



Coherent-state representation of reduced density matrices of correlated electronic systems

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Abstract

The one-particle reduced density matrix of correlated electronic systems is computed by expressing the many-electron wavefunction as a superposition of generalized coherent states, each representing a single Slater determinant. This representation could be used for developing a density matrix functional theory. The sensitivity of the density matrix to the parameters is demonstrated. © 2000 Published by Elsevier Science B.V.

1. Introduction

The notion that the ground-state properties of a many-electron system can be unambiguously characterized in terms of the 1-particle density, originally formulated by Hohenberg and Kohn [1,2], marked the advent of density functional theory (DFT). The Kohn–Sham (KS) formulation [3] of DFT has since developed into one of the most popular ground-state methods of modern quantum chemistry [1,2]. Its extension to the time-dependent case by Runge and Gross [4] has triggered considerable efforts for improving time-dependent density functional theory (TDDFT) as a tool for studying the dynamics of many-electron systems [5–7]. One practical problem in TDDFT is that the resulting frequency-dependent exchange-correlation potential is a strongly non-local functional of the density. Consequently, there gener-

ally exists no consistent local density approximation for this crucial quantity. Vignale and Kohn therefore proposed to go one step beyond the description of dynamical exchange-correlation effects in terms of the density [8], an approach which historically grew out of the traditional DFT. They demonstrated that a local density approximation does exist when choosing the current density rather than the charge density as the basic variable.

The present Letter is based on the observation that the charge density of a many-electron system is given by the diagonal elements of the 1-particle reduced density matrix ρ , whereas the current density is represented by the nearest to the diagonal elements. To develop a unified description of the original TDDFT and its current density extension, it would be desirable to construct a time-dependent density matrix functional theory (TDDMFT) which uses the 1-particle density matrix as the basic variable. Optically induced changes in the ground-state density matrix carry considerable information about

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optical coherences in the off-diagonal elements [9]. Using this information may facilitate the development of a new class of useful approximations to the exchange-correlation functional.

Several studies on the properties of time-independent energy functionals depending solely on the 1-particle reduced density matrix have been conducted since the 1970s [10–32]. Gilbert investigated the generalization of the Hohenberg–Kohn theorem to non-local external potentials [10]. He found that in this case a non-degenerate ground-state energy is a universal functional of the 1-particle reduced density matrix ρ , that ρ and the functional derivative of the energy with respect to ρ , $\delta E/\delta\rho$, can be simultaneously diagonalized, and that all partially occupied eigenvectors ϕ_i of ρ belong to the same degenerate eigenvalue ϵ_i of $\delta E/\delta\rho$. If we expand ρ in its eigenvectors, i.e.

$$\rho(x', x) = \sum_i n_i \phi_i^*(x) \phi_i(x'), \quad (1a)$$

then $0 \leq n_i \leq 1$, and an eigenvector is said to be *partially occupied* if $1 < n_i < 1$. (x in Eq. (1a) denotes both space and a spin variables.) Berrondo and Goscinski expressed the Gibbs free energy as a functional of the 1-particle reduced density matrix, showed that it fulfills a variational principle, and obtained the ground-state energy by taking the limit $T \rightarrow 0$, where T is the temperature [11]. Donnelly and Parr considered a non-canonical representation of the 1-particle density matrix,

$$\rho(x', x) = \sum_{ij} n_{ij} \psi_i^*(x) \psi_j(x'),$$

and derived a set of coupled integral equations for determining the ground-state energy [12,13]. This method, however, relies on using the unknown functional derivative of the energy with respect to ρ . In addition to reproducing Gilbert's results, they found, more specifically, that the chemical potential μ is the same for all partially occupied eigenvectors of ρ , i.e. $\mu = \epsilon_i/n_i$. Levy formulated both DFT and DMFT in terms of a constrained-search algorithm and showed that the v -representability requirement of both the charge density in DFT as well as of the density matrix in DMFT can be replaced by the much less restrictive N -representability condition [16–19]. (A charge density n (density matrix ρ) is

