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Pair Density Functional Theory - a Generalized Density Functional Theory *

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Abstract

The idea of a pair-density-functional theory for Fermions is presented. Whereas in the conventional Hohenberg-Kohn-Sham theory for the ground state of an interacting N-particle system the particle density is the key quantity and the sum of the kinetic and the interaction energy is a universal functional of this density, here the pair distribution function (PDF) is the key quantity and the kinetic energy is a universal functional of this PDF. With an appropriate ansatz for the PDF and the kinetic energy in terms of antisymmetric geminals a two-particle equation with an effective local interaction potential and a corresponding expression for the total energy are derived. Besides this a way is described how to obtain from the solution of the effective two-particle equation also the one-particle density matrix via the first link of the equation of motions for the reduced density matrices.

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1. Introduction

Within the Born-Oppenheimer approximation of the electron theory of molecules, clusters, and solids, it remains the task to solve the many-electron and the multi-centre problems. For the many-electron problem, effective one-particle descriptions like the Hartree, Hartree-Fock or Hohenberg-Kohn-Sham approaches are widely used. In particular, the generalized gradient approximation beyond the local-density approximation has led to a breakthrough for the use of the density-functional theory (DFT) in quantum chemistry. The key quantity in these effective one-particle approaches is the electronic density $n(\mathbf{r})$. From its approximate calculations follows then the total energy of the ground state, E . (For recent monographs on DFT cf. Refs. 1-4.)

On the other hand this total energy E , if considered as the expectation value of the Hamiltonian needs for its calculation the one-particle density matrix (1PDM) and the pair distribution function (PDF). Apart from this aspect, knowledge of the 1PDM and the PDF could give deeper insight into the details of electron correlation. Furthermore from the 1PDM follows the momentum distribution which determines the Compton scattering and - in the case of metals - the Fermi surface. (For recent monographs on reduced DM's cf. Refs. 5,6.) Recently, natural-occupation numbers have been used to measure the non-idempotency of the 1PDM and simultaneously the correlation strength [7]. (For recent monographs on electron correlation cf. Refs. 8,9.)

The question arises whether a generalized DTF can be developed which allows to calculate not only the density, but also the mentioned 1PDM and the PDF. Here it is shown that such a generalized DTF can be constructed. Its key quantities are the PDF and the kinetic energy as a universal functional of the PDF (defined via the constrained-search method). This is in analogy with the conventional DFT, where the density and the sum of kinetic and interaction energy as a universal functional of the density are the decisive quantities. The next steps in the construction of a pair-density-functional theory (PDFT) are:

- to study the *anatomy* of the reduced DM's in terms of natural one-particle orbitals and natural two-particle orbitals (geminals),
- to deduce from such a study an appropriate ansatz for the PDF in terms of geminals yet to be determined, as is done in the Kohn-Sham(KS) theory for the density in terms of one-particle orbitals, and
- to split the universal pair-density functional T into a part T_0 in terms of the mentioned geminals and an unknown remainder T_{XC} , somewhat as this is done in the KS theory for the density functional.

Finally, variation yields a two-particle Schrödinger equation with an effective particle interaction. Its solution gives a set of geminals from which the PDF follows via the above mentioned ansatz. Using this result in the equation of motion for the 1PDM this should allow to determine also the latter.

The paper is organized as follows:

Sec. 2 describes the class of systems under consideration.

Sec. 3 deals with reduced DM's, their corresponding cumulant matrices (CM's), and reduced distribution functions (density, PDF).

Sec. 4 gives the reduced DM's in terms of natural orbitals or geminals,

Sec. 5 derives the effective two-particle equation.

Sec. 6 shows how the results of Sec. 5 can be used to construct the 1PDM in addition to the PDF.

Sec. 7 lists other versions of the scheme presented in Sec. 2-6, and open questions.

