Aufbau derived from a unified treatment of occupation numbers in Hartree–Fock, Kohn–Sham, and natural orbital theories with the Karush–Kuhn–Tucker conditions for the inequality constraints $n_i \leq 1$ and $n_i \geq 0$

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(Received 9 January 2010; accepted 16 April 2010; published online 18 May 2010)

In the major independent particle models of electronic structure theory—Hartree–Fock, Kohn–Sham (KS), and natural orbital (NO) theories—occupations are constrained to 0 and 1 or to the interval [0,1]. We carry out a constrained optimization of the orbitals and occupation numbers with application of the usual equality constraints $\Sigma_i^\infty n_i = N$ and $\langle \phi_i | \phi_j \rangle = \delta_{ij}$. The occupation number optimization is carried out, allowing for fractional occupations, with the inequality constraints $n_i \geq 0$ and $n_i \leq 1$ with the Karush–Kuhn–Tucker method. This leads in all cases to an orbital energy spectrum with (only for NO and KS) possibly fractionally occupied degenerate levels at energy equal to the Lagrange multiplier ϵ for the first equality constraint, completely occupied levels at lower energies and completely unoccupied levels at higher energies. Aufbau thus follows in all cases directly from this general derivation. © *2010 American Institute of Physics*.
[doi:10.1063/1.3426319]

I. INTRODUCTION

In effective, one-electron theories such as Hartree–Fock (HF), the Kohn–Sham (KS) approach to density functional theory (DFT), and one-body reduced density matrix functional theory(DMFT), one-electron Hamiltonians are derived which have the one-electron states (orbitals) as eigenfunctions. Occupation numbers are often (in HF and KS calculations) fixed to 0 and 1, and in assigning occupations to the orbitals, the orbital energy spectrum is commonly used, assuming that application of the Aufbau principle will yield the lowest energy solution. However, we will show that the Aufbau solution can actually be derived from the minimum energy condition using the Karush–Kuhn–Tucker (KKT) conditions[1,2] for the handling of inequality constraints like $n_i \geq 0$ and $n_i \leq 1$.

All theories have in common that the energy can be written as a functional of a one-body reduced density matrix (1RDM), $E[\gamma]$, where the 1RDM is defined as

$$\gamma(\boldsymbol{x},\boldsymbol{x}') \equiv \sum_K \mathrm{d}_K \langle \Psi_K | \hat{\psi}^\dagger(\boldsymbol{x}') \hat{\psi}(\boldsymbol{x}) | \Psi_K \rangle. \tag{1}$$

The 1RDM can be expanded in its spectral representation,

$$\gamma(\boldsymbol{x},\boldsymbol{x}') = \sum_k n_k \phi_k(\boldsymbol{x}) \phi_k^*(\boldsymbol{x}). \tag{2}$$

The eigenfunctions of the 1RDM, $\phi_k(\boldsymbol{x})$, are called natural orbitals (NOs). These NOs are the HF and KS orbitals in the HF and DFT cases, respectively, and the true NOs in the DMFT case. We will occasionally refer to them collectively as NOs. The eigenvalues, n_k, are called occupation numbers.