called v -representable if there exists a potential v such that the ground-state wavefunction Ψ_g of the corresponding molecular Hamiltonian yields the given $n(\rho)$. $n(\rho)$ is called N -representable, if there exists some many-electron wavefunction Ψ (which need not be the ground state of any Hamiltonian) that reproduces the given charge density n (density matrix ρ). Valone extended Levy's work from pure state to ensemble density matrices [20,21]. Henderson applied Levy's formulation of DMFT to show the existence of a universal variational functional of the 1-particle reduced density matrix in momentum space [22]. In all of these investigations, however, the functional dependence of the energy on the density matrix remains unknown. Zumbach and Maschke used the variational principle for the energy as a functional of the 1-particle density matrix, where the variation in ρ is performed by separately varying its eigenvectors ϕ_i and occupation numbers n_i [23,24]. The variation in ϕ_i for fixed n_i leads to a set of self-consistent equations which are similar to the Hartree–Fock (HF) and KS equations. The variation in n_i , however, poses difficulties, since the non-analytical constraint $0 \leq n_i \leq 2$ cannot be expressed by means of a Lagrange multiplier. This difficulty appears to limit the usefulness of this approach. Yasuda and Nakatsuji calculated the 2-particle reduced density matrix by using the so-called density equation [27,28]. Klein and Dreizler derived a variational principle for the ground-state energy of a many-electron system as a functional of the 1-particle density matrix which contains the HF theory as a special case [29]. To this end, they accounted for correlation terms not only in the energy functional but also in the constraints for the density matrix. Chernyak and Mukamel proposed a time-dependent density matrix functional approach in Liouville space [30].

Developing a density-, current-density-, or density matrix-functional theory, requires addressing the question of the representability of all relevant values of the functional argument by a many-body wavefunction of some many-electron system. In the case of DFT this means that any charge density can be represented as the expectation value of the charge density operator on some pure state of a many-electron system. As indicated earlier, the constrained-search principle introduced by Levy and Lieb [16–19] rendered the more restrictive v -representability con-

dition for the charge density unnecessary. However, even though the less restrictive N -representability condition solves some of the formal problems in the development of a functional theory, this is still not sufficient for practical implementations. DFT became a practical tool only after it had been formulated using the KS orbitals. The KS formulation is based on the representability of any charge density distribution as an expectation value of the charge density operator on a many-body state, represented by a single Slater determinant [8,16–19]. More generally, a functional theory becomes an effective tool when any relevant value of the functional argument can be represented by a many-body state that belongs to some manageable manifold \mathcal{M} of trial states. In DFT, \mathcal{M} is simply the manifold of single Slater determinants. To build a DMFT analogue to the KS scheme one needs to find a suitable manifold \mathcal{M} of trial states. \mathcal{M} should be broad enough to represent all relevant single-electron density matrices and narrow enough to keep all computations manageable. Lieb has presented an example of a single-electron density matrix that cannot be represented by a pure many-body state [19]. However, this is a rather pathological example in view of the following: It can be easily demonstrated that if a single-electron density matrix ρ is represented by a pure state $|\Omega\rangle$, i.e.

$$\rho_{mn} = \langle \Omega | \hat{a}_m^\dagger \hat{a}_n | \Omega \rangle \quad (1b)$$

and it has a certain number of zero and unit eigenvalues, then $|\Omega\rangle$ can be represented as a direct product

$$|\Omega\rangle = |\Omega_0\rangle \otimes |\Omega_1\rangle \otimes |\Omega_r\rangle, \quad (1c)$$

where $|\Omega_0\rangle$ denotes a state with no particles corresponding to the zero-block of ρ , $|\Omega_1\rangle$ is a state with no holes, representing the unit-block of ρ , and $|\Omega_r\rangle$ refers to the relevant state corresponding to that block of ρ with fractional occupation numbers $n \in (0,1)$. In Lieb's example, the space of relevant states is two-dimensional, where all states are single-Slater determinants and the non-representability of a non-idempotent ρ is obvious. It can be easily shown by comparing the dimensionality of certain manifolds that the problem of representability of a single-electron density matrix starts with the relevant dimension 6 with three particles that belong to the

relevant space. In summary, the representability of a single-electron density matrix with $0 < n < 1$ and high dimension is still an open problem.

In this Letter, we start from the general idea of the KS method, i.e., replacing the system by a simple auxiliary reference system which has the same desired 1-particle quantity. In DFT, where this desired quantity is the charge density, one can choose a non-interacting system as an auxiliary system, i.e., one can find, in principle, a single Slater determinant which will reproduce the correct charge density of the interacting system. If, however, the desired quantity is the 1-particle density matrix, then this approach will obviously not work, since the 1-particle density matrix of a single Slater determinant has only eigenvalues 1 and 0. We examine a generalized ansatz for the many-electron wavefunction which contains the ansatz of a non-interacting system as a limiting case and represents density matrices with fractional occupation numbers within the interval $[0,1]$. This is a necessary ingredient for developing a KS-type DMFT. To this end, we consider superpositions of Slater determinants representing the many-electron wavefunction. The Slater determinants are given in a generalized coherent state representation, known as the Thouless parameterization [33,34]. We then study the dependence of the density matrices on the parameters. In Section 2, we introduce the Thouless parameterization. In Section 3, we consider the parameterization of the density matrix for a wavepacket given by a discrete superposition of Thouless states. Section 4 presents a study of the sensitivity of the density matrix of a correlated system to the parameters of the wavepacket. The results are discussed in Section 5.

