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Generalization of the Kohn-Sham system enabling representing arbitrary one-electron density matrices

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Density functional theory is currently the most widely applied method in electronic structure theory. The Kohn-Sham method, based on a fictitious system of non-interacting particles, is the workhorse of the theory. The particular form of the Kohn-Sham wave function admits only idempotent one-electron density matrices whereas wave functions of correlated electrons in post-Hartree-Fock methods invariably have fractional occupation numbers. Here we show that by generalizing the orbital concept, and introducing a suitable dot-product as well as a probability density a non-interacting system can be chosen that can represent the one-electron density matrix of any system, even one with fractional occupation numbers. This fictitious system ensures that the exact electron density is accessible within density functional theory. It can also serve as the basis for reduced density matrix functional theory. Moreover, to aid the analysis of the results the orbitals may be assigned energies from a mean-field Hamiltonian. This produces energy levels that are akin to Hartree-Fock orbital energies such that conventional analyses based on Koopmans theorem are available. Finally, this system is convenient in formalisms that depend on creation and annihilation operators as they are trivially applied to single-determinant wave functions.

I. INTRODUCTION

The dominant approach in electronic structure theory is density functional theory (DFT). Its foundations were laid with the Hohenberg-Kohn theorems [1]. The theory was turned into a practical approach by the Kohn-Sham method [2]. A central component of the method is a fictitious system of non-interacting electrons. The wave function that represents this system is supposed to be able to generate the exact electron density. In practice the Kohn-Sham wave function has the same form as the Hartree-Fock wave function. This wave function can only generate idempotent density matrices whereas all post-Hartree-Fock methods, including Full-CI, generate density matrices with fractional occupation numbers. In this paper we show that it is possible to generalize the Kohn-Sham wave function such that it can generate any one-electron density matrix. At the same time this generalized wave function remains representative of a system of non-interacting electrons, i.e. a single-determinant wave function. Incidentally, this wave function can also serve as a basis for reduced density matrix functional theory (RDMFT). This theory is an extension of DFT to density matrices formulated by Gilbert [3]. A particular feature of Gilbert's theory is that at convergence all orbitals with fractional occupation numbers are degenerate. In this work that requirement results in all correlated electrons being degenerate.

An interesting aspect of this wave function is that as it is a single-determinant wave function it is also possible to formulate one-electron properties. For instance it is possible to calculate single-electron energy levels akin to Hartree-Fock energies even if the wave function is a solution of RDMFT. Furthermore, it is trivial to apply annihilation and creation operators to a single-determinant wave function. Hence it is easy to generate excited determinants as well.

In the remainder of the paper Section II defines the generalized wave function. It is shown that the single-determinant wave function is indeed capable of generating an arbitrary one-electron density matrix. Section III explains how the wave function may be optimized. It is shown that the equations are actually in part the same as the Kohn-Sham equations, only another set of very similar equations is needed to describe the correlated electrons. Section IV describes how the wave function can be canonicalized to yield a Hartree-Fock like one-electron picture. Finally, section V shows some simple applications to demonstrate the features of the approach proposed.

II. DEFINING THE WAVE FUNCTION

The approach outlined in this article addresses the fact that for an n_b -dimensional density matrix there does not exist an n_b -dimensional transformation that only changes the occupation numbers. Nevertheless, such a transformation can be effected by mapping the problem into an n_b^2 -dimensional space, applying suitably chosen rotations, and projecting the result back into the original n_b -dimensional space. In this section the definition of an orbital is generalized such that it maps the density matrix from an n_b -dimensional to an n_b^2 -dimensional space. In addition the probability density is chosen to generate the projection from the n_b^2 -dimensional density matrix back to an n_b -dimensional one. An illustrative example of these operations is provided in the Supplementary Material [4]. Also a dot-product for the generalized orbitals is chosen.

It is shown that the generalized orbitals form an orthonormal set of the same dimension as the conventional orbitals. It is also shown that the density matrix of a single generalized orbital matches the appropriate N-presentability conditions [5] whereas it may distribute the electron over any set of conventional orbitals. Finally it is shown that these generalized orbitals may be used to define a single Slater determinant wave function. Combining the orthonormality as well as the density matrix implied in the probability density it is shown that the resulting Slater determinant can generate any one-electron density matrix, even one of a correlated state, i.e. a non-idempotent one.

