



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.

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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.

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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 canonical 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 \hat{W} :

$$\hat{H} = \hat{T} + \hat{V} + \hat{W}. \quad (1)$$

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

$$\hat{D} = \sum_i w_i |\Psi_i\rangle\langle\Psi_i|, \quad w_i \geq 0, \quad \sum_i w_i = 1. \quad (2)$$

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

$$\gamma(x, x') = \text{tr}\{\hat{D}\hat{\psi}^+(x')\hat{\psi}(x)\}, \quad (3)$$

where $\{\hat{\psi}(x)\}$ 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

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

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]:

$$0 \leq n_i \leq 1, \quad (5)$$

$$\sum_i n_i = N, \quad (6)$$

$$\{\phi_i\} \text{ is a complete orthonormal set.} \quad (7)$$

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

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

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

$$E[\gamma] = T[\gamma] + V_{\text{ext}}[\gamma] + W[\gamma], \quad (9)$$

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

where

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

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

$$N[\gamma] = \int dx \gamma(x, x) \quad (13)$$

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

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

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

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:

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

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

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 $0 \leq n_i \leq 1$, and most importantly, the orthonormality constraints of the NOs. Usually, the orthonormality of the NOs will be enforced by applying an orthonormalization 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

functional (Eqs. (9) and (10)) coincide (remember that the external potentials of the interacting and effective noninteracting Hamiltonians differ).

$$\frac{\delta\Omega_0[\gamma]}{\delta\gamma(x, x')} = \frac{\delta E[\gamma]}{\delta\gamma(x, x')}. \quad (18)$$

Because of the possibility of pinned states, this equation does not have to be fulfilled exactly. Therefore, as mentioned before, our minimization routine may not reach the exact minimum but will approach it arbitrarily closely. The effective Hamiltonian in spatial representation then becomes

$$h^{\text{eff}}[\gamma](x, x') = t[\gamma](x, x') + v_{\text{ext}}(x, x') + \mu\delta(x - x') + 1/\beta\sigma[\gamma](x, x') + v_w[\gamma](x, x'). \quad (19)$$

The functional derivatives are given by

$$v_w[\gamma](x, x') = \frac{\delta W[\gamma]}{\delta\gamma(x, x')}, \quad (20)$$

$$\sigma[\gamma](x, x') = \frac{\delta S_0[\gamma]}{\delta\gamma(x, x')}. \quad (21)$$

We want to use the chain rule for the functional derivative. We therefore need the derivatives of the ONs and NOs with respect to γ . They can be obtained using first-order perturbation theory, yielding

$$\frac{\delta n_k}{\delta\gamma(x', x)} = \phi_k^*(x')\phi_k(x), \quad (22)$$

$$\frac{\delta\phi_k(y)}{\delta\gamma(x', x)} = \sum_{l \neq k} \frac{\phi_l^*(x')\phi_l(x)}{n_k - n_l} \phi_l(y), \quad (23)$$

$$\frac{\delta\phi_k^*(y)}{\delta\gamma(x', x)} = \sum_{l \neq k} \frac{\phi_k^*(x')\phi_l(x)}{n_k - n_l} \phi_l^*(y). \quad (24)$$

In the following, it will be useful to work in the basis of NOs. An arbitrary function $g(x, x')$ is then represented by g_{ij} , where

$$g_{ij} = \int dx dx' \phi_i^*(x)g(x, x')\phi_j(x'). \quad (25)$$

The matrix elements h_{ij}^{eff} of the effective Hamiltonian then become

$$h_{ij}^{\text{eff}} = \delta_{ij} \left(\frac{\partial E[\gamma]}{\partial n_i} + \mu + \frac{\sigma_i}{\beta} \right) + \frac{1 - \delta_{ij}}{n_i - n_j} \times \int dy \left(\frac{\delta E[\gamma]}{\delta\phi_i(y)} \phi_j(y) - \frac{\delta E[\gamma]}{\delta\phi_j^*(y)} \phi_i^*(y) \right), \quad (26)$$

where the entropic contribution σ_i is given by

$$\sigma_i = \frac{\partial S_0[\gamma]}{\partial n_i} = \ln \left(\frac{1 - n_i}{n_i} \right). \quad (27)$$

The offdiagonal elements are exactly the ones Pernal [19] derived in her approach for the derivation of an effective potential for RDMFT. They are also simply related to the ones Piris and Ugalde [20] introduced in their method for an orbital minimization. It has to be noted, however, that in our approach the diagonal elements are not free to choose but are determined by the thermodynamic ensemble. The temperature of the Kohn–Sham system has no physical meaning and can be varied to influence the convergence behavior of the minimization routine. If β was small, i.e. if the corresponding effective temperature was high, due to the entropic term σ_i/β the diagonal part of \hat{H}^{eff} will be bigger compared to the offdiagonal parts. Therefore, after a diagonalization of \hat{H}^{eff} , the orbitals will change less. Accordingly, in the limit of $\beta \rightarrow 0$, the offdiagonal elements of \hat{H}^{eff} can be neglected and the diagonal

elements will be given by the entropic contribution σ_i/β , i.e. $h_{ij}^{\text{eff}} = \delta_{ij}\varepsilon_i = \delta_{ij}\sigma_i/\beta$. If one would now, starting from a set of ONs $\{n_i\}$, construct a new set of ONs $\{n'_i\}$ from this effective Hamiltonian via Eqs. (16) and (17) then one finds that the ONs are left invariant, i.e. $n'_i = n_i$. We will further investigate the behavior of our self-consistent minimization scheme for small β later on in this work.