2. The system

The class of systems we consider here is described by the Hamiltonian $\hat{H} = \hat{T} + \hat{V}$ with

$$\hat{T} = \int d\mathbf{l} \frac{\mathbf{p}_1^2}{2m} \hat{\gamma}(1, 1')|_{1'=1}, \quad (1)$$

where $\mathbf{p}_1 = (\hbar/i)(\partial/\partial \mathbf{r}_1)$ and $\hat{V} = \hat{V}_{\text{ext}} + \hat{V}_{\text{int}}$, where

$$\hat{V}_{\text{ext}} = \int d\mathbf{l} \hat{n}(1) v_{\text{ext}}(1), \quad (2)$$

$$\hat{V}_{\text{int}} = \int \frac{d\mathbf{l} d\mathbf{2}}{2!} \hat{n}(1, 2) v_{\text{int}}(1, 2). \quad (3)$$

$\mathbf{l} = (\mathbf{r}_1, \sigma_1)$ and $\int d\mathbf{l} = \sum_{\sigma_1} \int d^3\mathbf{r}_1$ are used as shorthands, $\hat{\gamma}(1, 1')$ and $\hat{n}(1, 2)$ are the operators of the 1PDM and the PDF, respectively. $\hat{n}(1, 2)$ is the diagonal of the corresponding 2PDM operator. $\hat{n}(1) = \hat{\gamma}(1, 1)$ is the operator of the particle density, so $\hat{N} = \int d\mathbf{l} \hat{n}(1)$ counts the particle number, while

$$\int \frac{d\mathbf{l} d\mathbf{2}}{2!} \hat{n}(1, 2) = \frac{\hat{N}(\hat{N} - 1)}{2!} \quad (4)$$

counts the number of the particle pairs. Note

$$\int d\mathbf{2} \hat{n}(1, 2) = \hat{n}(1)(\hat{N} - 1), \quad (5)$$

from which follows Eq. (4). $v_{\text{ext}}(1)$ is the external potential acting equally on all particles and $v_{\text{int}}(1, 2)$ is the particle interaction (e.g. Coulomb repulsion e^2/r_{12}).

3. The ground state and its reduced density matrices

The N -particle ground state of $\hat{H}$ is characterized by an energy E , a correlated N -particle Fermion wave function (WF) $\Phi(1, \dots, N)$ with

$$P_{ij}\Phi(\dots i \dots j \dots) = -\Phi(\dots i \dots j \dots),$$

$$\int \frac{d1 \dots dN}{N!} |\Phi(1, \dots, N)|^2 = 1 \quad (6)$$

and following from $\Phi(\dots)$ by the sequence of reduced DM's

$$\gamma(1, 1') = \int \frac{d2 \dots dN}{(N-1)!} \Phi(1, 2 \dots N) \Phi^*(1', 2 \dots N), \quad (7)$$

$$n(1, 2; 1', 2') = \int \frac{d3 \dots dN}{(N-2)!} \Phi(1, 2, 3 \dots N) \Phi^*(1', 2', 3 \dots N). \quad (8)$$

$n(1, 1'; 2, 2'; 3, 3')$ etc. or equivalently by the corresponding CM's

$$\gamma(1, 1'), \gamma(1, 1'; 2, 2'), \gamma(1, 1'; 2, 2'; 3, 3') \text{ etc.}$$

The latter quantities appear in the cumulant expansion of the DM's. The CM of a given order is that term of the DM of the same order, that cannot be reduced to irreducible CM's of lower order, e.g.

$$n(1, 1'; 2, 2') = \gamma(1, 1')\gamma(2, 2') - \gamma(1, 2')\gamma(2, 1') + \gamma(1, 1'; 2, 2'). \quad (9)$$

(On the one-particle level the analog equation $n(1, 1') = \gamma(1, 1')$ would be only a change of notation.) The cumulant construction is important for the thermodynamic limit because the CM's $\gamma(\dots)$ lead to the proper size scaling ($\sim N$).

The diagonals $n(1) = \gamma(1, 1)$ and $n(1, 2) = n(1, 1; 2, 2)$ are the particle density and the PDF, respectively. The diagonal $u_X(1, 2)$ of

$$u_X(1, 1'; 2, 2') = \gamma(1, 2')\gamma(2, 1') \quad (10)$$

can be referred to as the 'cumulant exchange (X) hole', and the diagonal of

$$u_C(1, 1'; 2, 2') = -\gamma(1, 1'; 2, 2') \quad (11)$$

as the 'cumulant correlation (C) hole'. With Eqs. (10) and (11) and with the XC-hole matrix

$$u_{XC}(1, 1'; 2, 2') = u_X(1, 1'; 2, 2') + u_C(1, 1'; 2, 2') \quad (12)$$

the 2PDM (9) can be written as

$$n(1, 1'; 2, 2') = \gamma(1, 1')\gamma(2, 2') - u_{XC}(1, 1'; 2, 2'). \quad (13)$$