The arguments in this section are most easily formulated in the form of matrix-vector equations. Note that the arguments given here can be formulated for a single spin-channel (either the α - or β -electron channel) without loss of generality. First we recall that the one-electron density matrix D for a system represented in n_b basis functions is a non-negative Hermitian matrix. Hence it may be diagonalized to produce an orthonormal set of eigenvectors, conventionally called natural orbitals, represented as matrix N , where each natural orbital is a column of N , and eigenvalues $1 \geq d_1 \geq d_2 \geq \dots d_{n_b} \geq 0$. These eigenvalues are referred to as occupation numbers. The natural orbitals may be expressed in an orthogonal basis such as plane waves or in a non-orthogonal basis such as Gaussian type orbitals. To accommodate all options an overlap matrix S is introduced, the elements of which are defined as

$$S_{ab} = \langle \chi_a(r) | \chi_b(r) \rangle \quad (1)$$

$$= \int \chi_a^*(r) \chi_b(r) dr \quad (2)$$

where a , b , and later c label basis functions, and $\chi_a(r)$ represents the basis functions. In the case of an orthogonal basis the overlap matrix is simply the unit matrix. As the natural orbitals N are an orthonormal set the following

condition holds

$$\langle N_i | N_j \rangle = \sum_{a,b=1}^{n_b} N_{ai}^* S_{ab} N_{bj} \quad (3)$$

$$= \delta_{ij} \quad (4)$$

Note that a matrix with one index, such as N_i , refers to a column. In this paper the indices i, j and later k label natural orbitals.

To represent the occupation numbers another set of n_b orthonormal vectors is introduced that are referred to as correlation functions that are columns of matrix C . The name refers to the fact that fractional occupation numbers that may be generated by these functions are directly related to electron correlation as in post Hartree-Fock methods. The correlation functions being expressed in terms of the natural orbitals are always represented in a orthonormal basis. In a system with n_e electrons of a given spin there are n_e occupied correlation functions and all others are unoccupied. The contribution from the r -th correlation function to the i -th occupation number is simply $C_{ir}^* C_{ir}$. For the correlation functions the condition

$$\langle C_r | C_s \rangle = \sum_{i,j=1}^{n_b} C_{ir}^* I_{ij} C_{js} \quad (5)$$

$$= \delta_{rs} \quad (6)$$

holds. Indices r, s and later t label correlation functions.

With the definitions above a set of n_b generalized orbitals G can be defined where every vector G_r can be expanded as

$$|G_s(r)\rangle = \sum_{a,i=1}^{n_b} G_{ai,s} |\chi_a(r)\rangle \quad (7)$$

$$= \sum_{a,i=1}^{n_b} N_{ai} C_{is} |\chi_a(r)\rangle \quad (8)$$

I.e. formally every generalized orbital has n_b^2 coefficients. As every correlation function has a one-to-one correspondence to a generalized orbital the indices r, s and t will be used to label the latter also. To define the dot-product between two vectors from G a metric S^G is constructed as a matrix by replicating the overlap matrix S n_b -times both horizontally and vertically as

$$S^G = \begin{pmatrix} S & S & \dots & S \\ S & S & \dots & S \\ \vdots & \vdots & \ddots & \vdots \\ S & S & \dots & S \end{pmatrix} \quad (9)$$

or equivalently

$$S_{ai,bj}^G = S_{ab} \quad (10)$$

In terms of this metric the dot-product for vectors from G can be written as

$$\langle G_r | G_s \rangle = \sum_{a,i=1}^{n_b} \sum_{b,j=1}^{n_b} G_{ai,r}^* S_{ai,bj}^G G_{bj,s} \quad (11)$$

$$= \sum_{i,j=1}^{n_b} C_{ir}^* C_{js} \left(\sum_{a,b=1}^{n_b} N_{ai}^* S_{ab} N_{bj} \right) \quad (12)$$

$$= \sum_{i,j=1}^{n_b} C_{ir}^* C_{js} \delta_{ij} \quad (13)$$

$$= \delta_{rs} \quad (14)$$

Hence it is clear that the vectors G form an orthonormal set. As the dimension of the basis set is n_b it is also obvious that there can only be n_b linearly independent vectors in this set. Note that if the only concern is to show that the

generalized orbitals constructed from a given set of natural orbitals and correlation functions form an orthonormal set then the metric of Eq. 9 can equally well be replaced by a block diagonal one. The advantage of Eq. 9 is that it also allows calculating the overlap between generalized orbitals generated from different sets of natural orbitals and correlation functions. A block diagonal metric would cause ambiguities in the latter case.

