f(r),
$$

\hspace{1cm} r = |r_1 - r'_1|, \hspace{1cm} f(0) = 1,

(10)

where the latter expression holds for a homogeneous system with the dimensionless 1-matrix $f(r)$. The property $f(0) = 1$ makes $\gamma(r_1|r'_1)$ correctly normalized. Note that for an spin-unpolarized system $\rho(1) = \rho(1)/2$, besides homogeneity makes $\rho(r) = \text{const} = \rho$.

The spin structure of $\gamma_2$ is [35]

$$
\gamma_2(1|1',2|2') = \frac{1}{2} \left( \delta_{\sigma_1,\sigma'_1}\delta_{\sigma_2,\sigma'_2} - \delta_{\sigma_1,\sigma'_2}\delta_{\sigma_2,\sigma'_1} \right) \delta_{\sigma_1,-\sigma_2}\gamma_+(1|1',2|2')
$$

$$
+ \frac{1}{2} \left( \delta_{\sigma_1,\sigma'_1}\delta_{\sigma_2,\sigma'_2} + \delta_{\sigma_1,\sigma'_2}\delta_{\sigma_2,\sigma'_1} \right) \gamma_-(1|1',2|2'),
$$

(11)
which gives rise to a singlet 2-matrix $\gamma_+$ and a triplet 2-matrix $\gamma_-$ with the normalizations

$$\text{Tr} \gamma_\pm = \frac{N}{2} (\frac{N}{2} \pm 1).$$

For a homogeneous system the diagonal elements of $\gamma_2$ define the spin-dependent dimensionless PD $g$ according to $\rho^2 g = \rho_2$,

$$g(1, 2) = \frac{1}{8} (1 - \delta_{\sigma_1, \sigma_2}) \delta_{\sigma_1, -\sigma_2} g_+(r_{12}) + \frac{1}{8} (1 + \delta_{\sigma_1, \sigma_2}) g_-(r_{12}), \quad r_{12} = |r_1 - r_2|. \quad (12)$$

Here $g_+(r)$ is the singlet PD and $g_-(r)$ is the triplet PD, which are normalized as

$$\int d^3r \frac{\rho}{2} [g_+(r) - 1] = \pm 1, \quad g_\pm(\infty) = 1. \quad (13)$$

Thus the PDs for spin-parallel ($g_p$) and spin-antiparallel ($g_a$) electron pairs can be defined with the help of $g_+$ and $g_-$ as

$$g_p(r) = g_-(r), \quad g_a(r) = \frac{1}{2} [g_+(r) + g_-(r)]. \quad (14)$$

They have the following normalizations

$$\int d^3r \frac{\rho}{2} [1 - g_p(r)] = 1, \quad \int d^3r \frac{\rho}{2} [1 - g_a(r)] = 0, \quad g_{p,a}(\infty) = 1. \quad (15)$$

With these definitions, the spin-summed PD is

$$g(r) = \frac{1}{2} [g_a(r) + g_p(r)] = \frac{1}{4} [g_+(r) + 3g_-(r)], \quad \int d^3r \rho [1 - g(r)] = 1, \quad g(\infty) = 1. \quad (16)$$

Note that in Refs. [29, 30] the $g_\pm(r)$ are defined differently, namely with a factor $\frac{1}{2}$, such that we have here $g_\pm(\infty) = 1$ (whereas in Refs. [29, 30] it is $\frac{1}{2}$).

Eqs. (13)-(16) may be equivalently written in terms of the dimensionless cumulant PD $h$ defined by $\rho^2 h = u$. Thus Eq. (17) takes the form

$$g(1, 2) = \frac{1}{4} - \frac{1}{4} \delta_{\sigma_1, \sigma_2} |f(r)|^2 - h(1, 2), \quad (17)$$

from which follows

$$g_p(r) = 1 - |f(r)|^2 - h_p(r), \quad g_a(r) = 1 - h_a(r). \quad (18)$$

With these definitions the normalization SRs (15) become

$$\int d^3r \frac{\rho}{2} h_p(r) = c, \quad \int d^3r \frac{\rho}{2} h_a(r) = 0, \quad h_{p,a}(\infty) = 0. \quad (19)$$
Next singlet/triplet terms \( h_\pm \) are defined - analog to Eq. (14) by \( h_p = h_- \) and \( h_a = \frac{1}{2}[h_++h_-] \). Their normalization SRs are

\[
\int d^3r \frac{\rho}{2} h_\pm(r) = \mp c, \quad c = 1 - \frac{2}{\rho} \int d^3r |f(r)|^2, \quad h_\pm(\infty) = 0, \tag{20}
\]

what follows from Eq. (19). Analog with Eq. (16), the spin-summed cumulant PD is

\[
h_\pm(r) = \frac{1}{4} \left[ h_a(r) + 3h_- (r) \right], \quad \int d^3r \rho h_\pm(r) = c, h(\infty) = 0. \tag{21}
\]