The diagonal of Eq.(13) gives the PDF

$$n(1, 2) = n(1)n(2) - u_{XC}(1, 2). \quad (14)$$

From the reduction of the 2PDM

$$\int d2 \, n(1, 1'; 2, 2) = (N-1)\gamma(1, 1') \quad (15)$$

follows the reduction of the XC-hole matrix

$$\int d2 \, u_{XC}(1, 1'; 2, 2) = \gamma(1, 1') \quad (16)$$

and normalization of the XC-hole (per particle)

$$\frac{1}{N} \int d1 d2 \, u_{XC}(1, 2) = 1. \quad (17)$$

With Eq.(12) and with the X-hole normalization (per particle)

$$x = \frac{1}{N} \int d1 d2 \, u_X(1, 2) \quad (18)$$

and with the C-hole normalization (per particle)

$$c = \frac{1}{N} \int d1 d2 \, u_C(1, 2)$$

the normalization sum rule (17) takes the form

$$x + c = 1. \quad (19)$$

With increasing correlation c , the (cumulant) X-hole normalization x decreases (correlation induced X-hole narrowing [10]).

Because of $E = \langle \hat{H} \rangle$, $n(1) = \langle \hat{n}(1) \rangle$, $\gamma(1, 1') = \langle \hat{\gamma}(1, 1') \rangle$ etc. the total energy is given by $E = T + V_{ext} + V_{int}$ and $V_{int} = V_H + V_X + V_C$ with

$$T = \int d1 \hat{i}(1) \gamma(1, 1')|_{1'=1}, \quad \hat{i}(1) = -\frac{\hbar^2}{2m} \Delta(1), \quad (20)$$

$$V_{ext} = \int d1 n(1) v_{ext}(1), \quad n(1) = \gamma(1, 1), \quad (21)$$

$$V_H = \int \frac{d1 d2}{2!} n(1) n(2) v_{int}(1, 2), \quad n(1) = \gamma(1, 1), \quad (22)$$

$$V_X = - \int \frac{d1 d2}{2!} u_X(1, 2) v_{int}(1, 2), \quad u_X(1, 2) = |\gamma(1, 2)|^2, \quad (23)$$

$$V_C = - \int \frac{d1 d2}{2!} u_C(1, 2) v_{int}(1, 2), \quad u_C(1, 2) = -\gamma(1, 1; 2, 2). \quad (24)$$

This describes E as a functional of $CM's$.

4. Natural orbitals and natural geminals

An essential step in the derivation of the KS equation is the ansatz for the particle density $n(1)$ in terms of orbitals $\varphi_k(1)$ to be determined from an effective one-particle Schrödinger equation. This ansatz can be viewed as having its origin in the representation of the 1PDM $\gamma(1, 1')$ in terms of its diagonalizing natural orbitals $\tilde{\varphi}_k(1)$ and corresponding occupation numbers n_k

$$\gamma(1, 1') = \sum_k \tilde{\varphi}_k(1) n_k \tilde{\varphi}_k^*(1'), \quad (25)$$

$$\langle \tilde{\varphi}_k | \tilde{\varphi}_{k'} \rangle = \delta_{k,k'}, \quad \sum_k n_k = N.$$

(For the concept of natural orbitals and geminals cf. Refs. 5, 6, 8, 11.) The true 1PDM is non-idempotent and the deviation of $x = (1/N) \sum_k (n_k)^2$ from 1 measures this non-idempotency. Eq. (19) expresses the relationship (at the two-particle level) between this non-idempotency x and the correlation strength c [7].