2. Coherent state representation of density matrices

The Hamiltonian of a molecule in an external optical electric field $\mathcal{E}(t)$ is given by

$$H = \sum_{i,j=1}^K h_{ij} a_i^\dagger a_j + \frac{1}{4} \sum_{i,j,k,l=1}^K V_{ij;kl} a_i^\dagger a_j^\dagger a_l a_k - \mathcal{E}(t) \sum_{i,j=1}^K \mu_{ij} a_i^\dagger a_j \quad (2a)$$

where

$$h_{ij} = \int \psi_i^*(\mathbf{r}) \left[\frac{-\hbar^2}{2m} \nabla^2 - \sum_{k=1}^{N_{at}} \frac{Z_k e^2}{|\mathbf{r} - \mathbf{R}_k|} \right] \psi_j(\mathbf{r}) \, d\mathbf{r} \quad (2b)$$

(Z_k is the atomic number of nucleus k), and where

$$V_{ij;kl} = \langle ij|kl \rangle - \langle ij|lk \rangle \quad (2c)$$

and

$$\begin{aligned} \langle ij|kl \rangle &= e^2 \int \frac{\psi_i^*(\mathbf{r}_1) \psi_j^*(\mathbf{r}_2) \psi_k(\mathbf{r}_1) \psi_l(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 \, d\mathbf{r}_2 \\ & \quad (2d) \end{aligned}$$

$V_{ij;kl}$ satisfy the symmetry properties

$$V_{ij;kl} = -V_{ji;kl} = -V_{ij;lk} = V_{ji;lk} \quad (2e)$$

If the external field $\mathcal{E}(t)$ is polarized along the z -axis, then

$$\mu_{ij} = e \int d^3r \psi_i^*(\mathbf{r}) z \psi_j(\mathbf{r}). \quad (2f)$$

The Thouless parameterization of single Slater determinants [33,34] occupied starts with a normalized reference Slater determinant $|\Phi_0\rangle$ composed of N (hole) orbitals.

$$\begin{aligned} |\Phi_0\rangle &= \prod_{h=1}^N a_h^\dagger |0\rangle, \\ \langle \Phi_0 | \Phi_0 \rangle &= 1, \end{aligned} \quad (2g)$$

$|0\rangle$ being the vacuum state (no electrons). Any Slater determinant $|z\rangle$ with $\langle z | \Phi_0 \rangle \neq 0$ can then be characterized by a set of complex parameters $\{z_{ph}\}$ as

$$\begin{aligned} |z\rangle &= [\det(1 + z^\dagger z)]^{-1/2} \\ &\times \prod_{h=1}^N \left(a_h^\dagger + \sum_{p=N+1}^K z_{ph} a_p^\dagger \right) |0\rangle, \end{aligned} \quad (2h)$$

which can also be written in terms of the reference Slater determinant as

$$\begin{aligned} |z\rangle &= [\det(1 + z^\dagger z)]^{-1/2} \\ &\times \prod_{h=1}^N \left(1 + \sum_{p=N+1}^K z_{ph} a_p^\dagger a_h \right) |\Phi_0\rangle. \end{aligned} \quad (2i)$$

Hereafter we use the indices $p, q, r, s, t = N+1, \dots, K$ for particle indices, $e, f, g, h = 1, \dots, N$ for hole indices, and $i, j, k, l = 1, \dots, K$ for the entire particle-hole space. Thus, a_p^\dagger and a_h^\dagger denote the creation operators for electrons and electron holes, respectively. The scalar product of two Thouless states $|z^{(n)}\rangle$ and $|z^{(m)}\rangle$ is [34]

$$\begin{aligned} \langle z^{(n)} | z^{(m)} \rangle &= [\det(1 + z^{(n)\dagger} z^{(n)})]^{-1/2} \\ &\times [\det(1 + z^{(m)\dagger} z^{(m)})]^{-1/2} \\ &\times \det(1 + z^{(n)\dagger} z^{(m)}). \end{aligned} \quad (2j)$$