Turning to the probability density given a vector from G we have

$$|G_s(r)\rangle \langle G_s(r')| = \sum_{a,b=1}^{n_b} |\chi_a(r)\rangle D_{ab}^s \langle \chi_b(r')| \quad (15)$$

where D is the density matrix. The elements of the density matrix generated by the single generalized orbital s are given by

$$D_{ab}^s = \sum_{i=1}^{n_b} N_{ai} C_{is} C_{is}^* N_{bi}^* \quad (16)$$

It is clear from the definition that the matrix D is non-negative, and from the normalization of the vectors C that the trace is 1. This is exactly what is required for the one-electron density matrix of a single electron.

Given the vectors G and assuming a system of n_e electrons in a particular spin channel we can write a single-determinant wave function in terms of these vectors as

$$\Psi(r_1, \dots, r_{n_e}) = |G_1(r_1)G_2(r_2) \dots G_{n_e}(r_{n_e})| \quad (17)$$

From this wave function the one-electron density matrix can be obtained as

$$\sum_{a,b=1}^{n_b} |\chi_a(r_1)\rangle D_{ab} \langle \chi_b(r'_1)| = n_e \int \Psi(r_1, r_2, \dots, r_{n_e}) \Psi^*(r'_1, r_2, \dots, r_{n_e}) dr_2 \dots dr_{n_e} \quad (18)$$

$$D_{ab} = \sum_{i=1}^{n_b} \sum_{s=1}^{n_e} N_{ai} C_{is} C_{is}^* N_{bi}^* \quad (19)$$

$$= \sum_{i=1}^{n_b} N_{ai} d_i N_{bi}^* \quad (20)$$

The occupation numbers d_i are obviously non-negative as they are a sum of squares. In addition because the correlation functions are an orthonormal set expressed in an orthonormal basis the matrix C is unitary. This means that

$$C^* C = C C^* = I \quad (21)$$

from which it follows that if only a subset of all columns of C are included then the diagonal elements $d_i \leq 1$. In addition the trace of the density matrix term of a single vector of G is 1 so that if n_e such vectors are included in the wave function the trace of the density matrix is n_e . Hence we have shown that a single-determinant wave function of the form presented here can generate any one-electron density matrix even non-idempotent ones. Trivially, an idempotent density matrix can be obtained when the correlation functions are unit vectors. Thus the original Kohn-Sham system is obtained as a special case of the wave function proposed.

III. OPTIMIZING THE WAVE FUNCTION

In the previous section a single-determinant wave function that can represent arbitrary one-electron density matrices was proposed. This wave function is expressed in terms of correlation functions and conventional natural orbitals. In order to deploy this wave function an approach to optimize it is required. Obviously this approach is based on an energy minimization. To keep the results as general as possible we consider energy expressions of the form

$$E = E(D^\alpha, D^\beta) \quad (22)$$

I.e. the energy is a functional of the one-electron density matrices of both spin channels. This type of expression encompasses a wide range of energy expressions including Hartree-Fock, DFT, and RDMFT. Furthermore, here only

the optimization w.r.t. one of the spin channels is discussed as the results for the other spin-channel are the same. Thus we consider the problem

$$L = E(D^\alpha(N^\alpha, C^\alpha); D^\beta) + \sum_{i,j=1}^{n_b} d_i \lambda_{ij}^{N^\alpha} \left(I_{ij} - \sum_{a,b=1}^{n_b} N_{ai}^{\alpha*} S_{ab} N_{bj}^\alpha \right) + \sum_{r,s=1}^{n_b} \lambda_{rs}^{C^\alpha} \left(I_{rs} - \sum_{i,j=1}^{n_b} C_{ir}^{\alpha*} I_{ij} C_{js}^\alpha \right) \quad (23)$$

$$\min_{N^\alpha, C^\alpha, \lambda_{ij}^{N^\alpha}, \lambda_{rs}^{C^\alpha}} L \quad (24)$$