We allow here in Eq. (1) for a 1RDM that is derived from an ensemble of states with weights $\mathrm{d}_K, 0 \leq \mathrm{d}_K \leq 1$, $\Sigma_K \mathrm{d}_K = 1$. The HF model is characterized by the restriction of the trial wave function to a single determinant, and the energy expression for the single determinant wave function [in terms of its γ, see Eq. (4)] is used. Lieb[3] proved that minimizing γ is actually always a pure state (single determinant) γ in the HF case, see below. In the KS case the energy is a functional of the diagonal of the 1RDM, the electron density $\rho(\boldsymbol{r})$. It is known that some exact ground state densities of interacting correlated electron systems are only ensemble, representable with the densities of the determinantal eigenstates of the KS independent particle system.[4,5] In that case Eq. (1) uses an ensemble of KS determinants. The exact solution in the KS case (with the exact $E[\rho]$) would yield the exact diagonal density $\rho(\boldsymbol{r})$, but not the exact γ. In DMFT one uses, in principle, the exact $E[\gamma]$, which exists according to the proof by Gilbert.[6] The 1RDM can be written with the exact wave function in Eq. (1), as the single term $\gamma(\boldsymbol{x},\boldsymbol{x}') \equiv \langle \Psi_0 | \hat{\psi}^\dagger(\boldsymbol{x}') \hat{\psi}(\boldsymbol{x}) | \Psi_0 \rangle$ (in the case of a nondegenerate ground state Ψ_0). It can also be written with the Ψ_K of Eq. (1) being the determinants constructed with the orbitals of the independent particle system of this case, i.e., the NOs. The determinants are degenerate states of the independent particle system since all fractionally occupied NOs obey one-electron equations with degenerate energies.[6] An ensemble is surely needed, with such weights d_K that the occu-

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pation numbers for the NOs in the exact wave function would result. We will return to the possible ensemble representation of γ in the various cases below.

So the energy can be written as a functional of the 1RDM for all the effective one-electron theories, and it can be split into one-body and two-body parts,

$$E[\gamma] = \sum_k n_k h_{kk} + W[\gamma]. \tag{3}$$

The one-body part contains the usual kinetic energy operator and the external potential. Since we are working on the spectral representation of the 1RDM of the particular method, the one-body part becomes an occupation number weighted sum over diagonal matrix elements of the one-body Hamiltonian in NO representation.

That the exact two-body part W is a functional of γ for *nonlocal* external potentials is the content of Gilbert's proof.[6] In DMFT we use, in principle, this exact $W[\gamma]$, or rather approximations since the exact $W[\gamma]$ is not known. We optimize the energy by variation in the components of γ, the NOs, and the occupation numbers. If the determinants in Eq. (1) are on the basis of the NOs, or if the exact wave function is expanded in NO-based determinants, it is easy to see that all occupation numbers must be between 0 and 1 for fermions and that the occupation numbers should sum to the total number of electrons.[7] It was proven by Coleman[8] that the requirements $0 \leq n_i \leq 1$ and $\Sigma_i n_i = N$ are not only necessary, but also sufficient conditions for γ to be ensemble N-representable.

If the external potential is restricted to be *local*, Hohenberg and Kohn[9] showed that only the diagonal of the 1RDM, i.e., the density $\rho(\boldsymbol{x}) = \gamma(\boldsymbol{x},\boldsymbol{x})$ is required to determine the exact energy. Therefore, in the case of DFT, the functional $W[\gamma]$ can be set to the Hartree plus (KS) exchange-correlation energy, $E_{Hxc}[\rho]$. The γ would correspond to the 1RDM of the KS system.[10] In KS-DFT, integer solutions for the n_i will result most of the time, but not always. In this case fractional occupation numbers are certainly allowed and indeed may be necessary.[4,5]

In the case of HF we can use the expression for the two-electron part of the energy in terms of the 1RDM when the wave function is restricted to one-determinantal form,

$$\begin{aligned} W^{\mathrm{HF}} &\equiv \frac{1}{2}\int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{x}' [\gamma(\boldsymbol{x},\boldsymbol{x})\gamma(\boldsymbol{x}',\boldsymbol{x}')w(\boldsymbol{x},\boldsymbol{x}') \\ &\quad - \gamma(\boldsymbol{x},\boldsymbol{x}')\gamma(\boldsymbol{x}',\boldsymbol{x})w(\boldsymbol{x},\boldsymbol{x}') \\ &= \frac{1}{2}\sum_{r,s} n_r n_s (w_{rssr} - w_{rsrs}), \end{aligned} \tag{4}$$

where $w(\boldsymbol{x},\boldsymbol{x}') = 1/|\boldsymbol{r}-\boldsymbol{r}'|$ is the electron-electron interaction potential. We use the following definition for the two-electron integrals:

$$w_{klrs} \equiv \int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{x}' \, \phi_k^*(\boldsymbol{x}) \phi_l^*(\boldsymbol{x}') w(\boldsymbol{x},\boldsymbol{x}') \phi_r(\boldsymbol{x}') \phi_s(\boldsymbol{x}). \tag{5}$$