Similar as for \( g_\pm \) the definition of \( h_\pm(r) \) differs from the definition used in Refs. [29, 30]. For the \( \gamma_\pm \) of Eq. (11) the contraction SRs

\[
\int d^3r_2 \gamma_\pm(r_1|r_1',r_2|r_2') = \frac{1}{2} \gamma(r_1|r_1') \left( \frac{N}{2} \pm 1 \right) \tag{22}
\]

hold, what contains the normalization SRs \( \text{Tr} \gamma_\pm = \frac{N}{2} \left( \frac{N}{2} \pm 1 \right) \) and agrees together with the spin structure Eq. (11) also with \( \int d^2\gamma_2(1|1',2|2) = \gamma(1|1')(N-1) \) of the contraction SR (4).

For \( \chi_\pm \), the cumulant part of \( \gamma_\pm \), defined by \( \gamma_\pm = \gamma_{\text{HF}}^\pm - \chi_\pm \), it follows from Eq. (22)

\[
\int d^3r_2 \chi_\pm(r_1|r_1',r_2|r_2') = \mp \frac{1}{2} \left[ \gamma(r_1|r_1') - \frac{1}{2} \int d^3r_2 \gamma(r_1|r_2')\gamma(r_2|r_1') \right], \tag{23}
\]

\( \text{Tr} \chi_\pm = \mp \frac{N}{2} c \). This contraction SR does not contain any non-size extensive term contrary to the rhs of Eq. (22). The difference \( \gamma_{\text{HF}}^\pm - \gamma_\pm \) makes the non-size extensively normalizable and contractable terms to cancel each other what is the prerequisite for the thermodynamic limit. The contraction SR (23) allows one for a homogeneous system to calculate the (non-ideal) momentum distribution \( n(k) \) by solving a quadratic equation provided that the cumulant matrices \( \chi_\pm \) are known e.g. from perturbation theory \( \chi_\pm \) is given by linked diagrams, but the RPA-like approximation used in Ref. [36] yields only the idempotent \( n^0(k) = \Theta(1-k) \) or from the natural geminals as solutions of an effective 2-body Schrödinger equation. What the latter means is described in the following. We start with the 1-matrix \( \gamma \), derive from this \( \gamma_{\text{HF}}^\pm \), the HF part of the 2-matrix, and use it in the definition \( \chi_\pm = \gamma_{\text{HF}}^\pm - \gamma_\pm \).

Natural orbitals and natural geminals

For a homogeneous system the natural orbitals of \( \gamma(r_1|r_1') \) are plane waves \( \varphi_k(r) = \frac{1}{\sqrt{\Omega}} e^{ikr} \) (\( \Omega = \text{normalization volume} \)) and their occupancies give the momentum distribution \( n(k) \),

\[
(\Omega = \text{normalization volume}) \text{ and their occupancies give the momentum distribution } n(k),
\]
resulting thus from the Fourier transform of the 1-matrix \( f(r) \)

\[
f(r) = \frac{2}{N} \sum_k n(k)e^{ikr}, \quad 0 < n(k) < 1, \quad \sum_k = \int \frac{\Omega d^3k}{(2\pi)^3}. \tag{24}
\]

\( n(k) \) allows one to analyze Compton scattering data. With increasing correlation, the quasi-particle weight \( z_F = n(1^-) - n(1^+) \) (being 1 for ‘no interaction’ or \( r_s = 0 \)) decreases. Note that in the more general spin-polarized case there are two different momentum distributions (for spin-up and spin-down). But for ‘no polarization’ they coincide. For recent parametrizations of the momentum distribution(s) cf. \[16, 35\].