In the subsequent derivations only the α -electron spin channel is considered hence the α label is dropped. The resulting equations directly transfer to the β -electron spin channel as well. For the orthogonality of the correlation functions we obtain from $\partial L / \partial \lambda_{rs}^C = 0$

$$\sum_{i,j=1}^{n_b} C_{ir}^* I_{ij} C_{js} = I_{rs} \quad (25)$$

For the natural orbitals $\partial L / \partial \lambda_{ij}^N = 0$ gives

$$d_i \left(I_{ij} - \sum_{a,b=1}^{n_b} N_{ai}^* S_{ab} N_{bj} \right) = 0 \quad (26)$$

which is also satisfied if the expression in brackets is zero leading to

$$\sum_{a,b=1}^{n_b} N_{ai}^* S_{ab} N_{bj} = I_{ij} \quad (27)$$

Furthermore, from $\partial L / \partial N_{ck}^* = 0$ we have for the natural orbitals

$$\left(\sum_{b=1}^{n_b} F_{cb} N_{bk} - \sum_{b,j=1}^{n_b} S_{cb} N_{bj} \lambda_{jk}^N \right) d_k = 0 \quad (28)$$

where F is the Fock matrix. The Fock matrix is the matrix representation of an effective one-electron operator which is derived from the total energy expression by differentiating it with respect to the density matrix. More specifically the Fock matrix elements F_{ab} are defined as

$$F_{ab} = \frac{\partial E(D)}{\partial D_{ab}} \quad (29)$$

Eq. 28 is also satisfied if we solve

$$\sum_{b=1}^{n_b} F_{cb} N_{bk} = \sum_{b,j=1}^{n_b} S_{cb} N_{bj} \lambda_{jk}^N \quad (30)$$

instead. For the correlation functions we find from $\partial L / \partial C_{kt}^* = 0$

$$0 = \sum_{i=1}^{n_b} F_{ki}^{N'} C_{ic} + \sum_{j=1}^{n_b} C_{kt} \lambda_{kj}^N \left(I_{kj} - \sum_{a,b=1}^{n_b} N_{ak}^* S_{ab} N_{bj} \right) - \sum_{j,s=1}^{n_b} I_{kj} C_{js} \lambda_{st}^C \quad (31)$$

$$F_{ki}^{N'} = \sum_{a,b=1}^{n_b} N_{ak}^* F_{ab} N_{bk} \delta_{ki} \quad (32)$$

where the second term in Eq. 31 is identical zero because of the orthogonality of the natural orbitals. Hence this equation simplifies to

$$\sum_{i=1}^{n_b} F_{ki}^{N'} C_{it} = \sum_{j,s=1}^{n_b} I_{kj} C_{js} \lambda_{st}^C \quad (33)$$

Therefore the wave function optimization problem translates into two secular equations. The first one, Eq. 30, is a secular equation for the natural orbitals and is in fact the same as the Kohn-Sham or Hartree-Fock equation. The second one, Eq. 33, seems very similar to the first one except that it solves for the correlation functions. One relevant difference is that the structure of the Fock matrix $F_{ki}^{N'}$ is special in that it is a diagonal matrix in the natural orbital basis. This may seem strange as it is counter intuitive that a non-trivial rotation can be obtained by diagonalizing a matrix based on a matrix that is diagonal already. To explain this situation consider the 2x2 problem

$$\begin{pmatrix} f_{11} & 0 \\ 0 & f_{22} \end{pmatrix} \begin{pmatrix} c_1 & -c_2 \\ c_2 & c_1 \end{pmatrix} = \begin{pmatrix} c_1 & -c_2 \\ c_2 & c_1 \end{pmatrix} \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} \quad (34)$$

There are two possible scenarios for the eigenvectors $(c_1, c_2)^T$ and $(-c_2, c_1)^T$. A trivial result is obtained by choosing the eigenvectors to be unit vectors, e.g. by choosing $c_1 = 1$ and $c_2 = 0$. In that case $\lambda_1 = f_{11}$ and $\lambda_2 = f_{22}$. The other case, when the eigenvectors are not unit vectors, i.e. $c_1 \neq 0$ and $c_2 \neq 0$, requires

$$\begin{pmatrix} f_{11}c_1 \\ f_{22}c_2 \end{pmatrix} = \lambda_1 \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \quad (35)$$

and therefore that $\lambda_1 = f_{11} = f_{22}$, and likewise for λ_2 . Therefore this scenario has a solution only when the diagonal elements are the same, and correspondingly, the eigenvalues are degenerate. As the diagonal elements are the expectation values of the natural orbitals this implies that the natural orbitals are degenerate as well. Such a solution clearly complies with the conditions set out in Gilbert's theorem for correlated orbitals. I.e. that at convergence the energies of all orbitals with fractional occupation numbers must be degenerate. Here this also translates into the corresponding generalized orbitals being degenerate. Because every generalized orbital represents a single electron in a single-determinant wave function this also implies that all correlated electrons are degenerate.