When we use the constraints $0 \leq n_i \leq 1$, this raises the question of the meaning of the expression for W^{HF} when fractional occupation numbers are allowed. Without going into the question of the physical meaning, Lieb[3] considered the completely unrestricted variational optimization of $E[\gamma]$ with W^{HF} of Eq. (4), allowing for fractional occupation numbers, i.e., under the conditions $0 \leq n_i \leq 1$ and $\Sigma_i n_i = N$. He proved that there is always a single determinant (integer occupations) with an energy that is a lower bound to $E^{\mathrm{HF}}[\gamma]$: $E^{\mathrm{HF}}[\gamma] \geq \langle \Phi_0 | \hat{H} | \Phi_0 \rangle$, where Φ_0 is the ground state HF determinant (or one of them in case of degeneracy). We can thus consider the general variation in Eq. (3) with W^{HF}, allowing for fractional occupation numbers, while we can be sure this will yield integer occupations in the HF case [see also comment below Eq. (32)].

So the ground state energy in all these theories is obtained by requiring that the variation in the energy due to variations in the 1RDM vanishes. If one assumes the functional to be differentiable, this condition can be formulated as

$$\frac{\delta E}{\delta \gamma(\boldsymbol{x},\boldsymbol{x}')} = 0. \tag{6}$$

This paper deals with the constraints that have to be applied on this variation and on the consequences of enforcing these constraints. We will optimize the energy with respect to the components of γ, the NOs, and occupation numbers. However, the 1RDM does not determine the phase of its eigenfunctions, the NOs, so the energy functional expressed in terms of orbitals and occupation numbers is only a true density matrix functional if it is independent of the NO phases. From this requirement we can immediately derive a condition on the NO derivatives.[11] First we make the phase of the NOs explicit by writing $\phi_k(\boldsymbol{x}) = e^{-i\alpha_k}\chi_k(\boldsymbol{x})$. Since the energy has to be invariant under phase changes, we have

$$\begin{aligned} 0 = \frac{\mathrm{d}E}{\mathrm{d}\alpha_k} &= \int \mathrm{d}\boldsymbol{x} \frac{\partial E}{\partial \phi_k(\boldsymbol{x})} \frac{\mathrm{d}\phi_k(\boldsymbol{x})}{\mathrm{d}\alpha_k} + \int \mathrm{d}\boldsymbol{x} \frac{\partial E}{\partial \phi_k^*(\boldsymbol{x})} \frac{\mathrm{d}\phi_k^*(\boldsymbol{x})}{\mathrm{d}\alpha_k} \\ &= i \int \mathrm{d}\boldsymbol{x} \left(\phi_k^*(\boldsymbol{x}) \frac{\partial E}{\partial \phi_k^*(\boldsymbol{x})} - \frac{\partial E}{\partial \phi_k(\boldsymbol{x})} \phi_k(\boldsymbol{x}) \right). \end{aligned} \tag{7}$$

This is an important requirement on any 1RDM functional. It is evidently obeyed by the DFT and (generalized) HF energies. Further, the following constraints have to be applied to ensure that the NOs and occupation numbers represent a proper 1RDM: (1) the NOs have to be orthonormal; (2) the occupation numbers have to sum the total number of electrons N; (3) the occupation numbers should obey $0 \leq n_k \leq 1$.[8] (1) and (2) are equality constraints that can easily be taken into account by Lagrange multipliers. However, it is generally believed that the inequality constraints $0 \leq n_k \leq 1$ cannot be incorporated by Lagrange multipliers. For example, Zumbach and Maschke[12] stated: "Unfortunately, the conditions $0 \leq n_k \leq 1$ cannot be expressed in terms of Lagrange parameters." However, the generalization of the method of Lagrange multipliers to inequality constraints has already been established in 1939 in a master thesis of Karush.[1] This result only reached a larger audience after a 1951 conference paper by Kuhn and Tucker.[2] We will give a brief introduction to the KKT technique in Sec. II. Then in Sec. III the application to the one-electron theories of HF, KS, and DMFT