In the following, we will show how the concept of a temperature tensor greatly enhances the adaptability of the Kohn–Sham system which will improve the performance of the minimization procedure.

3.2. Temperature tensor

To understand how the concept of a temperature tensor improves the performance of the minimization scheme, the following considerations will be helpful. In a self-consistent minimization scheme, for a given 1RDM, we construct a known (noninteracting) functional whose first derivative coincides with the one from the interacting functional. For a fixed β , the parameter μ is determined by the requirement of particle number conservation. β can then be varied to modify how narrow the noninteracting energy surface should be. However, second derivatives with respect to the ONs may differ quite substantially and a value of β which describes the energy surface along one ON well might describe others quite badly. A simple example is the following quadratic two-state model functional $E[n_1, n_2]$ without orbital dependence.

$$E[n_1, n_2] = \frac{\alpha_1}{2}(n_1 - 0.5)^2 + \frac{\alpha_2}{2}(n_2 - 0.5)^2, \quad (28)$$

$$= E_1[n_1] + E_2[n_2]. \quad (29)$$

The choice of $\alpha_1 = 50$ and $\alpha_2 = 1$ leads to $h_{11}^{\text{eff}} = \varepsilon_1 = -0.225 + \mu$ and $h_{22}^{\text{eff}} = \varepsilon_2 = 0.00450 + \mu$ in Eq. (26). The corresponding projected grand potential surfaces from Eq. (15) are plotted in Fig. 1 for $\beta = 0.11$. As one can see, the choice of $\beta = 0.11$ models the first energy surface quite well, but the second one fails to be reproduced. One would like to have some sort of state-dependent β_i which can be related to the second derivatives. However, before one can use such a construct, one has to confirm that it corresponds to an energy-surface whose minimum can easily be found.

We are now going to show that this is possible by a slight variation of the definition of grand canonical ensembles. We consider the following generalized SDO-grand potential functional

$$\mathfrak{G}[\hat{D}] = \text{tr}\{\hat{D}(\hat{B}(\hat{H} - \mu\hat{N}) + \ln \hat{D})\}, \quad (30)$$

where \hat{B} is an arbitrary hermitean operator on the Fock-space. The same proof as in [21] now leads to the following variational principle

$$\mathfrak{G}[\hat{D}] \geq \mathfrak{G}[\hat{D}_{\text{eq}}], \quad (31)$$

where the equality is only fulfilled if $\hat{D} = \hat{D}_{\text{eq}}$, with

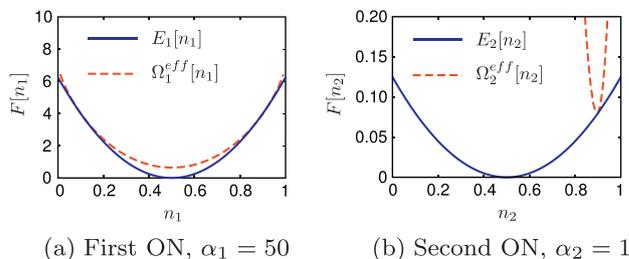


Fig. 1. Projected energy surfaces for the model of Eq. (28) with $\alpha_1 = 50$, $\alpha_2 = 1$, $\beta = 0.11$.

$$\widehat{D}_{eq} = e^{-\widehat{B}(\widehat{H}-\mu\widehat{N})}/Z_{eq}, \quad (32)$$

$$Z_{eq} = \text{tr}\{e^{-\widehat{B}(\widehat{H}-\mu\widehat{N})}\}. \quad (33)$$

For a noninteracting Hamiltonian and a \widehat{B} for which $[\widehat{B}, \widehat{H}] = 0$ the Fermi Dirac relation reads

$$n_i = \frac{1}{e^{\beta_i(\varepsilon_i - \mu)} + 1}, \quad (34)$$

$$\varepsilon_i - \mu = \frac{1}{\beta_i} \ln\left(\frac{1 - n_i}{n_i}\right), \quad (35)$$

where β_i denotes the i th eigenvalue of \widehat{B} . This leads to the following expression for the grand potential

$$\Omega_0[\gamma] = \sum_i (n_i(\varepsilon_i - \mu) + \frac{1}{\beta_i} (n_i \ln n_i + (1 - n_i) \ln(1 - n_i))), \quad (36)$$

$$= \sum_i \Omega_{0i}[n_i, \beta_i], \quad (37)$$

where in the case of a scalar temperature we just had one parameter to construct our effective noninteracting system, we now have one for each ON. A straightforward utilization of this freedom would be to let the second derivatives of the energy functional with respect to the ONs of the interacting functional and the noninteracting one be proportional to each other.