Another corollary of these considerations is that starting a calculation choosing the correlation functions to be unit vectors is a particularly bad choice. Because these unit vectors are always a solution to Eq. 33 there is no way to find a correlated state even if the energy expression accounts for electron correlation. Instead calculations have to be started assuming that initially the electrons are distributed over all relevant natural orbitals. If the energy expression accounts for electron correlation the expressions will converge towards degenerate correlation functions that distribute the electrons over the natural orbitals. If the energy expression has no electron correlation that favors fractionally occupied natural orbitals the correlation functions will converge towards unit vectors.

Although it would seem that Eq. 30 and 33 can be solved straightforwardly in conventional matrix diagonalization based ways the degeneracies cause complications. As at convergence all correlated orbitals are degenerate we find that any arbitrary rotation among those orbitals is an equally valid solution of the matrix diagonalization. In practice only some of these solutions minimize the total energy but diagonalizing the Fock operator cannot identify those solutions. Hence attempts to solve these equations using a diagonalization based approach will very likely fail.

Instead we construct gradients as

$$F_{ij}^N = \sum_{a,b=1}^{n_b} N_{ai}^* F_{ab} N_{bj} \quad (36)$$

$$F_{rs}^C = \sum_{i,j=1}^{n_b} C_{ir}^* F_{ij}^{N'} C_{js} \quad (37)$$

and from these skew symmetric matrices are formed as

$$T^N = \begin{pmatrix} 0 & -F_{12}^N & \dots & -F_{1n_b}^N \\ F_{21}^N & 0 & \dots & -F_{2n_b}^N \\ \vdots & \vdots & 0 & \vdots \\ F_{n_b1}^N & F_{n_b2}^N & \dots & 0 \end{pmatrix} \quad (38)$$

$$T^C = \begin{pmatrix} 0 & -F_{12}^C & \dots & -F_{1n_b}^C \\ F_{21}^C & 0 & \dots & -F_{2n_b}^C \\ \vdots & \vdots & 0 & \vdots \\ F_{n_b1}^C & F_{n_b2}^C & \dots & 0 \end{pmatrix} \quad (39)$$

Rotation matrices for the natural orbitals and correlation functions may be written as

$$R^N = e^{\sigma_N T^N} \quad (40)$$

$$R^C = e^{\sigma_C T^C} \quad (41)$$

The values of σ_N and σ_C are established by a line search [6] for the minimum of the total energy. After updating the natural orbitals and correlation functions a new line search is started. The iterations over line searches continue until the optimal σ -s are zero. By explicitly choosing rotations that minimize the total energy the indeterminateness of the eigenvectors of a degenerate matrix is circumvented. At present the line searches are performed alternately between σ_N and σ_C .

A. Equations of motion

In order for the expression proposed in Eq. 17 to be a proper wave function it must satisfy certain equations of motion. Of course one can substitute this expression into the time dependent Schrödinger equation. As the expression is only a single-determinant wave function and one that only generates the exact one-electron density matrix (without any considerations to the accuracy of the corresponding two-electron density matrix) there seems to be little to be gained over Hartree-Fock by doing that. Instead it seems wise to focus on the one thing the wave function can represent exactly, the one-electron density matrix, and consider its equation of motion which is given by the von Neumann equation [7]

$$i\hbar \frac{dD}{dt} = [H, D] \quad (42)$$

In the case that the Hamiltonian is time independent the time dependent density matrix is given by

$$D(t) = e^{-iHt/\hbar} D(0) e^{iHt/\hbar} \quad (43)$$

It would seem that the most straightforward way to evaluate the time dependent density matrix is to make use of Eq. 8 allowing the generalized orbital to be written as a vector. In addition the Hamiltonian can be generalized to

$$H = \begin{pmatrix} F & 0 & \dots & 0 \\ 0 & F & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & F \end{pmatrix} \quad (44)$$

where F is the effective one-electron Hamiltonian, the Fock matrix, of Eq. 29 replicated along the diagonal so that

$$H_{ai,bj} = \delta_{ij} F_{ab} \quad (45)$$

This approach is similar to the approach applied to the metric S^G but here the block diagonal representation is favored over the form of Eq. 9. The reason is that the Fock matrix of Eq. 44 is to be used specifically with a orthonormal set of generalized orbitals associated with a particular single-determinantal wave function. The form of the metric in Eq. 9 on the contrary has been generalized to allow calculating the overlap between generalized orbitals of different single-determinant wave functions.

