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Minimization procedure in reduced density matrix functional theory by means of an effective noninteracting system

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ABSTRACT

In this work, we propose a self-consistent minimization procedure for functionals in reduced density matrix functional theory. We introduce an effective noninteracting system at finite temperature which is capable of reproducing the groundstate one-reduced density matrix of an interacting system at zero temperature. By introducing the concept of a temperature tensor the minimization with respect to the occupation numbers is shown to be greatly improved.

1. Introduction

Since 1964, after the pioneering work of Hohenberg and Kohn [1], density functional theory (DFT) became the standard tool for the calculation of groundstate (gs) properties of quantum-mechanical systems. There are, however, some physical problems which are difficult to address in the framework of DFT. These include the description of strongly correlated systems, such as the dissociation of closed shell molecules into open shell fragments, and the fundamental gap in Mott insulators. Recently, a promising alternative to DFT was introduced which showed success in various fields, ranging from small molecules [2–9] to infinite solids [10–12], including the difficult cases mentioned above. This method features the one-reduced density matrix (1RDM) as central variable and is called reduced density matrix functional theory (RDMFT). In the theoretical framework of RDMFT, the functional form of the kinetic as well as of the exchange energy are known exactly in terms of the 1RDM and only the correlation part of the two-particle interaction energy has to be approximated. However, a minimization of functionals in RDMFT is complicated by the fact that at zero temperature there is no noninteracting system reproducing the 1RDM of the interacting system. This is in contrast to DFT where the Kohn–Sham system [13] allows for an efficient self-consistent minimization. Therefore, in RDMFT one usually resorts to direct minimization routines.

In the present work, we show that one can indeed construct a noninteracting system which reproduces a given 1RDM to arbitrary accuracy, if one considers this system to be in grand canoncial equilibrium at finite temperature. We therefore effectively model a zero-temperature interacting system by a finite-temperature noninteracting one. This allows one to construct a self-consistent Kohn–Sham minimization scheme for functionals in RDMFT.

Capitalizing on the freedom of choice for the temperature of the Kohn–Sham system, we will furthermore introduce the concept of a temperature tensor. This concept will later on be shown to greatly improve the performance of our minimization procedure.

We will then argue, why the energy value in a numerical minimization of a RDMFT functional is not a good measure of convergence. As alternatives we introduce two convergence measures which rely solely on the functional derivative of the RDMFT functional w.r.t. the 1RDM.

Finally, we will investigate the performance of the new minimization scheme by applying a common RDMFT functional to LiH. It will be shown that the self-consistent scheme is very efficient and avoids conceptual difficulties prevalent in many other minimization procedures.

2. Theoretical foundations

In this work, we will consider systems governed by a Hamiltonian $\hat{H}$ consisting of the kinetic energy $\hat{T}$, the external one-particle potential V, and the two-particle interaction $\widehat{W}$:

$$\hat{H} = \hat{T} + \hat{V} + \widehat{W}. \tag{1}$$

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A quantum-mechanical system is generally described by a statistical density operator (SDO) $\widehat{D}$ being a weighted sum of projection operators on the Hilbert space under consideration

$$\widehat{D} = \sum_i w_i |\Psi_i\rangle\langle\Psi_i|, \quad w_i \geqslant 0, \quad \sum_i w_i = 1. \tag{2}$$

The 1RDM $\gamma(x, x')$, corresponding to a particular SDO $\widehat{D}$, is defined as

$$\gamma(x,x') = \mathrm{tr}\{\widehat{D}\hat{\psi}^+(x')\hat{\psi}(x)\}, \tag{3}$$

where $\{\widehat{\psi}(x)\}$ are the common field operators and the variable x denotes a combination of spacial coordinate $\mathbf{r}$ and spin index σ ($x = (\mathbf{r}, \sigma)$). An integration over x is therefore to be interpreted as an integration over $\mathbf{r}$ and a summation over σ. By construction, $\gamma(x, x')$ is hermitean and can therefore be written in spectral representation

$$\gamma(x,x') = \sum_i n_i \phi_i^*(x')\phi_i(x). \tag{4}$$

The $\{\phi_i(x)\}$ are traditionally called the natural orbitals (NOs) and the $\{n_i\}$ are the occupation numbers (ONs) [14]. The conditions that ensure that a given $\gamma(x, x')$ is ensemble-N-representable, i.e. that it comes from a SDO of the form of Eq. (2), are the following [15]:

$$0 \leqslant n_i \leqslant 1, \tag{5}$$

$$\sum_i n_i = N, \tag{6}$$

$$\{\phi_i\} \text{ is a complete orthonormal set.} \tag{7}$$

The set of all ensemble-N-representable 1RDMs is given by

$$\Gamma^N = \{\gamma(x,x') | \gamma(x,x') \text{ fulfills Eqs.}(5), (6), \text{ and } (7)\}, \tag{8}$$

which is closed and convex.

Following from the theorems of Hohenberg and Kohn [1], we know that one can formulate a functional theory of the 1RDM for the determination of the gs energy. It was Gilbert [16] who showed that this theoretical framework is also capable of describing systems subject to nonlocal external potentials, a task not possible via DFT. We have furthermore shown in [17] that this methodology can be extended to the case of quantum-mechanical systems in grand canonical equilibrium.