With this spectral resolution of the 1-matrix \( \gamma \) one can easily write down \( \gamma_2^{HF} = A\gamma\gamma \) and from this follow its singlet/triplet components \( \gamma_{\pm}^{HF} \). Thereby the geminals \( \frac{1}{\sqrt{\Omega}}e^{iKR} \frac{1}{\sqrt{\Omega}}e^{ikr} \) with \( R = \frac{1}{2}(r_1 + r_2) \) and \( r = r_1 - r_2 \) appear together with the weight \( n(k_1)n(k_2) \) as the probability of finding two electron momenta \( k_{1,2} = \frac{1}{2}K \pm k \) where \( K = k_1 + k_2 \) is the total momentum and \( k = \frac{1}{2}(k_1 - k_2) \) is the half relative momentum. The first factor describes the free-particle center-of-mass motion, whereas \( \frac{1}{\sqrt{\Omega}}e^{ikr} = \frac{4\pi}{\sqrt{\Omega}} \sum_L^\pm i^lj_L(kr)Y_L^*(e_k) \), \( j_L(kr) = j_i(kr)Y_L(e_r) \), \( L = (l, m_l) \) describes the relative motion for \( \gamma_2^{HF} \). Starting with \( \gamma_2^{HF} = A\gamma\gamma \) and defining \( \gamma_{\pm}^{HF} \) according to the spin structure Eq.(11), it results

\[
\gamma_{\pm}^{HF} = \sum_{k_{1,2}} n(k_1)n(k_2) \varphi_{\pm}^0(r_1, r_2; k_1, k_2) \varphi_{\pm}^0(r_1', r_2'; k_1, k_2) \tag{25}
\]

with \( \varphi_0^0 = \frac{1}{\sqrt{\Omega}}e^{iKR} \frac{4\pi}{\sqrt{\Omega}} \sum_L^\pm i^lj_L(kr)Y_L^*(e_k) \) and

\[
\text{Tr}\gamma^{HF} = \sum_{k_{1,2}} n(k_1)n(k_2) \left[ 1 \pm \delta_{k_1, k_2} \right] = \frac{N}{2} \left( \frac{N}{2} \pm 1 \right) + \frac{N}{2}c. \tag{26}
\]

So, the spectral resolution (25) can be written in terms of free-electron geminals \( j_i(kr) \) and an occupancy matrix

\[
\mu_{LL'}(K, k) = \int \frac{d\Omega_k}{4\pi} Y_L^*(e_k)n(k_1)n(k_2)Y_{L'}(e_k). \tag{27}
\]

Its diagonalization yields an \( L \)-mixing [29].

With the aim to get finally \( \chi_{\pm} = \gamma_{\pm}^{HF} - \gamma_{\pm} \), it is assumed that \( \gamma_{\pm} \) has the same form as \( \gamma_{\pm}^{HF} \) in Eq.(25) with the only difference of replacing the free-electron geminals \( \varphi_{\pm}^0 \) or \( j_i(kr) \)
by interacting-electron geminals \( \varphi_{\pm} \) or \( R_l(r,k) \):

\[
\gamma_{\pm}(r_1r'_1, r_2r'_2) = \sum_{k_{1,2}} n(k_1)n(k_2)\varphi_{\pm}(r_1, r_2; k_1, k_2) \varphi_{\pm}^*(r'_1, r'_2; k_1, k_2). \tag{28}
\]

If these interacting-electron geminals \( R_l \) together with the momentum distribution \( n(k) \) are available, then the PDs \( g_{\pm} \) follow from

\[
g_{\pm}(r) = 2 \sum_{L}^{\pm} \frac{2}{N} \sum_{k} \mu(k) R_l^2(r,k), \quad \mu(k) = \frac{2}{N} \sum_{K} n(k_1)n(k_2) \tag{29}
\]

with \( \frac{2}{N} \sum_{k} \mu(k) = 1 \) and \( \mu(0) = 2^3(1 - c) \).

Assuming that the \( R_l \) are scattering solutions of a radial Schrödinger equation (cf. next Sec.) with a large-\( r \) asymptotics (phase shifted compared with \( j_l \)) according to

\[
R_l(r,k) \rightarrow \frac{1}{kr} \sin(kr - l\frac{\pi}{2} + \eta_l(k)), \quad j_l(kr) \rightarrow \frac{1}{kr} \sin(kr - l\frac{\pi}{2}), \tag{30}
\]

the normalization SRs \( \text{(13)} \) or \( \text{(20)} \) take the form \( \text{(29)} \)

\[
\frac{2}{\pi} \sum_{L}^{\pm} \int_{0}^{\infty} dk \left[ -\frac{\mu(k)}{dk} \right] \eta_l(k) = \pm c. \tag{31}
\]