$$\beta_i = \eta \frac{\partial^2 S_0[\gamma]}{\partial n_i^2} \bigg/ \frac{\partial^2 E[\gamma]}{\partial n_i^2}, \quad (38)$$

$$= \eta \frac{1}{n_i(1 - n_i)} \left(\frac{\partial^2 E[\gamma]}{\partial n_i^2} \right)^{-1}, \quad (39)$$

where η , the proportionality factor, is the only global parameter. In our model (Eq. (28)), this yields

$$\beta_i = \frac{\eta}{\alpha_i n_i(1 - n_i)}. \quad (40)$$

$\eta = 1$ lets the second derivatives of interacting and noninteracting functional be equal whereas an increase (decrease) of η leads to a spreading (compression) of the noninteracting energy surface. As can be seen from Fig. 2, with a good choice of η (in our model $\eta = 0.5$) one can reproduce the different energy surfaces simultaneously.

We can now construct a self-consistent scheme for the minimization of $E[\gamma]$ which we sketch in Fig. 3. Every iteration of this scheme requires a change in NOs and therefore an update of the derivatives w.r.t. the NOs. This might prove to be expensive and one might be interested in a procedure which only minimizes the ONs and leaves the NOs invariant. Fortunately, the minimization scheme can easily be modified to accomplish this task. The effective Hamiltonian H^{eff} is simply assumed to be diagonal, i.e. one only populates the diagonal elements following Eq. (26). The

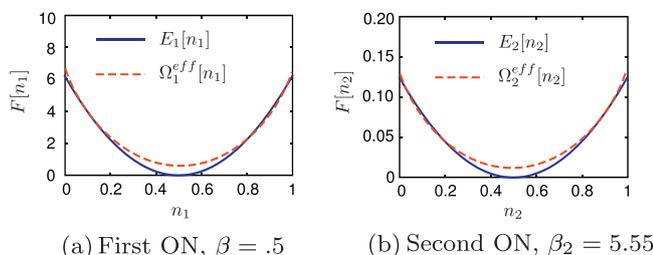


Fig. 2. Projected energy surfaces for the model of Eq. (28) with $\alpha_1 = 50$, $\alpha_2 = 1$. The choice of $\eta = 0.5$ leads to $\beta_1 = 0.11$ and $\beta_2 = 5.55$.

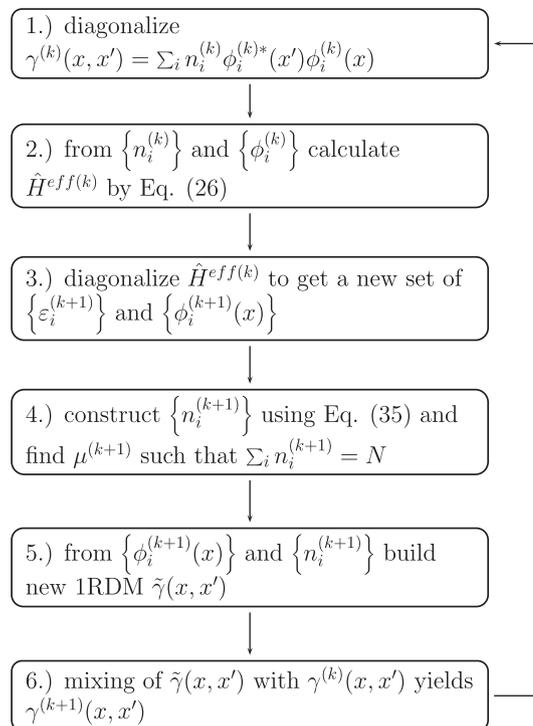


Fig. 3. Self-consistent minimization scheme in RDMFT.

eigenvalues, i.e. the diagonal elements, of H^{eff} , will then yield a new set of ONs via Eq. (16). Assigning the new ONs to the frozen orbitals is straightforward because a given ON n_i leads to a specific $\varepsilon'_i = h_{ii}^{eff}$ which in turn leads to an unambiguously defined n'_i .

The last step in the minimization scheme, the mixing of 1RDMs, is straightforward, because Γ^N is a convex set.