The functional for the energy $E[\gamma]$ of the interacting and for the grand potential $\Omega_0[\gamma]$ of a noninteracting system in grand canonical equilibrium are given as

$$E[\gamma] = T[\gamma] + V_{ext}[\gamma] + W[\gamma], \tag{9}$$

$$\Omega_0[\gamma] = T[\gamma] + V_{ext}[\gamma] - \mu N[\gamma] - 1/\beta S_0[\gamma], \tag{10}$$

where

$$T[\gamma] = \int dx' \lim_{x \to x'} \left(-\frac{\nabla^2}{2}\right) \gamma(x', x) \tag{11}$$

$$V_{ext}[\gamma] = \int dx dx' \, v_{ext}(x,x')\gamma(x',x) \tag{12}$$

$$N[\gamma] = \int dx \gamma(x,x) \tag{13}$$

$$S_0[\gamma] = -\sum_i (n_i \ln n_i + (1-n_i)\ln(1-n_i)). \tag{14}$$

The functional $W[\gamma]$ for the interaction contribution is not known exactly and has to be approximated in practice. The noninteracting grand potential can be written solely in terms of the one-particle eigenenergies and the ONs as

$$\Omega_0[\gamma] = \sum_i \left(n_i(\varepsilon_i - \mu) + \frac{1}{\beta}(n_i \ln n_i + (1-n_i)\ln(1-n_i)) \right). \tag{15}$$

In the context of this work, the question of noninteracting (ni)-V-representability, i.e. the question which 1RDMs correspond to a groundstate or equilibrium of a noninteracting system, will become important. The sets of all zero-temperature ni-V-representable and finite-temperature ni-V-representable 1RDMs will be denoted by Γ_0^V and Γ_T^V, respectively. In the case of zero temperature a nondegenerate system assumes a pure groundstate and the corresponding noninteracting 1RDM will be idempotent. Therefore, Γ_0^V is on the boundary of Γ^N. We have shown in [17] that the gs-1RDM of a Coulomb system is in the interior of Γ^N and, therefore, we cannot use a noninteracting system at zero temperature to find the minimum of an RDMFT functional. In simple terms: the 1RDM of interacting particles is never idempotent and, hence, it cannot be represented as the 1RDM of a Kohn–Sham-type noninteracting system at zero temperature. At finite temperature, however, for a noninteracting system with one-particle eigenvalues $\{\varepsilon_i\}$, the ONs are given by the Fermi–Dirac distribution [18] which can easily be inverted:

$$n_i = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1}, \tag{16}$$

$$\varepsilon_i - \mu = \frac{1}{\beta} \ln\left(\frac{1-n_i}{n_i}\right). \tag{17}$$

This implies that all 1RDMs in the interior of Γ^N are in Γ_T^V. Therefore, for every 1RDM in Γ^N there is a 1RDM from Γ_T^V arbitrarily close to it which allows the utilization of a noninteracting system in grand canonical equilibrium in a self-consistent minimization scheme. We emphasize the term "arbitrarily close" because pinned ONs (i.e. 0 or 1) cannot be reproduced by a system at finite temperature (see Eq. (17)), but every ON arbitrarily close to 0 or 1 can. The error introduced by these pinned states therefore becomes arbitrarily small.

3. Self-consistent minimization

The biggest stumbling stone in the numerical minimization of RDMFT functionals is the incorporation of the auxiliary constraints on the ONs and NOs of the 1RDM. These are particle number conservation $\sum n_i = N$, the fermionic constraint $0 \leqslant n_i \leqslant 1$, and most importantly, the orthonormality constraints of the NOs. Usually, the orthonormality of the NOs will be enforced by applying an orthonomalization algorithm to the NOs after they have been modified, using the information provided by the functional derivatives $\delta E[\gamma]/\delta\phi_i$. These orthonormalization procedures can change several orbitals quite significantly which can lead to a slow convergence of the minimization routines.

The main idea of a self-consistent minimization scheme is now to approximate the energy surface $E[\gamma]$ by a simpler one whose minimum, incorporating all auxiliary constraints, can be found easily. In our situation, we take the information about the derivatives of $E[\gamma]$ at γ and construct an effective noninteracting system in grand canonical equilibrium whose grand potential functional $\Omega_0[\gamma]$ has the same functional derivative in γ. The minimum of this energy surface is found by a diagonalization of the effective Hamiltonian and an occupation of the new ONs according to the Fermi–Dirac distribution. The resulting eq-1RDM will then serve as the starting point for the subsequent iteration. This method automatically incorporates the constraints on the ONs and NOs and we will not have to apply subsequent orthonormalizations and the like. The success of this scheme, of course, relies on the similarity of the energy surfaces of $E[\gamma]$ and $\Omega_0[\gamma]$.

We will now proceed to derive the variational equations, guiding the determination of γ.

3.1. Effective Hamiltonian

The effective noninteracting system is constructed such that the derivatives of the interacting as well as of the noninteracting