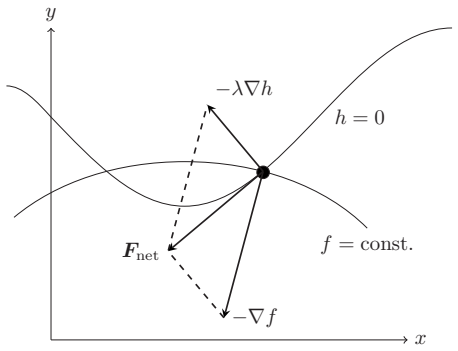

FIG. 1. The force of the objective function $-\nabla f$ and the force of the constraint $-\lambda\nabla h$ are imbalanced. A net force $\boldsymbol{F}_{\text{net}}$ remains.

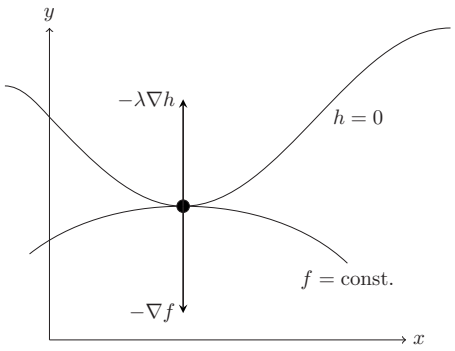

FIG. 2. At the optimal point the forces of the constraint $-\lambda\nabla h$ exactly cancels the force of the objective function $-\nabla f$, so there is no net force.

will be given. The main result is that the eigenvalue spectrum for the one-electron equations that can be obtained in each case has a very similar structure. All fractionally occupied orbitals (if any) are degenerate, with energy ϵ, with ϵ as the Lagrange multiplier for the electron number constraint $\Sigma_i n_i = N$. For them, the inequality constraints are not "binding." For all fully occupied orbitals the inequality constraint $n_i \leq 1$ is binding and their orbital energies ϵ_i are equal to $\epsilon_i = \epsilon - \epsilon_i^1$, with ϵ_i^1 as the corresponding positive Lagrange multiplier. All fully occupied orbitals have therefore energies *below* ϵ. All completely empty orbitals, for which the constraint $n_i \geq 0$ is active, have orbital energies $\epsilon_a = \epsilon + \epsilon_a^0$, all *above* ϵ since also the Lagrange multipliers ϵ_a^0 are positive. In the case of HF important previous results were already obtained by Lieb and co-workers.[3,13] In the case of DFT, our treatment generalizes the ones of Slater[14,15] and Janak.[16] These authors introduced fractional occupations without physical justification; the issue was clarified by the introduction of ensembles in DFT.[4,17,18] In the case of DMFT, the degeneracy of the fractionally occupied orbitals was an important result of Gilbert.[6] The behavior of the orbital energies for the completely occupied and unoccupied NOs (if any) in the DMFT case has often been conjectured or just assumed, but we are not aware of any proof.

II. THE KARUSH–KUHN–TUCKER CONDITIONS

We will not present a rigorous mathematical treatment of the KKT conditions. A more rigorous treatment can be found in literature on optimization and nonlinear programming, e.g., Refs 19–21. We will use a graphical illustration to just bring out the essential points. First consider a general two dimensional optimization problem with an equality constraint,

$$\min_{x,y\in\mathbb{R}} f(x,y),$$

$$\text{subject to } h(x,y)=0. \tag{8}$$

Now consider an arbitrary feasible point (x,y), i.e., a point that satisfies the constraint $h(x,y)=0$ (Fig. 1). In general, this point will not be optimal so there will exist a nonvanishing gradient at this point, $\nabla f \neq \mathbf{0}$. Therefore, one could obtain a lower value by moving down the gradient. The physical picture is to consider a particle at (x,y) in a potential f. The potential will exert a force $-\nabla f$ on the particle and it will attain its lowest potential energy if the force is zero, i.e., it reached a local minimum.