3.3. Small step investigation

We showed in the previous considerations that one can employ the finite temperature Kohn–Sham system in RDMFT to construct a self-consistent minimization scheme. However, this does not ensure that an application of this scheme will actually lead to a minimum of the functional. This is a common problem of minimization schemes, but in the following we are going to show that for small steplengths our method will definitely lead to a decrease of the value of the functional under consideration. As we argued before, choosing a smaller β will lead to smaller changes in ONs and NOs. Starting from a given 1RDM γ , we therefore apply first-order perturbation theory to get the modified 1RDM γ' . By the virtue of Eq. (26), γ leads to the effective Hamiltonian \widehat{H}^{eff} . A diagonalization under the assumptions of first-order perturbation theory then yields the following new eigenvalues ε'_i and eigenstates ϕ'_i .

$$\varepsilon'_i = h_{ii}^{eff}, \quad (41)$$

$$\phi'_i(x) = \phi_i(x) + \sum_{j \neq i} \frac{h_{ji}^{eff}}{\varepsilon_i - \varepsilon_j} \phi_j(x). \quad (42)$$

The new ONs, resulting from our modified eigenenergies, become

$$n'_i = \frac{1}{1 + e^{\beta_i(\varepsilon'_i - \mu - \Delta_\mu)}}, \quad (43)$$

where one had to introduce the chemical potential correction Δ_μ to ensure particle number conservation. With Eqs. (26) and (27) one gets

$$n'_i = \frac{n_i}{n_i + (1 - n_i)e^{\beta_i \left(\frac{\partial E[\gamma]}{\partial n_i} - A_\mu \right)}}. \quad (44)$$

Expanding Eq. (44) in orders of β_i and retaining the leading contribution, we get

$$\delta n_i = n'_i - n_i, \quad (45)$$

$$= \beta_i n_i (n_i - 1) \left(\frac{\partial E[\gamma]}{\partial n_i} - A_\mu^{(0)} \right). \quad (46)$$

This result is very similar to the steepest-descent method with an additional factor of $n_i(n_i - 1)$. This additional term tries to keep the ONs in the allowed set $0 < n_i < 1$. $A_\mu^{(0)}$ can now be found by the requirement of particle number conservation,

$$A_\mu^{(0)} = \frac{\sum_i \beta_i n_i (n_i - 1) \frac{\partial E[\gamma]}{\partial n_i}}{\sum_i \beta_i n_i (n_i - 1)}. \quad (47)$$

The overall change in the 1RDM up to first order in β_i is then given by

$$\Delta \gamma_{ij} = \gamma'_{ij} - \delta_{ij} n_i, \quad (48)$$

$$= \delta_{ij} \delta n_i + (1 - \delta_{ij}) \frac{n_i - n_j}{\varepsilon_i - \varepsilon_j} h_{ij}^{\text{eff}}. \quad (49)$$

The energy changes accordingly as

$$\Delta E = \int dx dx' \frac{\delta E[\gamma]}{\delta \gamma(x, x')} \Delta \gamma(x', x), \quad (50)$$

$$= \sum_{ij} \frac{\delta E[\gamma]}{\delta \gamma_{ij}} \Delta \gamma_{ij}, \quad (51)$$

$$= \underbrace{\sum_i \delta n_i \frac{\partial E[\gamma]}{\partial n_i}}_{\Delta E_1} + \underbrace{\sum_{i \neq j} \frac{n_i - n_j}{\varepsilon_i - \varepsilon_j} |h_{ij}^{\text{eff}}|^2}_{\Delta E_2}. \quad (52)$$

We see that the energy change ΔE separates into two parts. One is determined by the change in ONs, and one comes from the change in NOs. In the following we are going to investigate these two different contributions separately.

3.3.1. Occupation number contribution

We will now show that the first term in Eq. (52), which is due to the change in ONs, is negative for appropriately small steplengths.

$$\Delta E_1 = \sum_i \delta n_i \frac{\partial E[\gamma]}{\partial n_i} \quad (53)$$

$$= \sum_i \beta_i n_i (n_i - 1) \left(\frac{\partial E[\gamma]}{\partial n_i} - A_\mu^{(0)} \right) \frac{\partial E[\gamma]}{\partial n_i}, \quad (54)$$

For brevity, we introduce $c_i = \frac{\beta_i n_i (n_i - 1)}{\sum_i \beta_i n_i (n_i - 1)}$. Using Eq. (47) then leads to

$$\begin{aligned} \Delta E_1 &= \left(\sum_j \beta_j n_j (n_j - 1) \right) \sum_i c_i \left(\left(\frac{\partial E[\gamma]}{\partial n_i} \right)^2 - \left(\sum_k c_k \frac{\partial E[\gamma]}{\partial n_k} \right)^2 \right) \\ &= \left(\sum_j \beta_j n_j (n_j - 1) \right), \end{aligned} \quad (55)$$

$$\sum_i c_i \left(\frac{\partial E[\gamma]}{\partial n_i} - \sum_k c_k \frac{\partial E[\gamma]}{\partial n_k} \right)^2. \quad (56)$$