Now the KS approach can be understood *a posteriori* as decomposing the true 1PDM $\gamma(1, 1')$ into an idempotent (KS) part $\gamma_0(1, 1')$, the diagonal of which agrees with the true diagonal $n(1) = \gamma(1, 1)$, and a non-idempotent part $\gamma_1(1, 1')$ with vanishing diagonal elements:

$$\gamma(1, 1') = \gamma_0(1, 1') + \gamma_1(1, 1'), \quad (26)$$

$$\gamma_0(1, 1') = \sum_k^{occ} \varphi_k(1) \varphi_k^*(1'), \quad \sum_k^{occ} 1 = N, \quad \gamma_1(1, 1) = 0.$$

The question arises whether the PDF $n(1, 2)$ and other two-particle quantities like $u_{XC}(1, 2)$ or $u_C(1, 2)$ can be treated in a similar way. In terms of diagonalizing natural geminals (two-particle orbitals) the 2PDM is given by [5]

$$n(1, 1'; 2, 2') = \sum_{\kappa} \tilde{\varphi}_{\kappa}(1, 2) n_{\kappa} \tilde{\varphi}_{\kappa}^*(1', 2') \quad (27)$$

with $\tilde{\varphi}_{\kappa}(2, 1) = -\tilde{\varphi}_{\kappa}(1, 2)$,

$$\int \frac{d1 d2}{2!} \tilde{\varphi}_{\kappa}^*(1, 2) \tilde{\varphi}_{\kappa'}(1, 2) = \delta_{\kappa, \kappa'} \quad (28)$$

and

$$\sum_{\kappa} n_{\kappa} = \frac{N(N-1)}{2}. \quad (29)$$

(The natural-geminal occupation numbers n_{κ} are not to be confused with the natural-orbital occupation numbers n_k .) Define with $\gamma_{\kappa}(1, 1') = \int d2 \tilde{\varphi}_{\kappa}(1, 2) \tilde{\varphi}_{\kappa}^*(1', 2)$ the 1PDM of the geminals $\tilde{\varphi}_{\kappa}(1, 2)$. Then the reduction equation (15) reads

$$\sum_{\kappa} n_{\kappa} \gamma_{\kappa}(1, 1') = (N-1) \gamma(1, 1'), \quad \int d1 \gamma_{\kappa}(1, 1) = 2. \quad (30)$$

Now the analog of Eq. (26) would be

$$\begin{aligned} n(1, 1'; 2, 2') &= n_0(1, 1'; 2, 2') + n_1(1, 1'; 2, 2'). \\ n_0(1, 1'; 2, 2') &= \sum_{\kappa}^{occ} \varphi_{\kappa}(1, 2) \varphi_{\kappa}^*(1', 2'), \\ \sum_{\kappa}^{occ} 1 &= \frac{N(N-1)}{2!}, \quad n_1(1, 1; 2, 2) = 0. \end{aligned} \quad (31)$$

For the purpose of the next Sec. even the weaker assumption with $2' = 2$ would be sufficient.

An example for Eqs. (27)-(31) would be a system of noninteracting particles with orbitals $\varphi_k^0(1)$ and energies ε_k^0 resulting from the diagonalization of the unperturbed one-particle Hamiltonian

$$\hat{h}_0(1) = \hat{i}(1) + v_{ext}(1). \quad (32)$$

The unperturbed ground state Φ^0 arises from the occupation of the N lowest states k . Then each geminal state κ is characterized by a pair of the unperturbed one-particle states, i.e. $\kappa = (k_1, k_2)$ with $k_1 \neq k_2$, and the geminals and their occupation numbers are

$$\varphi_{\kappa}^0(1, 2) = \det \begin{vmatrix} \varphi_{k_1}^0(1) & \varphi_{k_1}^0(2) \\ \varphi_{k_2}^0(1) & \varphi_{k_2}^0(2) \end{vmatrix} \quad (33)$$

and

$$n_{\kappa}^0 = \begin{cases} 1 & \text{for } k_1 = occ \text{ and } k_2 = occ \text{ and } k_1 \neq k_2 \\ 0 & \text{for } k_1 \neq occ \text{ or } k_2 \neq occ \text{ or } k_1 = k_2. \end{cases} \quad (34)$$

In this case in Eq. (31) the correction term beyond the KS part $n_0(\dots)$ vanishes: $n_1(\dots) = 0$.

5. Pair density functional theory

With the constrained-search method of M. Levy [12], a functional

$$T[n(1,2)] = \min_{\Phi \rightarrow n(1,2)} \frac{(\Phi, \hat{T}\Phi)}{(\Phi, \Phi)} \quad (35)$$

is defined. In the Hilbert space of antisymmetric N -particle states that subspace is considered, the N -particle wave functions of which yield a given N -particle PDF $n(1,2)$. Within this subspace, the expectation value of $\hat{T}$ is minimized. The kinetic energy T as a universal functional of the PDF $n(1,2)$ results.