However, in our case the particle is not free to move over the potential surface but is constraint to the curve defined by $h(x,y)=0$. To keep the particle at this curve, an additional force is required which is perpendicular to the curve, $-\lambda\nabla h$, where λ is some scaling factor to give the force $-\nabla h$ the right magnitude to keep the particle on the curve $h(x,y,)=0$. The total force on the particle will now be the sum of the two forces,

$$\boldsymbol{F}_{\text{net}} = -\nabla f - \lambda \nabla h. \tag{9}$$

Similar to the unconstrained case, the particle will attain its lowest potential energy if the *total* force is zero (Fig. 2), so we obtain the usual first-order optimality condition for equality constraints,

$$\boldsymbol{F}_{\text{net}} = -\nabla f - \lambda \nabla h = 0, \tag{10}$$

where the scaling factor λ of the force due to the constraint is generally known as the Lagrange multiplier.

Now consider a minimization problem with an inequality constraint,

$$\min_{x,y\in\mathbb{R}} f(x,y),$$

$$\text{subject to } g(x,y)\leq 0. \tag{11}$$

The inequality constraint $g(x,y)\leq 0$ effectively defines a region where the solution is feasible with a boundary $g(x,y)=0$. There are two situations possible at the optimal point: (1) the constraint is binding so the particle is at the boundary of the constraint, $g(x,y)=0$, and we need a force $-\xi\nabla g$ to keep the optimal point at the boundary, or (2) the constraint is not binding, $g(x,y)\leq 0$, and no force is required. The constraint is not active when the corresponding Lagrange multiplier is zero, $\xi=0$. So we have $g(x,y)=0$ or $\xi=0$, which can be formulated as

$$\xi g(x,y) = 0. \tag{12}$$

This condition is known as the complementary slackness condition. There is also the possibility that the unconstrained optimal point happens to be at the boundary of the feasible region. In that case we have $g(x,y)=\xi=0$, which is also covered by condition (12).

Note that using the gradient to constrain the problem can fail if $\nabla g=0$ at some point for which $g=0$, so using $-\lambda\nabla g$ as a force to keep the solution in the feasible region does not work. Therefore, one usually has to check if the constraints are "qualified" so that the optimal point will not have $\nabla g=0$ and $g=0$, since such an optimal point will not be recognized by the KKT conditions. However, our constraints for the occupation numbers are linear so this problem will not arise. Further, it is usually never checked if the constraints for the orbitals (orthonormality) are qualified. However, this follows directly from the fact that their gradients are linearly independent if the solution is feasible. For more details about constraint qualification consult literature on optimization, e.g., Refs 19–21.

Further the constraining force is only allowed to work in one direction. It should only push the particle into the feasible region and not outside it. Therefore, the corresponding Lagrange multiplier has to be positive [if the sign of the condition is chosen as $g(x,y)\leq 0$],

$$\xi \geq 0. \tag{13}$$

It has been shown by KKT that these conditions [Eqs. (12) and (13)] are necessary conditions for a local minimum (or maximum). So an optimization problem with inequality constraints can be treated in the same way as a problem with equality constraints with the only difference that the complementary slackness condition and the positivity of the Lagrange multipliers must be taken into account. So the first-order stationarity conditions for a general minimization problem,

$$\min_{\mathbf{x}\in\mathbb{R}^N} f(\boldsymbol{x}),$$

$$\text{subject to } g_i(\boldsymbol{x})\leq 0 \quad \text{for } i=1,\ldots,m,$$

$$h_j(\boldsymbol{x})=0 \quad \text{for } j=1,\ldots,l, \tag{14}$$

can be formulated with the help of the following Lagrangian:

$$L(\boldsymbol{x},\boldsymbol{\xi},\boldsymbol{\lambda})=f(\boldsymbol{x})+\sum_{i=1}^{m}\xi_i g_i(\boldsymbol{x})+\sum_{j=1}^{l}\lambda_i h_i(\boldsymbol{x}). \tag{15}$$