The Thouless states are generalized coherent states and therefore, even though they are over-complete, there exists a resolution of the unity:

$$\begin{aligned} \hat{1} &= c \int \prod_{h=1}^N \prod_{p=N+1}^K dx_{ph} dy_{ph} \\ &\times [\det(1 + z^\dagger z)]^{-K} |z\rangle \langle z|, \end{aligned} \quad (2k)$$

$$c^{-1} = \int \prod_{h=1}^N \prod_{p=N+1}^K dx_{ph} dy_{ph} [\det(1 + z^\dagger z)]^{-K+1}, \quad (2l)$$

where we denoted $x_{ph} = \text{Re } z_{ph}$, $y_{ph} = \text{Im } z_{ph}$, and a few other properties of these states which will be used in the following derivations are listed below. Introducing the 1-particle transition density matrices between two Thouless states

$$\Gamma_{ji}(z^{(n)\dagger}, z^{(m)}) = \frac{\langle z^{(n)} | a_i^\dagger a_j | z^{(m)} \rangle}{\langle z^{(n)} | z^{(m)} \rangle} \quad (2m)$$

we have

$$\begin{aligned} \Gamma_{ji}(z^{(n)\dagger}, z^{(m)}) &= \left[\left(\frac{1}{z^{(m)}} \right) (1 + z^{(n)\dagger} z^{(m)})^{-1} (1, z^{(n)\dagger}) \right]_{ji}. \end{aligned} \quad (2n)$$

The 2-particle transition density matrix

$$\Gamma_{ij;kl}^{(2)}(z^{(n)\dagger}, z^{(m)}) = \frac{\langle z^{(n)} | a_i^\dagger a_j^\dagger a_l a_k | z^{(m)} \rangle}{\langle z^{(n)} | z^{(m)} \rangle} \quad (2o)$$

may be computed by using the Wick theorem

$$\Gamma_{ij;kl}^{(2)} = \Gamma_{lj} \Gamma_{ki} - \Gamma_{li} \Gamma_{kj}. \quad (2p)$$

Eq. (2p) that constitutes an exact relation between the matrix elements of the two-particle operators in terms of their single-particle counterparts is a generalization of the standard Wick theorem represented by Eq. (2p) when $z^{(n)} = z^{(m)}$. Eq. (2p) can be easily derived by evaluating the quantity

$$\text{Tr}\{a_i^\dagger a_j^\dagger a_l a_k \exp[-H^{(m)}\tau - H^{(n)}\tau]\}$$

where $H^{(j)}$ is a harmonic Hamiltonian with the ground state $|z^{(j)}\rangle$ using the Wick theorem for the imaginary-time (Matsubara) Green functions [35] and taking the $\tau \rightarrow +\infty$ limit.

3. Superposition of Thouless states

An interesting moment method of computing the propagation of coherent state wavepackets with a continuous distribution of parameters was developed and applied to conjugated polymers [36]. We will consider a discrete superposition of M Thouless states, each represented by a different set of Thouless parameters $z_{ph}^{(n)}$:

$$|\Psi\rangle = \sum_{n=1}^M k_n |z^{(n)}\rangle. \quad (3a)$$

This ansatz is reminiscent of a CI expansion, however the orthogonal CI basis set is entirely different from the basis employed here. Using this ansatz, the energy assumes the form

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = E^{(1)} + E^{(2)} + E^{\text{ext}}, \quad (3b)$$

where

$$E^{(1)} = \sum_{i,j=1}^K h_{ij} \rho_{ji}, \quad (3c)$$

$$E^{(2)} = \frac{1}{4} \sum_{i,j,k,l=1}^K V_{ij;kl} \rho_{ij;kl}^{(2)}. \quad (3d)$$

We have defined the 1-electron reduced density matrix

$$\rho_{ji} = \frac{\langle \Psi | a_i^\dagger a_j | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (3e)$$

and the 2-electron density matrix

$$\rho_{ij;kl}^{(2)} = \frac{\langle \Psi | a_i^\dagger a_j^\dagger a_l a_k | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (3f)$$

The energy term E^{ext} due to the time dependent external electric field is analogous to $E^{(1)}$ with h_{ij} replaced by $-\mathcal{E}\mu_{ij}$.