Next V_{ext} of Eq. (21) is rewritten as

$$V_{ext} = \int \frac{d1d2}{2!} \frac{1}{(N-1)} n(1,2) [v_{ext}(1) + v_{ext}(2)] \quad (36)$$

and a pair-density functional

$$E[n(1,2)] = T[n(1,2)] + \int \frac{d1d2}{2!} n(1,2) \left\{ \frac{1}{(N-1)} [v_{ext}(1) + v_{ext}(2)] + v_{int}(1,2) \right\} \quad (37)$$

is defined. Then the ground state energy E follows from

$$E = \min_{n(1,2) \rightarrow N} E[n(1,2)]. \quad (38)$$

Next the variational ansatz

$$n(1,2) = \sum_{\kappa}^{\text{occ}} |\varphi_{\kappa}(1,2)|^2, \quad \langle \varphi_{\kappa} | \varphi_{\kappa} \rangle = \int \frac{d1d2}{2!} |\varphi_{\kappa}(1,2)|^2 = 1 \quad (39)$$

is made according to the discussion around Eq. (31). The antisymmetric geminals $\varphi_{\kappa}(1,2)$ are anticipated as the solutions of an effective two-particle equation yet to be determined. Remember: The KS wave function is an antisymmetrized product of N single-particle (KS) orbitals arising from a local effective one-particle potential. The analog here is an antisymmetrized

product of $N(N-1)/2$ (antisymmetric) geminals with a local effective two-particle potential. Again analog the KS approach via

$$T[n(1,2)] = T_0[n(1,2)] + T_{XC}[n(1,2)], \quad (40)$$

$$T_0[n(1,2)] = \frac{1}{N-1} \sum_{\kappa}^{\text{occ}} \langle \varphi_{\kappa} | [\hat{i}(1) + \hat{i}(2)] | \varphi_{\kappa} \rangle$$

a functional $T_{XC}[n(1,2)]$ is defined; the notation

$$\langle \varphi_{\kappa} | \hat{a}(1,2) | \varphi_{\kappa} \rangle = \int \frac{d1d2}{2!} \varphi_{\kappa}^*(1,2) \hat{a}(1,2) \varphi_{\kappa}(1,2)$$

is used. Then the variation

$$\frac{\delta}{\delta \varphi_{\kappa}^*(1,2)} \{ E[n(1,2)] - \varepsilon_{\kappa} \langle \varphi_{\kappa} | \varphi_{\kappa} \rangle \} = 0 \quad (41)$$

yields

$$\begin{aligned} & \{ \hat{h}_0(1) + \hat{h}_0(2) + (N-1)[v_{int}(1,2) + v_{XC}(1,2)] \} \varphi_{\kappa}(1,2) = \\ & = \varepsilon_{\kappa} \varphi_{\kappa}(1,2) \end{aligned} \quad (42)$$

with $\hat{h}_0(1) = \hat{i}(1) + v_{ext}(1)$, $\varepsilon_{\kappa} = (N-1)\varepsilon_{\kappa}$, and

$$v_{XC}(1,2) = \frac{\delta T_{XC}[n(1,2)]}{\delta n(1,2)}. \quad (43)$$

This is an effective two-particle Schrödinger equation for geminals $\varphi_{\kappa}(1,2)$, from which follows the PDF $n(1,2)$ according to Eq. (39) and then the density according to Eq. (5) or (15), i.e.

$$n(1,2) = \sum_{\kappa}^{\text{occ}} |\varphi_{\kappa}(1,2)|^2, \quad n(1) = \int \frac{d2}{N-1} n(1,2). \quad (44)$$

To obtain the ground state energy an aufbau principle for geminals is used. The two-particle Schrödinger equation (42) contains an effective particle interaction

$$v_{eff}(1,2) = v_{int}(1,2) + v_{XC}(1,2), \quad (45)$$

where the second term beyond the bare particle interaction arises because the two particles move in the sea of all the other particles. For two-particle systems it would be $T_{XC} = 0$, $v_{XC} = 0$, $N - 1 = 1$, and only one geminal would determine the PDF $n(1, 2)$.