The first-order stationarity conditions are traditionally grouped into three:[21] the primal feasibility conditions,

$$g_i(\boldsymbol{x})\leq 0, \quad \forall\, i=1,\ldots,m, \tag{16a}$$

$$h_j(\boldsymbol{x})=0, \quad \forall\, j=1,\ldots,l, \tag{16b}$$

the dual feasibility conditions,

$$\nabla_{\boldsymbol{x}} L=\nabla f(\boldsymbol{x})+\sum_{i=1}^{m}\xi_i\nabla g_i(\boldsymbol{x})+\sum_{j=1}^{l}\lambda_i\nabla h_i(\boldsymbol{x})=0, \tag{17a}$$

$$\xi_i\geq 0, \quad \forall\, i=1,\ldots,m, \tag{17b}$$

and the complementary slackness conditions,

$$\xi_i g_i(\boldsymbol{x})=0, \quad \forall\, i=1,\ldots,m. \tag{18}$$

III. APPLICATION OF THE KKT CONDITIONS TO EFFECTIVE ONE-ELECTRON THEORIES

Now that we have the KKT conditions to deal with the inequality constraints, we introduce the following Lagrangian for the energy functional:

$$\Omega\equiv E-\sum_{rs}\lambda_{sr}(\langle\phi_r|\phi_s\rangle-\delta_{rs})-\epsilon\left(\sum_r n_r-N\right)+\sum_r\epsilon_r^0(-n_r)+\sum_r\epsilon_r^1(n_r-1), \tag{19}$$

where we introduced Lagrange multipliers for the orthonormality of the NOs, for the $\Sigma n_k-N=0$ condition, and for the inequality constraints $-\boldsymbol{n}\leq\mathbf{0}$ and $\boldsymbol{n}-\mathbf{1}\leq\mathbf{0}$, respectively. The first of the dual feasibility conditions [Eq. (17a)] implies that the derivative of the Lagrangian Ω with respect to the NOs and occupation numbers has to be set to zero,

$$\frac{\partial E}{\partial\phi_k(\boldsymbol{x})}-\sum_r\lambda_{kr}\phi_r^*(\boldsymbol{x})=0, \quad \forall_k, \tag{20a}$$

$$\frac{\partial E}{\partial\phi_l^*(\boldsymbol{x})}-\sum_s\phi_s(\boldsymbol{x})\lambda_{sl}=0, \quad \forall_l, \tag{20b}$$

$$\frac{\partial E}{\partial n_k}-\epsilon_k^0+\epsilon_k^1-\epsilon=0, \quad \forall_k. \tag{20c}$$

The second of the dual feasibility conditions [Eq. (17b)] shows that the Lagrange multipliers of the inequality constraints have to be positive,

$$\epsilon_k^0\geq 0, \tag{21a}$$

$$\epsilon_k^1\geq 0. \tag{21b}$$

Additionally, we have the complementary slackness conditions for the inequality constraints [Eq. (18)],

$$\epsilon_k^0 n_k=0, \quad \forall_k, \tag{22a}$$

$$\epsilon_k^1(n_k-1)=0, \quad \forall_k. \tag{22b}$$

Of course the optimal point also has to obey the primal feasibility conditions [Eq. (16)] (the constraints),

$$\langle\phi_k|\phi_l\rangle=\delta_{kl}, \tag{23a}$$

$$n_k\geq 0, \tag{23b}$$

$$n_k\leq 1, \tag{23c}$$

$$\sum_k n_k=N. \tag{23d}$$

There are many equations that have to be solved simultaneously. However, the Lagrange multipliers for the orthonormality of the NOs, $\boldsymbol{\lambda}$, can be eliminated all together. Therefore, we project Eq. (20a) to $\phi_l(\boldsymbol{x})$ and Eq. (20b) to $\phi_k^*(\boldsymbol{x})$, which gives

$$\int d\boldsymbol{x}\frac{\partial E}{\partial\phi_k(\boldsymbol{x})}\phi_l(\boldsymbol{x})-\lambda_{kl}=0, \quad \forall_k, \tag{24a}$$

TABLE I. Relation between the occupation numbers and orbital energies as given by the KKT conditions.