The norm of the wavepacket follows immediately from Eq. (3a)

$$S_0(k^\dagger, z^\dagger, k, z) \equiv \langle \Psi | \Psi \rangle = \sum_{n,m=1}^M k_n^* k_m \langle z^{(n)} | z^{(m)} \rangle, \quad (3g)$$

where $\langle z^{(n)} | z^{(m)} \rangle$ is given in Eq. (2j). Here and throughout the remainder of this section, k^\dagger , k , z^\dagger and z in the argument of a function denote symbolically a dependence on the entire array of coefficients and Thouless parameters, i.e. $k^\dagger \equiv (k_1^*, \dots, k_M^*)$, $z^\dagger \equiv (z^{(1)\dagger}, \dots, z^{(M)\dagger})$, $k \equiv (k_1, \dots, k_M)$, $z \equiv (z^{(1)}, \dots, z^{(M)})$.

For the 1- and 2-electron density matrices we obtain

$$\begin{aligned} \rho_{ji} &= \rho_{ji}(k^\dagger, z^\dagger, k, z) \\ &= \frac{1}{S_0} \sum_{n,m=1}^M k_n^* k_m \Gamma_{ji}(z^{(n)\dagger}, z^{(m)}) \langle z^{(n)} | z^{(m)} \rangle, \end{aligned} \quad (3h)$$

and

$$\begin{aligned} \rho_{ij;kl} &= \rho_{ij;kl}(k^*, z^\dagger, k, z) = \frac{1}{S_0} \\ &\times \sum_{n,m=1}^M k_n^* k_m \Gamma_{ij;kl}^{(2)}(z^{(n)\dagger}, z^{(m)}) \langle z^{(n)} | z^{(m)} \rangle, \end{aligned} \quad (3i)$$

where the transition density matrices are given by Eqs. (2m) and (2o), and the scalar product between is given by Eq. (2j).

In summary, Eqs. (3b), (3f), (3h), (3i) and (2p), yield for the single-body energy

$$\begin{aligned} E^{(1)} &= E^{(1)}(k^\dagger, z^\dagger, k, z) = \frac{1}{S_0} \sum_{i,j=1}^K h_{ij} \\ &\times \sum_{n,m=1}^M k_n^* k_m \Gamma_{ji}(z^{(n)\dagger}, z^{(m)}) \langle z^{(n)} | z^{(m)} \rangle \end{aligned} \quad (3j)$$

and for the two-body energy

$$\begin{aligned}
 E^{(2)} &= E^{(2)}(k^\dagger, z^\dagger, k, z) \\
 &= \frac{1}{4S_0} \sum_{i,j,k,l=1}^K V_{ij;kl} \sum_{n,m=1}^M k_n^* k_m \times \langle z^{(n)} | z^{(m)} \rangle \\
 &\quad \times \left\{ \Gamma_{lj}(z^{(n)\dagger}, z^{(m)}) \Gamma_{ki}(z^{(n)\dagger}, z^{(m)}) \right. \\
 &\quad \left. - \Gamma_{li}(z^{(n)\dagger}, z^{(m)}) \Gamma_{kj}(z^{(n)\dagger}, z^{(m)}) \right\}. \quad (3k)
 \end{aligned}$$

4. Numerical study of the 1-particle density matrix

The discrete superposition ansatz is ideal for exploring the sensitivity of the density matrix to the choice of wavepacket parameters $z^{(n)}$. Since our goal is to represent arbitrary density matrices with a simple wavepacket ansatz, we try to assess whether it is possible to generate density matrices with an arbitrary eigenvalue spectrum.

We consider a short polyene, C_6H_{10} (*trans*-hexadiene) shown in the bottom of Fig. 1.

We have calculated the ground state using the INDO/S semi-empirical Hamiltonian which has four atomic orbitals per carbon atom, and one per hydrogen atom, which amounts to a total of 34 orbitals. Since each molecular orbital accommodates two electrons, we are dealing with $N = 17$ hole orbitals and $K - N = 17$ particle orbitals. We include 34 electrons in the calculation and did not split the density matrix into particle and hole parts. Thus we have $4N^2$ independent elements in the (Hermitian) density matrix ρ . Below we consider a discrete superposition of two Thouless states $z^{(1)}$ and $z^{(2)}$ of the form (Eq. (3a)) and set the coefficients $k_1 = k_2 = 1$. Since each set of Thouless parameters consists of $N(K - N)$ complex elements, this gives us $4N^2$ independent wavepacket parameters, which matches the number of variables of a general density matrix. In principle this should make it possible to represent an arbitrary density matrix.