Assume for $v_{XC}(1, 2)$ reasonable approximations can be found and Eq. (42) can be solved, then the total energy follows according to

$$E = \frac{1}{N-1} \sum_{\kappa}^{\text{occ}} \varepsilon_{\kappa} + T_{XC}[n(1, 2)] - \int \frac{d1 d2}{2!} n(1, 2) \frac{\delta T_{XC}[n(1, 2)]}{\delta n(1, 2)}. \quad (46)$$

Note that in this expression V_{ext} and V_H or V_X are no longer present.

6. The reduced DM's equation of motion

The hierarchy of equations of motion for the reduced DM's (quantum analog of the classical BBGKY hierarchy) starts with

$$\begin{aligned} & [\hat{h}_0(1) - \hat{h}_0^*(1')] \gamma(1, 1') + \\ & + \int d2 [v_{\text{int}}(1, 2) - v_{\text{int}}^*(1', 2)] n(1, 1'; 2, 2) = 0. \end{aligned} \quad (47)$$

This follows from $\langle [\hat{H}, \hat{\gamma}(1, 1')]_- \rangle = 0$. In the limit $1' \rightarrow 1$, Eq. (47) reduces to the continuity equation:

$$\frac{\partial}{\partial \tau} j(\tau) = 0, \quad j(\tau) = \frac{\tilde{p}}{m} \gamma(\tau, \tau')|_{\tau'=\tau}, \quad \tilde{p} = \frac{1}{2}(p^* + p), \quad (48)$$

where $\gamma(\tau, \tau') = \Sigma_{\sigma} \gamma(\tau, \sigma | \tau', \sigma)$. (In Ref. 13 Eq. (47) has been used to derive the local momentum balance.) For $1' \neq 1$ Eq. (48) can be used to determine the 1PDM $\gamma(1, 1')$ with the results of Eq. (42) and with the approximation

$$n(1, 1'; 2, 2) \approx \sum_{\kappa}^{\text{occ}} \varphi_{\kappa}(1, 2) \varphi_{\kappa}^*(1', 2). \quad (49)$$

With the eigenstates of the unperturbed one-particle Hamiltonian $\hat{h}_0(1)$, cf. text before Eq. (32), Eq. (47) takes the form

$$(\varepsilon_k^0 - \varepsilon_{k'}^0) \gamma_{k,k'} = m_{k,k'}, \quad (50)$$

from which - for given r.h.s. - follow the off-diagonal elements of the 1PDM (in the φ_k^0 representation). The diagonal elements $\gamma_{k,k}$ may be adjusted to obey the continuity equation (48), i.e.

$$\sum_{k,k'} \gamma_{k,k'} \frac{\partial}{\partial \tau} [Im \sum_{\sigma} [\varphi_{k'}^0(x)]^* \frac{\partial}{\partial \tau} \varphi_k^0(x)] = 0 \quad (51)$$

(here $x = (\tau, \sigma)$) and to the given quantities $n(\tau)$ of Eq. (44) and $T[n(1, 2)]$ of Eq. (40) via

$$\sum_{k,k'} \gamma_{k,k'} \sum_{\sigma} [\varphi_{k'}^0(x)]^* \varphi_k^0(x) = n(\tau) \quad (52)$$

and

$$\sum_{k,k'} \gamma_{k,k'} < \varphi_{k'}^0 | \hat{t} | \varphi_k^0 > = T[n(1, 2)] \quad (53)$$

(possibly with the help of information theory).

Having this $\gamma_{k,k'}$ or $\gamma(1, 1') = \sum_{k,k'} \varphi_k^0(1) \gamma_{k,k'} [\varphi_{k'}^0(1')]^*$ approximately available, then V_X can be calculated from Eq. (23). V_{int} follows from Eqs. (3) and (44) and V_H from Eqs. (22) and (44), finally $V_C = V_{\text{int}} - V_H - V_X$ results, cf. Eq. (24). So within this PDFT also the 1PDM and all the 'components' of the total energy $E = T + V$ with $V = V_{\text{ext}} + V_{\text{int}}$ and $V_{\text{int}} = V_H + V_X + V_C$ are available.

The natural-occupation numbers n_k of the 1PDM can be used to construct the non-idempotency measures

$$c_{\nu} = 1 - \frac{1}{N} \sum_k (n_k)^{\nu} \quad \text{and} \quad s = -\frac{1}{N} \sum_k n_k \log(n_k)$$

and so to characterize type and strength of the correlation present in the system under consideration [7].