NO energies	⇒	occupation
$\epsilon_k < \epsilon$		$n_k = 1$
$\epsilon_k = \epsilon$		$0 \le n_k \le 1$
$\epsilon_k > \epsilon$		$n_k = 0$

$$\int d\boldsymbol{x}\, \phi_k^*(\boldsymbol{x}) \frac{\partial E}{\partial \phi_l^*(\boldsymbol{x})} - \lambda_{kl} = 0, \quad \forall_l. \tag{24b}$$

Subtracting these equations from each other eliminates the Lagrange multipliers $\boldsymbol{\lambda}$,

$$\int d\boldsymbol{x} \left(\frac{\partial E}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) - \phi_k^*(\boldsymbol{x}) \frac{\partial E}{\partial \phi_l^*(\boldsymbol{x})} \right) = 0. \tag{25}$$

Note that this equation is valid for all k,l pairs. However, as we have shown before, for $k=l$ this equation is automatically satisfied for proper energy functionals [Eq. (7)], i.e., energy functionals that are invariant under the phase of the NOs. So we only need to consider pairs $k \neq l$.

Now consider the dual feasibility condition with the occupation number derivative [Eq. (20c)]. It contains three Lagrange multipliers, ϵ_k^0, ϵ_k^1, and ϵ. To simplify the expression, we define the quantity ϵ_k,

$$\epsilon_k \equiv \epsilon + \epsilon_k^0 - \epsilon_k^1, \tag{26}$$

which we will show as the orbital energy in the effective one-electron equations for the NOs that will be derived. From the complementary slackness conditions [Eq. (22)], we find that for fractional occupation numbers $\epsilon_k^0 = \epsilon_k^1 = 0$ so the orbital energies are all equal to ϵ. However, for fully occupied or completely empty NOs, the orbital energy will differ from ϵ. Taking the positivity of the Lagrange multipliers ϵ_k^0 and ϵ_k^1 into account [Eq. (21)], one obtains the Aufbau solution as detailed in Table I. Although Aufbau has commonly been assumed in all effective one-electron models and has been proven for (completely) unrestricted HF,[3,13] we are not aware of a general proof based on the proper treatment of the constraints on the occupation numbers.

We proceed with the derivation of the effective one-electron equations. Using Eq. (3) for the energy, Eq. (25) [from the orbital derivatives Eqs. (20a) and (20b)] can be written as Eq. (27a), and the occupation number derivative (20c) yields Eq. (27b),

$$(n_l - n_k) h_{kl} + (W_{kl}^\dagger - W_{kl}) = 0, \quad \forall\, k \neq l, \tag{27a}$$

$$h_{kk} + \frac{\partial W}{\partial n_k} = \epsilon_k, \quad \forall\, k, \tag{27b}$$

where we introduced

$$W_{kl} \equiv \int d\boldsymbol{x} \frac{\partial W}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}). \tag{28}$$

By dividing Eq. (27a) by $(n_l - n_k)$, both stationarity equations can be combined into the following effective one-electron eigenvalue equations:

$$\hat{h}^{\text{eff}} \phi_k = (\hat{h} + \hat{v}^{\text{eff}}) \phi_k = \epsilon_k \phi_k, \tag{29}$$

where $\hat{v}^{\text{eff}}$ is determined by its matrix elements,

$$v_{kl}^{\text{eff}} \equiv \begin{cases} \dfrac{(W_{kl}^\dagger - W_{kl})}{(n_l - n_k)} & \text{for } k \neq l \\ \dfrac{\partial W}{\partial n_k} & \text{for } k = l. \end{cases} \tag{30}$$

The off-diagonal matrix elements were derived before by Pernal[22] for the case that the energy is not an explicit functional of $\boldsymbol{\gamma}$, but a functional of the NOs and occupation numbers. One way to do this is by applying the chain rule to Gilberts' expression for the potential, $v^{\text{eff}}(\boldsymbol{x},\boldsymbol{x}') = \delta E / \delta \gamma(\boldsymbol{x},\boldsymbol{x}')$. We use condition (20c) on the occupation number derivative to also fix the diagonal elements v_{kk}^{eff}, and therefore, the orbital energies that afford the results in Table I.