To illustrate the sensitivity of the parameterized density matrix to variations in $z^{(1)}$, $z^{(2)}$, we took these parameters to be independent random variables with a uniform distribution in an interval $[-W, W]$. We then varied W and observed its effect on the

density matrix. Table 1 shows the eigenvalues of the density matrix for one realization for $W = 0.1$, and $W = 1$. As W is increased, the eigenvalue spectrum of the single-electron density matrix deviates increasingly from the HF limit and shows a qualitatively different behavior in the two cases ($W = 0.1$, and $W = 1$). In the case of an uncorrelated state ($W = 0$) given by a single Slater determinant the spectrum of ρ is strongly degenerate: ρ has 17 eigenvectors with $\lambda = 2$ (occupied orbitals) and 17 eigenvectors with $\lambda = 0$ (unoccupied orbitals). For a weakly correlated state ($W = 0.1$) the eigenvectors of ρ can still be partitioned into two groups: there are 17 eigenvectors with eigenvalues close to 2 and 17 eigenvectors with eigenvalues close to 0. The spectrum of ρ still has a well pronounced gap of $\Delta\lambda \approx 0.4 \ll 2$. When the correlations become strong ($W = 1$) the eigenvalues of ρ span the whole interval $[0, 2]$ of possible eigenvalues and the gap disappears. This demonstrates the capability of the discrete superposition of only two Slater determinants to interpolate between the weakly and the strongly correlated case at least on the level of the single-electron density matrix.

Fig. 1 shows contour plots of the averaged 1-particle density matrix $\sqrt{\rho_s^2 + \rho_{p_x}^2 + \rho_{p_y}^2 + \rho_{p_z}^2}/2$, where ρ_s , ρ_{p_x} , ρ_{p_y} , and ρ_{p_z} are the 1-particle density matrices for the four INDO/S-atomic orbitals. The labels on the x and y axis of each contour plot corresponds to the atomic labels of the carbon atoms (cf. labeling of molecule at bottom of Fig. 1). The (1,1) element of the density matrix is given in the lower left corner. The bottom right panel shows the HF-ground state. The three top rows depict the deviation from the ground-state density matrix $\delta\rho$ for $W = 0.01$ (first row), 0.1 (second row), and 1 (third row). Each panel has a different color code. The first column of the three top rows shows one specific realization of the wavepacket parameters. The fine structure of $\delta\rho$ may vary for each realization of parameters. However, the scale of $\delta\rho$ reflects increasing deviation from the HF density matrix by increasing W . The maximum value of $\delta\rho$ for $W = 0.01$, 0.1, and 1 is 0.01, 0.11, and 0.9, respectively.

We have also considered an ensemble average over 500 states, each being a superposition of 2 Thouless states, characterized by a set of Thouless parameters which are randomly picked from an interval of a certain width (just as in the left column of