Subsequently evaluating

$$G_{ai,r}(t) = \sum_{b,j=1}^{n_b} e^{-iHt/\hbar} G_{bj,r}(0) \quad (46)$$

the generalized orbitals at time t are obtained from which $D(t)$ can be constructed according to

$$D_{ab}(t) = \sum_{i=1}^{n_b} \sum_{r=1}^{n_e} G_{ai,r}(t) G_{bi,r}^*(t) \quad (47)$$

This equation is essentially the same as Eq. 19 except that nor the natural orbitals nor the correlation functions are explicitly referenced. In order to return the generalized orbitals to the form of Eq. 8 the density matrix $D(t)$ can be diagonalized to obtain the natural orbitals at time t . Furthermore time dependent correlation functions can be optimized that generate the occupation numbers at time t .

The approach to optimizing the correlation functions simply involves writing the correlation functions at time t in terms of the correlation functions at time 0 as

$$C_{ir}(t) = \sum_{s=1}^{n_b} C_{is}(0) U_{sr}(t) \quad (48)$$

where U is a unitary matrix. Subsequently the error

$$R = \sum_{i=1}^{n_b} (d'_i(t) - d_i(t))^2 + \sum_{r,s=1}^{n_b} \lambda_{rs} \left(\delta_{rs} - \sum_{i=1}^{n_b} C_{ir}(t) C_{is}^*(t) \right) \quad (49)$$

$$d'_i(t) = \sum_{r=1}^{n_e} C_{ir}(t) C_{ir}^*(t) \quad (50)$$

as a function of U is minimized to obtain the eigenvalue equation

$$2 \sum_{i,s=1}^{n_b} C_{ir}^*(0) (d'_i(t) - d_i(t)) C_{is}(0) U_{st} = \sum_{s=1}^{n_b} U_{rs} \lambda_{st} \quad (51)$$

where $d_i(t)$ are the occupation numbers obtained from the diagonalization of $D(t)$. This equation needs to be solved iteratively as $d'_i(t)$ depends on the solution.

Supposedly this approach can also be extended to time dependent Hamiltonians by introducing sufficiently small time steps. Hence it would seem that the equations of motion as given by the von Neumann equation can be applied relatively straightforwardly in the present context. Admittedly to date we have not tested this approach as yet.

IV. WAVEFUNCTION ANALYSIS

Once the wave function has been converged we have a set of orbitals and the total energy of the system. Moreover, if there are degenerate energy levels with fractional occupation numbers in the natural orbitals the corresponding orbital energies equal the chemical potential. For the orbitals obtained we know that they generate the one-electron density matrix that minimizes the total energy. In practice the corresponding set of orbitals is not unique. Like in Hartree-Fock or Kohn-Sham theory the total energy is invariant under some rotations among the orbitals. Furthermore, in Hartree-Fock theory Koopmans theorem [8] can be used to estimate ionization potentials and electron affinities from the orbital energies. The chemical potential obtained at the end of the optimization does not afford the same rich set of information. In this section we will show that in our approach some of the information resulting from a Hartree-Fock calculation can be obtained from our wave function as well with modest extra effort.

The first important point to note is that as the energy is a functional of the one-electron density matrix any transformations of the wave function that leave this matrix unchanged do not affect the total energy either. In practice this means that rotations among natural orbitals with equal occupation numbers leave the total energy unchanged. Likewise rotations amongst the occupied correlation functions, or rotations amongst the unoccupied correlation functions do not affect the total energy. While the total energy for the ground state remains unchanged under these rotations processes that change the orbital occupations might be very sensitive to the particulars of the orbitals. An example of such a process is the excitation of an electron. Hence, specific orbital representations that support meaningful interpretations are highly desirable.

In practice the natural orbitals cannot be canonicalized. For the natural orbitals the ordering is critical to maintain the link with the correlation functions. This fact in combination with the degeneracies cause any approach to canonicalization to fail on these orbitals.

The correlation functions can be canonicalized in a more informative way. To this end the Fock matrix of the traditional Hartree-Fock energy is evaluated. The expectation values of the natural orbitals over this matrix feed into the Fock matrix for the correlation functions. This Fock matrix is transformed into the correlation function basis and the occupied-unoccupied block zeroed to suppress mixings that change the density matrix. The resulting matrix is diagonalized to obtain canonical correlation functions. Because the Fock matrix of the Hartree-Fock energy has few degenerate states the resulting orbitals and their energies are Hartree-Fock like. Nevertheless, these orbitals still generate the same correlated one-electron density matrix. This combination suggests that the orbitals can be interpreted similarly to the ones from Hartree-Fock theory. This option was obtained at the cost of a single Fock matrix construction which is modest compared to the few dozen Fock matrix constructions that are required in the self consistent field procedure. Obviously the correlation functions may be canonicalized over any operator. Which operator to choose depends on what the results are to be used for.