One may compare these SRs with the well-known Friedel SR for point defects in metals with their screening cloud around an impurity. If the spectral resolutions \( \text{(25)} \) and \( \text{(28)} \) are used in \( \chi_{\pm} = \gamma_{\pm}^{\text{HF}} - \gamma_{\pm} \), the contraction SRs \( \text{(23)} \) can be written as \( \text{(30)} \)

\[
\frac{2}{\pi} \sum_{L}^{\pm} \int_{0}^{\infty} dk \left[ -\frac{\partial^2 \mu(2\kappa,k)}{\partial k} \right] \eta(k) + b_{\pm}(\kappa) = \pm n(\kappa)[1 - n(\kappa)],
\]

\[
\mu(K,k) = \int \frac{d\Omega_k}{4\pi} n(k_1)n(k_2). \tag{32}
\]

The quantity \( b_{\pm}(\kappa) \) is defined in the next Section. With \( \sum_{\kappa} b_{\pm}(\kappa) = 0 \), the contraction SRs \( \text{(32)} \) contain the normalization SRs \( \text{(31)} \) as special cases. Thereby \( \frac{2}{N} \sum_{\kappa} 2^3 \mu(2\kappa,k) = \mu(k) \) is used. The contraction SR \( \text{(32)} \) may be considered as the spectral resolution of the normalization SR \( \text{(31)} \). Both Eq.\( \text{(31)} \) and Eq.\( \text{(32)} \) are relations between the 1-body quantity \( n(k) \) and the 2-body quantities \( R_l(r,k) \) in addition to the virial theorem.
Now the question is, where to get from the geminals \( R_l(r, k) \). In Refs. [23, 24, 25] it is intuitively assumed that they are (at least for the parametrization [29] of the PDs) the solution of the radial Schrödinger equation

\[
\left[ -\frac{1}{r}\frac{\partial^2}{\partial r^2} r + \frac{l(l + 1)}{r^2} + v_\pm(r) - k^2 \right] R_l(r, k) = 0, \tag{33}
\]

which arises from a 2-body Schrödinger equation with an effective interaction potential \( v_\pm(r) = \frac{1}{r} + v_\text{scr}(r) \) possibly different for \( + \) (= even \( l \)) and \( - \) (= odd \( l \)). This is the Coulomb repulsion between two electrons effectively screened by the Fermi-Coulomb hole around each electron. This therefore attractive screening potential comes in the Hartree description [26] from the Poisson equation \( \Delta v_\text{scr}(r) = 4\pi \rho[1 - g(r)] \), which makes the approach a self-consistent one: \( g^0(r) \to v_\pm^0(r) \to R_l^0(r, k) \to g^1(r) \to \cdots \). The results of this approach are in excellent agreement with the quantum-Monte-Carlo data of Refs. [37, 38]. They have been further improved with the inclusion of exchange and correlation in Ref. [27]. Meanwhile also the spin-polarized HEG has been treated in this way [28]. These successes say that this approach contains at least some truth, even if it is not exact and it confirms the above assumption that only the wave functions change from \( \varphi^0 \) to \( \varphi \) when going from the known \( \gamma_{HF}^\pm \) to the unknown \( \gamma_\pm \) leaving the occupancy weight unchanged.

One generalization is the assumption that the PD geminals of Eq.(33) can be used in the spectral resolution [28] also as 2-matrix geminals. This allows one to calculate not only the PDs \( g_\pm(r) \) but also the momentum distribution \( n(k) \) through the contraction SRs [32] - at least in principle. The quantity \( b_\pm(r) \) therein is defined by

\[
b_\pm(\kappa) = -\frac{1}{2}(4\pi)^2 \sum_{\substack{L, L' \geq 0 \\text{all}\ \kappa_{1,2}}} \frac{1}{N^2} \sum \tilde{v}_\pm(\kappa_{12}) \times \frac{2}{N} \sum_k \left[ \mu_{LL'}(2(\kappa - \kappa_1), k) - \mu_{LL'}(2(\kappa - \kappa_2), k) \right] \times \left[ \tilde{R}_L(\kappa_1, k) \frac{\partial \tilde{R}_{L'}^{*}(\kappa_2, k)}{\partial k^2} - \frac{\partial \tilde{R}_L^{*}(\kappa_1, k)}{\partial k^2} \tilde{R}_{L'}(\kappa_2, k) \right], \tag{34}
\]