Because every ON n_i fulfills $0 < n_i < 1$ and every β_i is greater 0, this leads to the conclusion

$$\Delta E_1 \leq 0. \quad (57)$$

3.3.2. Natural orbital contribution

We can now turn to the second term in Eq. (52) which represents the energy change due to the change in NOs.

$$\Delta E_2 = \sum_{i \neq j} \frac{n_i - n_j}{\varepsilon_i - \varepsilon_j} |h_{ij}^{\text{eff}}|^2. \quad (58)$$

By using Eq. (35) this transforms to

$$\Delta E_2 = \sum_{i \neq j} \frac{n_i - n_j}{\frac{1}{\beta_i} \ln \left(\frac{1 - n_i}{n_i} \right) - \frac{1}{\beta_j} \ln \left(\frac{1 - n_j}{n_j} \right)} |h_{ij}^{\text{eff}}|^2. \quad (59)$$

We see that for an arbitrary choice of β_i , we cannot ensure the negativity of ΔE_2 . But if we use a constant β , we get

$$\Delta E_2 = \beta \sum_{i \neq j} \frac{n_i - n_j}{\ln \left(\frac{n_i(1 - n_i)}{n_i(1 - n_j)} \right)} |h_{ij}^{\text{eff}}|^2, \quad (60)$$

which is nonpositive for $0 < n_i < 1$:

$$\Delta E_2 \leq 0. \quad (61)$$

We have shown that for small enough β_i , the ON change will always decrease the grand potential, regardless of whether one chooses a constant temperature or a temperature tensor. When considering changes in the NOs, one has to fall back to constant temperature to ensure a decrease of the functional value. We will use these findings in our numerical implementation of the minimization scheme as demonstrated later on in this work.

3.4. Convergence measures

We have now all the necessary tools at hand to iteratively minimize a functional $E[\gamma]$. We need, however, some measures to judge if a calculation is converged. There are two main reasons why using the energy itself as convergence measure is disadvantageous.

Firstly, often the calculation of derivatives is not accurate and consequently a derivative-based minimization may lead to a fix-point where $E[\gamma]$ is not minimal. This leads to a sign change of the convergence measure and implementing the strict decrease of energy as a requirement of the minimization procedure will then lead to a starting point dependent result. To illustrate this problem we consider a simple parabola $E(x) = ax^2$ whose minimum is at $x = 0$. Let us now assume that the calculation of the derivative is only approximate and leads to a constant error δ . The derivatives then do not describe the surface given by $E(x)$ but rather one defined by $\bar{E}(x) = ax^2 + \delta x$ whose minimum will be at $\bar{x} = -d/(2a)$. If one would now approach this minimum coming from the left with a series of positions $\{x_i\}$, then $E(x_i)$ will be monotonously decreasing. At the point of convergence its value will be $E(\bar{x}) = d^2/(4a)$. If, on the other hand, we would have approached the minimum coming from the right, i.e. starting at $x = \infty$, then we would have passed through the minimum of $E(x)$ and the series $E(x_i)$ would exhibit a valley. Incorporating the energy $E(x)$, or rather the change in energy, as convergence measure would therefore prevent the minimization to approach the true minimum of $\bar{E}(x)$ and lead to two different points of convergence, depending on the starting position.

Secondly, because the true minimal energy is not known, one would have to judge convergence from the change in $E[\gamma]$ after iterating the minimization routine, i.e. a small change in $E[\gamma]$ indicates a relative closeness to the real minimum. This might pose a problem if the minimum of the energy-surface, as defined by the derivatives of $E[\gamma]$, is very shallow or, worse, if the minimization procedure leads to a slow approach to the minimum. An example for such a situation is discussed in the summary.

Because of these problems, we would rather use a strictly positive convergence measure which goes to 0 if the 1RDM approaches

the minimum of the energy-surface, as defined by the derivatives of $E[\gamma]$. We will establish our choice of convergence measures on the following two observations.

- In the minimum, the derivatives with respect to the ONs will be equal for unpinned states.
- In the minimum, the effective Hamiltonian \hat{H}^{eff} will be diagonal.

The first observation allows us to define a convergence measure χ_n^2 for a minimization with respect to the ONs:

$$\chi_n^2 = \frac{1}{N_{unpinned}} \sum_i^{N_{unpinned}} \left(\frac{\partial E}{\partial n_i} - \bar{\mu} \right)^2, \quad (62)$$

$$\bar{\mu} = \frac{1}{N_{unpinned}} \sum_i^{N_{unpinned}} \frac{\partial E}{\partial n_i}. \quad (63)$$

The second statement leads to the following definition of χ_ϕ^2 as a convergence measure for a minimization with respect to the NOs:

$$\chi_\phi^2 = \frac{1}{N-1} \frac{\sum_{i \neq j}^N |h_{ij}^{eff}|^2}{\sum_i \epsilon_i^2}. \quad (64)$$

If a minimization is converging, both measures should approach 0.