7. Some discussions and outlook

- Further work must make explicit the spin dependence and distinguish between spin-parallel PDF and spin-antiparallel PDF.
- In addition to the version of a PDFT presented here, other versions can be constructed [14] where the 'bare' one-particle Hamiltonian $\hat{h}_0(1)$ is replaced e.g. by the Hartree Hamiltonian

$$\hat{h}_H(1) = \hat{h}_0(1) + v_H(1), \quad v_H(1) = \int d2 \, n(2) v_{int}(1, 2)$$

or by the Hartree-Fock Hamiltonian

$$\hat{h}_{HF}(1) = \hat{h}_H(1) + \hat{v}_X(1),$$

$$\hat{v}_X(1) \varphi_k(1) = - \int d2 \, \gamma(1, 2) v_{int}(1, 2) \varphi_k(2).$$

By the way, these versions do not contain the particle number N explicitly (as this is the case with Eq. (42)), so they directly apply to extended systems.

- The eigenstates of these one-particle Hamiltonians can be used in configurational interaction (CI) expansions of the geminals $\varphi_\kappa(1, 2)$. - Can the $\varphi_\kappa(1, 2)$ be discussed in terms of Brueckner orbitals [8] ?
- In the cases of a *Hooke* atom or of a homogeneous system the two-particle equation can be transformed, replacing the original particle coordinates $\underline{r}_1$ and $\underline{r}_2$ by their *centre of mass* $\underline{R} = (1/2)(\underline{r}_1 + \underline{r}_2)$ and *relative coordinate* $\underline{r} = \underline{r}_1 - \underline{r}_2$. Then separation of the (harmonic respectively free) centre-of-mass motion leaves behind formally only a 'one-particle' problem for the relative motion. (The case of a Hooke atom with two electrons has been studied recently by Taut [15], cf. also Refs. 16, 17.)
- To each of these versions belong different effective interactions and each effective interaction can be used to define a dielectric function. Their relations to other dielectric functions known in electron-gas theory are yet to be studied.

- Are the sufficient conditions for a two-point function to be a PDF, i.e. to arise from a correlated many-body WF known (N representability) ? Or: Is it possible to construct from a given PDF a many-body WF that yields then again this PDF (similar as one can construct within conventional DFT a many-body WF from the density)?
- Which are the *scaling properties* of the new pair-density functionals $T[n(1, 2)]$ and $T_{XC}[n(1, 2)]$?
- Relations to other two-particle schemes like Bethe-Goldstone equation [18], (independent and coupled) pair approximations and Nesbet hierarchy [8], coupled cluster approach and many-body perturbation theory, and papers of Lieb [19], Chayes et al. [20], Valone [21], Krotscheck [22] have yet to be worked out.
- What are the relations between PDFT and conventional DFT ? As a simple example the density functional $F[n(1)]$ results from

$$F[n(1)] = \min_{n(1, 2) \rightarrow n(1)} \left\{ T[n(1, 2)] + \int \frac{d1 d2}{2!} n(1, 2) v_{int}(1, 2) \right\}.$$

Is it possible to get better insight into the density functional $E_{XC}[n(1)]$ by solving (approximately) the effective two-particle problem ? Is it possible to find $\delta V_{XC}/\delta n(1)$ or $\delta V_C/\delta n(1)$ from the construction mentioned at the end of Sec. 6 ?

- The conventional DFT is based on the one-to-one correspondence between the external potential $v_{ext}(1)$ and the density $n(1)$. [On variation the particle interaction $v_{int}(1, 2)$ is kept fixed.] The above derivation makes use of the one-to-one correspondence between the particle interaction $v_{int}(1, 2)$ and the PDF $n(1, 2)$. [On variation the external potential $v_{ext}(1)$ is kept fixed.] To prove $n(1, 2) \rightarrow v_{int}(1, 2)$, one should try to apply Hohenberg-Kohn type arguments as used for $n(1) \rightarrow v_{ext}(1)$. Now: Is it possible or useful to develop a scheme of coupled effective one- and two-particle equations based on the correspondence between $v_{ext}(1)$ and $v_{int}(1, 2)$ on the one hand and $n(1)$ and $n(1, 2)$ on the other hand, knowing that $v_{ext}(1)$ and $v_{int}(1, 2)$ are independent from each other, while $n(1, 2)$ yields $n(1)$?

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