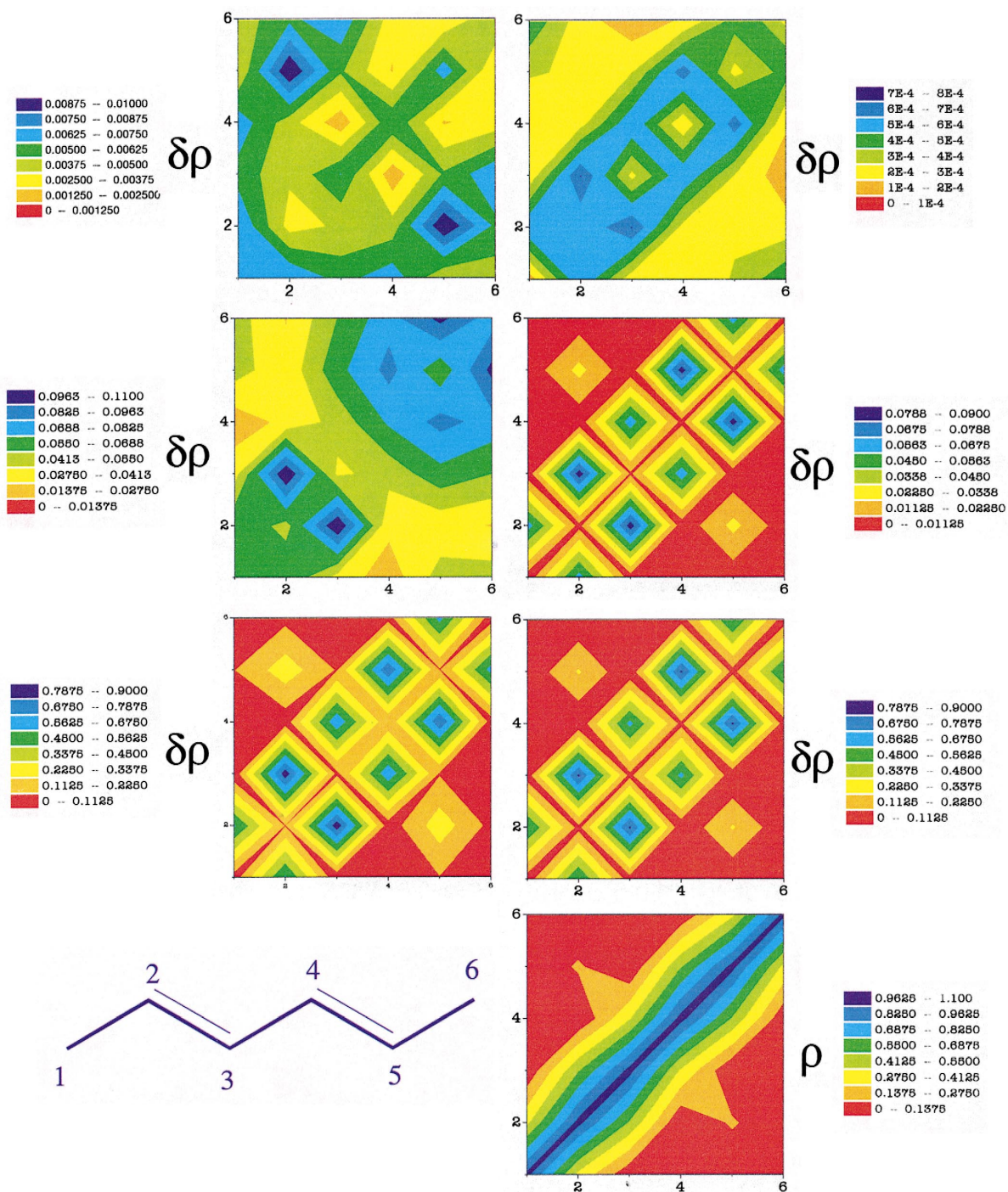


Fig. 1. Deviation from the HF ground-state density matrix for $W=0.01$ (first row), 0.1 (middle row) and 1 (third row), for one specific realization of the wavepacket parameters (left column, top three rows) and an ensemble-average over 500 different wavepackets (right column, top three rows). The molecular structure and the HF density matrix are shown in the bottom row.

Table 1
Eigenvalues of the single electron density matrix ρ for the wavepacket ansatz and two different parameters

$W = 0.1$	$W = 1$
2.00e+00	2.00e+00
2.00e+00	1.99e+00
2.00e+00	1.99e+00
1.99e+00	1.98e+00
1.99e+00	1.97e+00
1.98e+00	1.93e+00
1.97e+00	1.89e+00
1.96e+00	1.88e+00
1.95e+00	1.84e+00
1.94e+00	1.83e+00
1.93e+00	1.78e+00
1.91e+00	1.66e+00
1.91e+00	1.65e+00
1.89e+00	1.44e+00
1.85e+00	1.32e+00
1.80e+00	1.20e+00
1.80e+00	1.08e+00
2.03e-01	9.18-01
1.46e-01	8.03-01
1.14e-01	6.85-01
1.09e-01	5.60-01
9.14e-02	3.52-01
8.26e-02	3.39-01
6.73e-02	2.23-01
5.69e-02	1.74-01
4.79e-02	1.57-01
3.56e-02	1.19-01
2.67e-02	1.10-01
1.76e-02	7.48-02
1.48e-02	3.07-02
9.50e-03	1.98-02
4.22e-03	1.30-02
1.15e-03	5.94-03
1.37e-04	4.55-04

Fig. 1). The resulting ensemble-averaged density matrices are shown in the right column and the three top rows of Fig. 1. $\delta\rho$ now actually reflects the molecular symmetry. We further observe, as in the left column, that the maximum range of $\delta\rho$ increases from 0.0008 through 0.09 to 0.9 as we vary W from 0.01, 0.1, and 1, respectively.

5. Discussion

Our numerical study of Section 4 clearly shows an increasing deviation of the 1-particle density ma-

trix from the uncorrelated HF density matrix as the range of the wavepacket parameters was increased. This indicates the potential usefulness of our proposed wavepacket ansatz. A rigorous development of a DMFT requires the inversion of Eq. (3h) together with (Eq. (3g)). If we could represent an arbitrary density matrix ρ by a set of parameters $z^{(m)}$ then the parameters would be a functional of the density matrix. By calculating the energy in terms of the parameters (according to Eqs. (2l) and (3k) we should obtain the energy as a functional of the density matrix. It remains an open question at this point whether this inversion is in general possible for the ansatz. Inverting Eqs. (3h) and (3g) amounts to solving a system of non-linear equations. The discrete superposition wavepacket yields a highly non-linear expression for the density matrix in terms of the Thouless parameters.