4. Example

We test the self-consistent procedure for the case of solid LiH at zero temperature by using the FP-LAPW code Elk [22]. The exchange–correlation energy will be modelled by the α functional $E_{xc}^\alpha[\gamma]$, as introduced in [12]. The interaction functional $W[\gamma]$ is then given as a sum of the classical Hartree energy functional $E_H[\gamma]$ and the exchange–correlation functional $E_{xc}^\alpha[\gamma]$.

$$E_{xc}^\alpha[\gamma] = -\frac{1}{2} \sum_{ij} n_i^\alpha n_j^\alpha \int dx dx' w(x, x') \phi_i^*(x') \phi_i(x) \phi_j^*(x) \phi_j(x'). \quad (65)$$

We choose this functional because it exhibits several properties making it difficult to be minimized. It will lead to several fully occupied, i.e. pinned states. Therefore, as argued before, there is no non-interacting system at finite temperature reproducing this 1RDM exactly but there will be one leading to an equilibrium 1RDM arbitrarily close. The minimization of the α functional is therefore a good test for the minimization scheme leading to boundary minima on Γ^N . Furthermore, the α functional exhibits divergencies in the derivatives w.r.t. the ONs for $n_i \rightarrow 0$. If, in the minimum, there are ONs close to 0 (and there will be if one considers enough NOs) this might lead to convergence problems of the minimization.

We will now investigate the performance of the self-consistent minimization scheme w.r.t. ON- and NO-convergence. It turned out in the course of our investigations that a mixing of 1RDMs, accord-

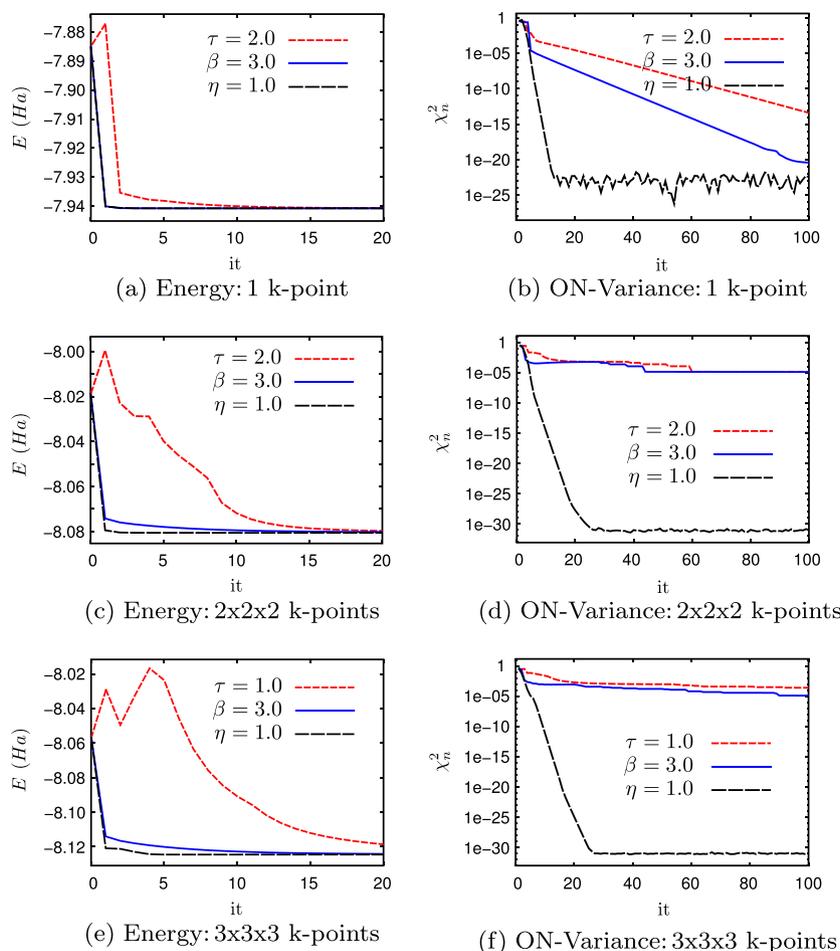


Fig. 4. Energy E and ON-convergence measure χ_n for ON minimizations of the α functional, with $\alpha = 0.565$, applied to LiH. The red, short dashed lines stand for a steepest-descent minimization, the blue, solid ones for a sc-Kohn–Sham minimization with constant β , and the black, long dashed ones for a sc-Kohn–Sham minimization with adaptive β . τ denotes the parameter value for *taurdmn* in Elk, whereas β and η are defined via Eqs. (10) and (38). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

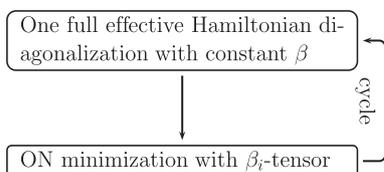


Fig. 5. Full minimization scheme.

ing to point 6 in Fig. 3, does not improve our results and we therefore abstain from it.