V. APPLICATION TO LIH AND BE

In order to demonstrate what the formalism introduced can provide it is applied to the systems LiH and Be. The reasons for this choice are that both systems are small so the results can be reported in detail. The Be atom

TABLE I. The total energies ($/E_H$) for Be in the 6-31G basis set for different methods

Hartree-Fock	-14.566764
WDMFT	-14.590417
Full-CI	-14.613545

TABLE II. Occupation numbers of the total one-electron density matrix for Be

Hartree-Fock	WDMFT	Full-CI
2.0000	2.0000	1.9999
2.0000	1.8502	1.8010
0.0000	0.0456	0.0657
0.0000	0.0457	0.0657
0.0000	0.0459	0.0657
0.0000	0.0042	0.0020
0.0000	0.0028	0.0000
0.0000	0.0028	0.0000
0.0000	0.0028	0.0000

is a system with well known near degenerate states whereas the LiH molecule is a weakly correlated system. The energy expression used is the power functional [9] with a power of 0.578 [10]. The formalism and the functional were implemented in a modified version of NWChem [11]. The electronic structure was described using the 6-31G basis set [12–14]. In LiH the bond length was 1.5957 Å.

The total energies for Be and LiH are reported in Tables I and V, respectively. The approach proposed in this work is referred to as Wave Function based Density Matrix Functional Theory (WDMFT). The occupation numbers for Be and LiH are compared with those of the Full-CI method in Tables II and VI. The orbital energies are given in Tables III and VII. The results under the columns "converged" are the orbital energies at the end of the power functional optimization. The results under the column "canonicalized" are the orbital energies obtained from the canonicalization of the correlation functions over the Fock matrix from Hartree-Fock. Finally, Tables IV and VIII give the total energies obtained from excited Slater determinants of generalized orbitals. The full wave functions for Be and LiH are given in the Supplemental Material [15].

The total energy obtained from the WDMFT method as well as the fractional occupation numbers for the natural orbitals show that correlation is accounted for to some degree. Obviously this is only to be expected from a reduced density matrix functional theory. More interesting is that the orbital picture behind the WDMFT method enables multiple perspectives on the results. The orbital energies from the power functional display the degeneracies that Gilbert's theorem calls for and reveal the chemical potential. Yet when the correlation functions are canonicalized over the regular Fock operator from Hartree-Fock energy levels similar to those of Hartree-Fock theory are recovered. Furthermore, moving one electron from one occupied correlation function to an unoccupied one a Slater determinant of an excited state is obtained. These latter features are trivial in this method but are cumbersome in other reduced density matrix functional approaches.

TABLE III. Orbital energies of Be

Hartree-Fock	WDMFT	
	converged	canonicalized
-4.7069	-3.7562	-4.7221
-0.3013	-0.1589	-0.2565
0.0824	-0.1589	0.0506
0.0824	-0.1589	0.0757
0.0824	-0.1589	0.0758
0.4398	-0.1589	0.4351
0.4649	-0.1589	0.4543
0.4649	-0.1589	0.4570
0.4649	-0.1589	0.4570

TABLE IV. Total energies of excited determinants of Be

Excitation	Hartree-Fock	WDMFT
ground state	-14.566764	-14.590417
$\alpha : 2 \rightarrow 3$	-14.425466	-14.475988
$\alpha : 2 \rightarrow 4$	-14.425466	-14.444019
$\alpha : 2 \rightarrow 5$	-14.425466	-14.444326

TABLE V. The total energies ($/E_H$) for LiH in the 6-31G basis set for different methods

Hartree-Fock	-7.979277
WDMFT	-7.985189
Full-CI	-7.998288

TABLE VI. Occupation numbers of the total one-electron density matrix for LiH

Hartree-Fock	WDMFT	Full-CI
2.0000	2.0000	1.9999
2.0000	1.9501	1.9564
0.0000	0.0297	0.0394
0.0000	0.0023	0.0016
0.0000	0.0023	0.0011
0.0000	0.0045	0.0011
0.0000	0.0009	0.0005
0.0000	0.0018	0.0000
0.0000	0.0018	0.0000
0.0000	0.0051	0.0000
0.0000	0.0013	0.0000