We finally note that our wavepacket ansatz can also be used for computing the time-dependent problem of electron dynamics of correlated systems, by invoking the time-dependent variational principle to derive equations of motion for the wavefunction.

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References

- [1] R. Erdahl, V.H. Smith Jr. (Eds.), Density Matrices and Density Functionals, Riedel, Dordrecht, 1987.
- [2] R.M. Dreizler, E.K.U. Gross, Density Functional Theory, Springer, Berlin, 1990.
- [3] W. Kohn, L.J. Sham, Phys. Rev. 140 A (1965) 1133.
- [4] E. Runge, E.K.U. Gross, Phys. Rev. Lett. 52 (1984) 997.
- [5] E.K.U. Gross, W. Kohn, Adv. Quantum Chem. 21 (1990) 255.
- [6] C.A. Ullrich, U.J. Grossmann, E.K.U. Gross, Phys. Rev. Lett. 74 (1995) 872.
- [7] M.E. Cassida, in: J.M. Seminario (Ed.), Recent Developments and Applications of Modern Density Functional Theory, Elsevier, Amsterdam, 1996, p. 391.
- [8] G. Vignale, W. Kohn, Phys. Rev. Lett. 77 (1996) 2037.
- [9] S. Mukamel, S. Tretiak, Th. Wagersreiter, V. Chernyak, Science 277 (1997) 781.

- [10] T.L. Gilbert, Phys. Rev. B 12 (1975) 2111.
- [11] M. Berrondo, O. Gosciniski, Int. J. Quantum Chem. Symp. 9 (1975) 67.
- [12] R.A. Donnelly, R.G. Parr, J. Chem. Phys. 69 (1978) 4431.
- [13] R.A. Donnelly, J. Chem. Phys. 71 (1979) 2874.
- [14] B. Laskowski, J. Diamond, A. Waleh, B. Hudson, J. Chem. Phys. 69 (1978) 5222.
- [15] J.K. Percus, Int. J. Quantum Chem. 13 (1978) 89.
- [16] M. Levy, Proc. Natl. Acad. Sci. USA 76 (1979) 6062.
- [17] M. Levy, Phys. Rev. A 26 (1982) 1200.
- [18] J.E. Osburn, M. Levy, Phys. Rev. A 33 (1986) 2230.
- [19] E.H. Lieb, Int. J. Quantum Chem. 24 (1983) 243.
- [20] S.M. Valone, J. Chem. Phys. 73 (1980) 1344.
- [21] S.M. Valone, J. Chem. Phys. 73 (1980) 4653.
- [22] G.A. Henderson, Phys. Rev. A 23 (1981) 19.
- [23] G. Zumbach, K. Maschke, Phys. Rev. A 28 (1983) 544.
- [24] G. Zumbach, K. Maschke, J. Chem. Phys. 82 (1985) 5604.
- [25] E.V. Ludeña, A. Sierraalta, Phys. Rev. A 32 (1985) 19.
- [26] A.K. Theophilou, N.H. March, Phys. Rev. A 34 (1986) 3630.
- [27] K. Yasuda, H. Nakatsuji, Phys. Rev. A 56 (1997) 2648.
- [28] H. Nakatsuji, Phys. Rev. A 14 (1976) 41.
- [29] A. Klein, R.M. Dreizler, Phys. Rev. A 57 (1998) 2485.
- [30] V. Chernyak, S. Mukamel, Phys. Rev. A 52 (1995) 3601.
- [31] J.C. Ramirez, J.M.H. Pérez, R.P. Sagar, R.O. Esquivel, M. Hô, V.H. Smith Jr., Phys. Rev. A 58 (1998) 1050.
- [32] J. Cioslowski, R. Lopez-Boada, J. Chem. Phys. 109 (1998) 4156.
- [33] J.-P. Blaizot, G. Ripka, Quantum Theory of Finite Systems, MIT Press, Cambridge, MA, 1986.
- [34] E. Deumens, A.D. Diz, R. Longo, Y. Öhrn, Rev. Mod. Phys. 66 (1994) 917.
- [35] A.A. Abrikosov, L.P. Gorkov, I.Ye. Dzyaloshinsky, Quantum Field Theoretical Methods in Statistical Physics, Oxford University Press, New York, 1965.
- [36] B. Laskowski, J. Diamond, A. Waleh, B. Hudson, J. Chem. Phys. 69 (1978) 5222.