4.1. Occupation number minimization

We have minimized the α functional for $\alpha = 0.565$ with three methods. First, we have used the steepest-descent method, as implemented in Elk. As we have pointed out before, by neglecting the offdiagonal elements of H^{eff} , the self-consistent minimization scheme can be used to only minimize w.r.t. the ONs while leaving the NOs invariant. Using this modification, our second method is the self-consistent RDMFT minimization with constant β , and finally we have employed a temperature tensor β_i of the form of Eq. (39) with parameter η . In all three methods, we chose all parameters to achieve fastest convergence. The results, which are shown in

Fig. 4a–f, show that both self-consistent Kohn–Sham minimizations lead to a faster convergence than steepest-descent. A dramatic improvement in the speed of convergence is achieved by employing a temperature tensor. The slow decrease of χ_n^2 in Fig. 4d and f for the steepest-descent and constant- β methods can be attributed to the following fact. For these two methods, the ONs, which will be pinned at the equilibrium, approach their final values quite slowly. Therefore, their derivatives contribute to χ_n^2 via Eq. (62) even after several iterations.

4.2. Full minimization

We can now turn to the problem of minimizing $E[\gamma]$ with respect to both ONs and NOs. We find that the overall performance of this full minimization is greatly improved by introducing a ON-minimization after every NO-minimization step (see Fig. 3). Because we have seen in the previous section that this can be done very efficiently, this increases the runtime of a full minimization run only negligibly. The deeper reason for the improvement of the convergence by inclusion of an ON-minimization is the following: It typically happens that two states ϕ_i and ϕ_j have similar eigenvalues in \hat{H}^{eff} but considerably different ONs. A diagonalization of \hat{H}^{eff} then yields a strong mixing between these states. If the ONs were not updated, one might be led away from the minimum of the grand potential functional. A subsequent ON-minimization remedies this problem and assigns the optimal