where \( \tilde{v}_\pm(\kappa_{12}) \) and \( \tilde{R}_L(\kappa, k) \) are the Fourier transforms of \( v_\pm(r) \) and \( R_L(r, k) \), respectively. If one starts with a PD \( g^0(r) \), then it follows (e.g. in the Hartree approximation) the effective
interaction potential $v^0_{\pm}(r)$ yielding geminals $R^0_0(r,k)$ with their phase shifts $\eta^0_0(k)$ and a PD $g^1(r)$. Next with a starting momentum distribution $n^0(k)$ the lhs of Eq. (32) can be calculated. The result is a quadratic equation. Its solution gives $n^1(k)$, etc., until self-consistency is reached finally. Whether this really works has to be checked. For the "PD to 2-matrix" generalization in terms of phase shift SRs for normalization and contraction cf. Refs. [29] and [30], respectively. For the generalization of these SRs to the case of the spin-polarized HEG cf. Ref. [35].

Another generalization concerns inhomogeneous systems. It has been already discussed in Ref. [26]. Here the problem is alternatively viewed for the case of an extended system (e.g. a jellium with a crystalline periodic background density). Then one has to solve the 2-body Schrödinger equation

$$\left\{ \sum_{i=1,2} \left[ t(r_i) + v_{\text{ext}}(r_i) + v_{\text{H}}(r_i) \right] + v_{\pm}(r_1, r_2) - \frac{1}{2}(k_1^2 + k_2^2) \right\} \varphi_{\pm} = 0 \quad (35)$$

with the local Hartree potential $v_{\text{H}}(r)$ and an appropriately screened Coulomb repulsion $v_{\pm}(r_1, r_2)$. The self-consistent procedure would have to start with a reasonable approximation for the natural orbitals and their occupancies. From this follows $\gamma_{\pm}^{\text{HF}}$. From the solution of Eq. (35) [where on the Hartree level, $\rho_2(r_1, r_2)$ is needed as an input for $v_{\pm}(r_1, r_2)$], follows also $\gamma_{\pm}$. This gives the new PD. But also $\chi_{\pm} = \gamma_{\pm}^{\text{HF}} - \gamma_{\pm}$ is then available, which - used in Eq. (38) - yields new natural orbitals and occupancies.

**Summary and outlook**

The Kimball-Overhauser approach for the pair density of the spin-unpolarized homogeneous electron gas (HEG) in terms of geminals is revisited from a reduced-density-matrix (RDM) point of view. We start with the definition of the 2-body RDM and its spectral resolution in terms of natural geminals. This gives quite naturally the Kimball-Overhauser parametrization of the pair density in terms of such geminals. Thereby it is assumed that the geminals which parametrize the pair density can be used also as natural geminals. This assumption has the advantage that also the 1-matrix can be calculated as a consequence of
the contraction properties of the 2-matrix. An important role plays the size-extensivity of the cumulants, which allows one to consider the thermodynamic limit. Open questions are:

- Does the asymptotics Eq. (30) of \( R_l(r, k) \) give [via Eq. (29)] the correct asymptotics of \( g_\pm(r) \)? If this is not the case, can this deficiency be removed by using non-local effective interaction potentials?

- Why the lhs of Eqs. (31) and (32) are not particle-hole symmetric?

- Is there a link to the concept of strongly orthogonal geminals?

- What are the contraction sum rules for the spin-polarized HEG [35]?

- Can the effective 2-body Schrödinger equations (33), (35) be derived from the hierarchy of contracted Schrödinger equations or from the Bethe-Salpeter equation or \( \cdots \)? To what extent is the Kimball-Overhauser approach and its generalizations related to a possible pair-density functional theory [22] and to 2-body cluster expansions [39]? How to treat finite systems in terms of a screened Coulomb repulsion?

- What are the peculiarities of \( \chi_\pm \) and \( v_\pm \) for bondbreaking situations, for metals, semiconductors, ferromagnets, antiferromagnets, superconductors, off-diagonal-long-range order, ferromagnetic superconductors, mixed valence compounds, heavy-fermion systems, non-Fermi liquid behavior, quantum criticality, \( \cdots \)?

In Ref. [40] calculational electronic-structure methods are reviewed including attempts to generalize density-functional theories (e.g. density-matrix functional theory), to further develop the RDM theory (contracted Schrödinger equations, \( N \)-representability [10]), to make the accurate quantum-chemical methods (configurational interaction, coupled cluster, Møller-Plesset) applicable also to extended systems (crystalline solids), and to treat systems with strong electron correlations from first principles.
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