TABLE VII. Orbital energies of LiH

Hartree-Fock	WDMFT	
	converged	canonicalized
-2.4533	-1.7574	-2.4561
-0.3007	-0.1068	-0.2893
0.0094	-0.1068	0.0033
0.0602	-0.1068	0.0588
0.0602	-0.1068	0.0596
0.1449	-0.1068	0.1413
0.2005	-0.1068	0.2005
0.2219	-0.1068	0.2196
0.2219	-0.1068	0.2205
0.3598	-0.1068	0.3546
1.3182	-0.1068	1.3091

TABLE VIII. Total energies of excited determinants of LiH

Excitation	Hartree-Fock	Total Energy
ground state	-7.979277	-7.985189
$\alpha : 2 \rightarrow 3$	-7.829456	-7.835788
$\alpha : 2 \rightarrow 4$	-7.789693	-7.794577
$\alpha : 2 \rightarrow 5$	-7.789693	-7.792494

VI. CONCLUSIONS

This paper demonstrates that a fictitious one-electron system can be formulated that can represent any arbitrary one-electron density matrix with a single-determinant wave function. This includes even density matrices corresponding to a correlated state. The formulation of the wave function requires the conventional natural orbitals as well as a new set referred to as correlation functions. Optimizing such a wave function requires solving the traditional Hartree-Fock or Kohn-Sham equations, with a suitable reduced density matrix functional, as well as a new set of equations for the correlation functions. Both sets of equations are very similar in structure. The analysis of the wave function allows for representations that are very similar to the orbital energies of Hartree-Fock theory. In addition excited determinants can easily be generated by applying the usual excitation operators to the ground state determinant.

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- [1] P. Hohenberg and W. Kohn. Inhomogeneous electron gas. *Physical Review*, 136(3B):B864, Nov 1964.
 - [2] W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Physical Review*, 140(4A):A1133, Nov 1965.
 - [3] T. L. Gilbert. Hohenberg-kohn theorem for nonlocal external potentials. *Physical Review B*, 12(6):2111, Sep 1975.
 - [4] See supplemental material at [url will be inserted by publisher] for a numerical example of the key transformations.
 - [5] A. J. Coleman. Structure of fermion density matrices. *Rev. Mod. Phys.*, 35(3):668, Jul 1963.
 - [6] Jorge Nocedal and Stephen J. Wright. *Numerical Optimization*, chapter 3, pages 30–65. Operations Research and Financial Engineering. Springer, New York, 2 edition, 2006.
 - [7] J. von Neumann. Wahrscheinlichkeitstheoretischer aufbau der quantenmechanik. *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-Physikalische Klasse*, 1927:245, 1927.
 - [8] T Koopmans. Über die zuordnung von wellenfunktionen und eigenwerten zu den einzelnen elektronen eines atoms. *Physica*, 1(1-6):104, Jan 1934.
 - [9] A.M.K. Müller. Explicit approximate relation between reduced two- and one-particle density matrices. *Physics Letters A*, 105(9):446, Nov 1984.
 - [10] N. N. Lathiotakis, S. Sharma, J. K. Dewhurst, F. G. Eich, M. A. L. Marques, and E. K. U. Gross. Density-matrix-power functional: Performance for finite systems and the homogeneous electron gas. *Physical Review A*, 79(4), Apr 2009.
 - [11] M. Valiev, E.J. Bylaska, N. Govind, K. Kowalski, T.P. Straatsma, H.J.J. Van Dam, D. Wang, J. Nieplocha, E. Apra, T.L. Windus, and et al. Nwchem: A comprehensive and scalable open-source solution for large scale molecular simulations. *Computer Physics Communications*, 181(9):1477, Sep 2010.
 - [12] W. J. Hehre. Selfconsistent molecular orbital methods. xii. further extensions of gaussian-type basis sets for use in molecular orbital studies of organic molecules. *J. Chem. Phys.*, 56(5):2257, 1972.
 - [13] James D. Dill. Self-consistent molecular orbital methods. xv. extended gaussian-type basis sets for lithium, beryllium, and boron. *J. Chem. Phys.*, 62(7):2921, 1975.
 - [14] Karen L. Schuchardt, Brett T. Didier, Todd Elsethagen, Lisong Sun, Vidhya Gurumoorthi, Jared Chase, Jun Li, and Theresa L. Windus. Basis set exchange: a community database for computational sciences. *J. Chem. Inf. Model.*, 47(3):1045, May 2007.
 - [15] See supplemental material at [url will be inserted by publisher] for the full wavefunctions of Be and LiH.