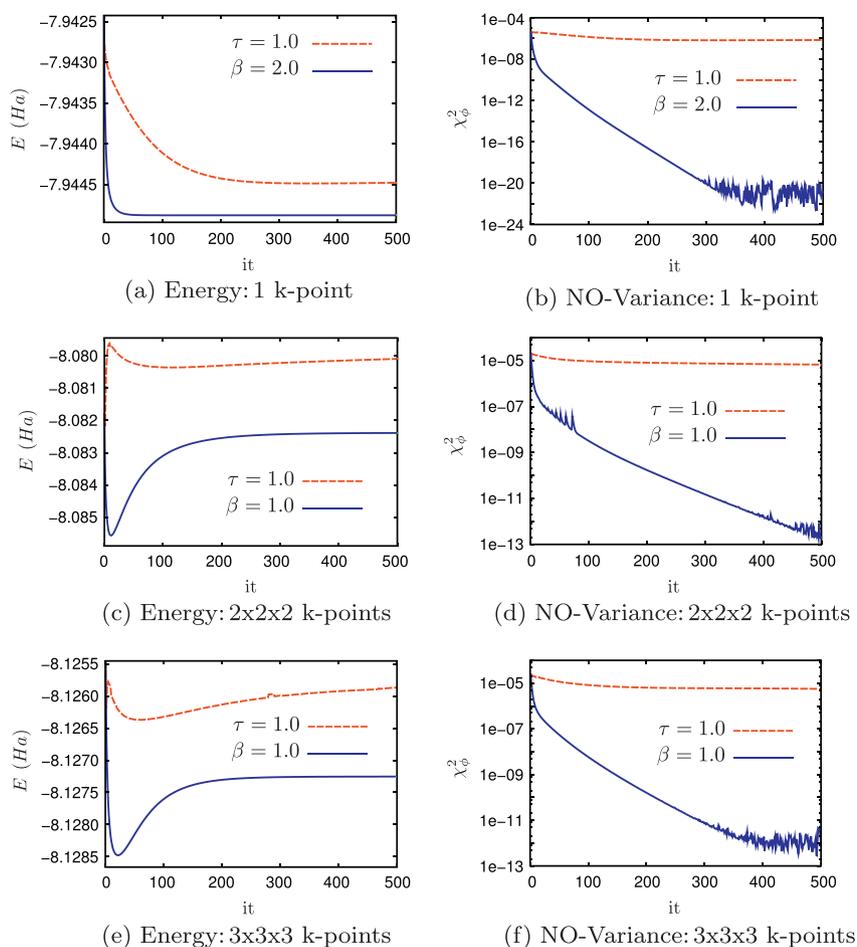


Fig. 6. Energy E and NO-convergence measure χ_ϕ for NO minimizations of the α functional, with $\alpha = 0.565$ applied to LiH. Both variables are plotted against the number of NO changes. After each change in NO there follows a complete ON minimization. The red, dashed lines stand for a steepest-descent minimization whereas the blue, solid ones depict a sc-Kohn–Sham minimization with constant β . τ denotes the parameter value for *taurdmc* in Elk, whereas β is defined via Eq. (10). The increase of energy is due to the fact that the derivatives are calculated only approximately. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ON for each NO. We show a sketch of the full minimization scheme in Fig. 5. An application of this scheme to LiH then leads to the results depicted in Fig. 6. Again, we see a tremendous increase in speed and accuracy for the self-consistent Kohn–Sham minimization scheme compared to the steepest-descent method. The steepest-descent method shows a very slow convergence, which can be attributed to the orthonormalization of NOs. The increase of the energy curves in Fig. 6c and e is due to the approximative nature of the derivatives. As we have pointed out before, the minimization procedure is only guided by the values of the derivatives (see Eq. (26)) and it will not minimize the energy surface defined by $E[\gamma]$ but rather one defined by the approximate derivatives. Coincidentally, the starting point for the minimization of $E[\gamma]$, as shown in Fig. 5, leads to a path to the minimum of the approximate energy surface which leads through a part of the exact surface which has a lower value. Coming from another starting point this would not necessarily have been the case. This starting point dependence always exists if the derivatives are approximate which solidifies the argument that the energy should not be used as convergence measure.

5. Summary and outlook

In the present work, we have introduced a self-consistent Kohn–Sham minimization scheme in the theoretical framework of RDMFT. In order to judge the convergence of a calculation without having to resort to the energy, we have then defined derivative-based convergence measures.

We used the novel minimization method for several functionals and materials, for which the α functional and LiH serve as examples in this work, and it generally proves to be superior in many respects compared to the steepest-descent method. Using a temperature tensor speeds up the ON-minimization considerably and the minimization w.r.t. to the NOs usually shows a more stable behavior. The important parameter in the minimization scheme is the effective temperature β and the speed of convergence crucially depends on it. In Figs. 7 and 8 we show the behavior of the minimization scheme for three different choices of β . $\beta = 1$ represents the optimal value, i.e. the value for which the convergence measure χ_ϕ^2 decreases the fastest. We see that the energy reaches its fixpoint after approximately 300 iterations. An increase of β to $\beta = 2$ seemingly speeds up the energy convergence, but from χ_ϕ^2 one can see that after about 100 iterations the minimization fails to diagonalize H^{eff} any further. The changes in the 1RDM, whose amplitudes are determined by β , become too big and the 1RDM jumps around the fixpoint of the energy. Without considering χ_ϕ^2 , this would have been difficult to detect which illustrates the importance of a convergence measure which is independent of the energy value. One might argue that this choice of β still leads to a fixpoint very close to the optimal one, but this cannot be ensured for all problems and all choices of β and therefore has to

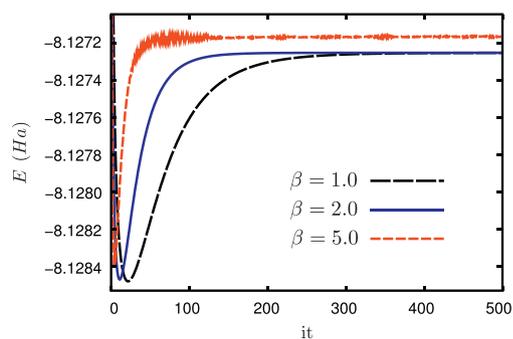


Fig. 7. Energy convergence for different effective temperatures.

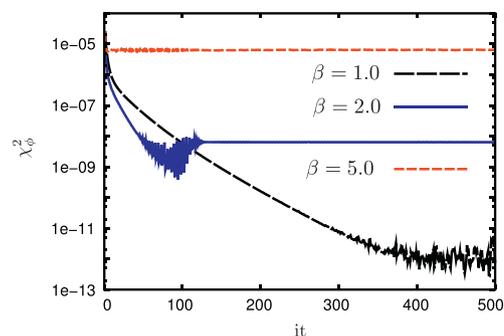


Fig. 8. NO-convergence for different effective temperatures.

be seen in the actual example as rather accidental, i.e. fortunate. A further increase of β to $\beta = 5$ then exposes this problem more dramatically. The energy apparently reaches a fixpoint. But this fixpoint is considerably above the optimal one. Just having the energy at hand, this would have been difficult to detect. But χ_ϕ^2 directly shows that the minimization is far from being converged.

One important feature, which can be extracted from Figs. 7 and 8, is that all three parameters lead to a similar energy vs. iteration curve. Apparently, a minimization-run with β being too big is able to lead to the vicinity of the fixpoint. An utilization of this fact would now be to use an adaptive β rather than a constant one. One could start with a big β till the energy does not change anymore and then decrease β until χ_ϕ^2 surpasses the convergence threshold.

We expect that our successful demonstration of an efficient minimization scheme in RDMFT will support the investigation and development of functionals and therefore encourage further work in this field of research.

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