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The electron-gas pair density and its geminal description

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Abstract: Attempts to generalize the density functional theory are summarized. A possible pair density functional theory is linked to the Overhauser parametrization of the electron-gas pair density. The importance of the cumulant partitioning is stressed and a modified Overhauser approach for the *cumulant* 2-body reduced density matrix, the contraction of which determines the 1-body reduced density matrix, is discussed.

Keywords: reduced density matrices, cumulant partitioning, generalized density functional theories, Kimball-Overhauser geminals

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The simplest quantum-kinematical quantity of a many-electron system (bound by $v_{\rm ext}(\mathbf{r})$, described by $\hat{H} = \hat{T} + \hat{V}_{\rm ext} + \hat{V}_{\rm int}$, ground state) is its (1-body) density $\rho(1)$ with $1 = (\mathbf{r}, \sigma)$. Density functional theory is an effective 1-body scheme, which provides the density $\rho(1)$ and the total energy E, supposed a certain density functional $E_{\rm xc}[\rho]$ is approximately known. But the 1-body reduced density matrix (1-matrix for short) $\gamma(1|1')$ and the pair density $\rho_2(1,2)$ remain unknown within this scheme. The 1-matrix $\gamma(1|1')$ contains not only the density with $\rho(1) = \gamma(1|1)$, but also the momentum distribution $n(k)$ (= diagonal of the Fourier transformed 1-matrix) and it enters the pair density in its cumulant partitioning $\rho_2(1,2) = \rho(1)\rho(2) - \gamma(1|2)\gamma(2|1) - u(1,2)$, where $u(1,2)$ is the diagonal of the cumulant 2-matrix $\chi(1|1',2|2')$. The corresponding partitioning of the interaction energy is $V_{\rm int} = V_{\rm H} + V_{\rm F} + V_{\rm C}$ with H = Hartree, F = Fock, C = cumulant. The more general density-matrix functional theory may be considered as an effective 1-body scheme for $\gamma(1|1')$ and E, supposed $V_{\rm C}$ is approximately known as a 1-matrix functional $V_{\rm C}[\gamma]$. But the cumulant pair density remains unknown within this scheme. Pair-density functional theory [1]-[11] may be considered as an effective 2-body scheme for $\rho_2(1,2)$ and E, supposed T is approximately known as a pair-density functional $T[\rho_2]$. But then the 1-matrix remains unknown.

It would be most desirable, if an effective 2-body scheme would be available for the cumulant geminals $\psi_K(1,2)$ and their occupancies ν_K, such that $\chi(1|1',2|2') = \sum_K \psi_K(1,2)\nu_K\psi^*_K(1',2')$ is the cumulant 2-matrix. Its diagonal gives the cumulant pair density $u(1,2) = \chi(1|1,2|2)$ and from the contraction sum rule

$$\int d2\ \chi(1|1',2|2) = \sum_\kappa \psi_\kappa(1)\nu_\kappa(1-\nu_\kappa)\psi^*_\kappa(1'), \quad \gamma(1|1') = \sum_\kappa \psi_\kappa(1)\nu_\kappa\psi^*_\kappa(1') \tag{1}$$

follows the 1-matrix by solving a quadratic equation. $\psi_\kappa(1)$ and ν_κ are the natural orbitals and their occupancies, respectively, which diagonalize the 1-matrix $\gamma(1|1')$. From $\rho(1) = \gamma(1|1)$ follow

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$V_{\rm ext}$ and $V_{\rm H}$, from $\gamma(1|1')$ follow T and $V_{\rm F}$, and from $u(1,2)$ follows $V_{\rm C}$: $E = T + V_{\rm ext} + V_{\rm H} + V_{\rm F} + V_{\rm C}$. Unfortunately almost nothing is known about the cumulant 2-matrix $\chi(1|1',2|2')$. In view of Eq. (1) it is sufficient to know the 3-point function $\chi(1|1',2|2)$.

One way to learn something about these cumulant quantities may be to study them for the spin-unpolarized uniform or homogeneous electron gas (HEG)[12]. The advantage of this model is, that in its weak-correlation limit $r_s \to 0$, the cumulant 2-matrix $\chi(1|1',2|2')$ can be controlled through the well-known random-phase-approximation results for $n(k)$ and $\rho_2(1,2)$ [13]-[16]. There is still another motivation for such a study. Namely, on the one hand, there is the idea of Kimball and Overhauser [17]-[33], to parametrize the (dimensionless) HEG pair density as

$$g(r) = 2\left(\frac{1}{4}\sum_L^{+} + \frac{3}{4}\sum_L^{-}\right)\langle \mu(k) R_l^2(r,k)\rangle \;, \quad \langle \cdots \rangle = \int_0^\infty d(k)^3 \;\cdots \tag{2}$$

in terms of pair-density geminals $R_l(r,k)$ and corresponding weights $\mu(k)$. $\pm$ stands for even, respectively, odd l, corresponding to the singlet, respectively, triplet components of $g(r)$. It turns out first a 2-body problem, which is easily treated separating-off the center-of-mass motion. It then remains a radial Schrödinger equation with an appropriately screened Coulomb repulsion and with scattering-state solutions $R_l(r,k)$. The geminal weight follows from $n(k)$ according to

$$\mu(k) = \int_0^\infty d(K)^3 \; n(|\frac{1}{2}\mathbf{K} + \mathbf{k}|) n(|\frac{1}{2}\mathbf{K} - \mathbf{k}|). \tag{3}$$

Notice the cumulant partitioning of the pair density as $g(r) = 1 - \frac{1}{2} f^2(r) - h(r)$ with $f(r) =$ Fourier transform of $n(k)$,

$$f(r) = \int_0^\infty d(k)^3 \; \frac{\sin kr}{kr} \; n(k), \quad \text{and} \quad 1 - \frac{1}{2} f^2(r) = 2\left(\frac{1}{4}\sum_L^{+} + \frac{3}{4}\sum_L^{-}\right)\langle \mu(k) j_l^2(kr)\rangle. \tag{4}$$

Treating the electron-electron repulsion $\alpha r_s/q^2$ as perturbation, the cumulant pair density $h(r)$ is given by *linked* Feynman diagrams. The results of the Overhauser approach are promising, but on the other hand, there is the insight, that this approach violates the plasmon sum rule [33]. Is the mentioned search for a scheme, which provides the *cumulant* geminals with scattering states $\tilde{R}_l(r,k)$ and bound states $\tilde{R}_{n,l}(r)$ and - following from them - the cumulant pair density

$$h(r) = 2\left(\frac{1}{4}\sum_L^{+} + \frac{3}{4}\sum_L^{-}\right)\left(\langle \tilde{\mu}(k) \tilde{R}_l^2(r,k)\rangle + \sum_n \tilde{\mu}_n \tilde{R}_{n,l}^2(r)\right) \tag{5}$$

a possible way out ? $h(r)$ should have the long-range asymptotics in agreement with the plasmon sum rule and it has of course also to obey the cusp condition for $r \to 0$ [17].

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