The division by the occupation number differences in Eq. (30) appears to be dangerous, in particular, if the orbital occupancies are (nearly) equal. However, we can show that the $(W_{kl}^\dagger - W_{kl})$ term exactly contains a $(n_l - n_k)$ term so the $(n_l - n_k)$ factor in the denominator cancels out in the off-diagonal matrix element of $\hat{v}^{\text{eff}}$. In the case of exactly degenerate occupancies, which will occur for the whole set of fully occupied orbitals in HF, and for the set of empty orbitals, Eq. (27a) becomes $(n_l - n_k) h_{kl}^{\text{eff}} = 0$ and is obeyed regardless of the value of the off-diagonal matrix element of $\hat{h}^{\text{eff}}$. Stationarity in the energy is then obtained leaving arbitrary rotations of these orbitals among themselves possible. Such rotations would of course affect the diagonal and off-diagonal elements of $\hat{h}^{\text{eff}}$. The rotations of the set of fully occupied NOs among themselves and similarly of the set of completely unoccupied NOs, which diagonalize $\boldsymbol{h}^{\text{eff}}$, yield the eigenfunctions of $\hat{h}^{\text{eff}}$ with the ϵ_k as eigenvalues. These NOs are known as the canonical HF and KS orbitals in the case of HF and DFT, respectively.

We will now derive explicit expressions for the effective potential for HF, KS, and DMFT. Depending on the definition of the general coordinate, either $\boldsymbol{x} = \boldsymbol{r}\sigma$ or $\boldsymbol{x} = \boldsymbol{r}$, we obtain equations for the completely unrestricted or spin free versions of these theories. The common closed shell case (equal spin up and spin down orbitals, always both occupied) is trivially included in these results. With "completely unrestricted" we denote the case that the orbitals are general functions of space and spin, and are not restricted to be either α or β spin orbitals. The formalism is also easily extended to the usual unrestricted versions where the number of α and β electrons is specified as N_α and N_β. For each spin the conditions $0 \le n_k^{\alpha/\beta} \le 1$ and $\Sigma_k n_k^{\alpha/\beta} = N_{\alpha/\beta}$ have to be enforced so each spin group has its own multipliers $\epsilon_k^{\alpha/\beta}$. Within these spin groups Aufbau is required for a minimum energy solution. However, between the α and β electrons Aufbau does not necessarily occur since the specific number of electrons is constrained to sum to N_α and N_β, respectively. A generalization to more complicated schemes such as restricted open-shell HF (ROHF), if at all possible, would be nontrivial in view of the special requirements for the Fock operator to obtain meaningful orbital energies (with Koopmans' type

interpretation[23]). Extension to ROHF is beyond the scope of this article. Here, we only demonstrate the versions with straightforward constraints: spin free or (completely) unrestricted.

For HF we can use W^{HF} [Eq. (4)]. The projected orbital derivative and the occupation number derivative of this definition of the HF two-body contribution to the energy yield

$$W_{kl}^{\mathrm{HF}} = n_k \sum_r n_r (w_{krrl} - w_{krlr}), \tag{31a}$$

$$\frac{\partial W^{\mathrm{HF}}}{\partial n_k} = \sum_r n_r (w_{krrk} - w_{krkr}). \tag{31b}$$

Therefore, the effective potential for HF can be written as

$$v_{kl}^{\mathrm{eff:HF}} = \sum_r n_r (w_{krrl} - w_{krlr}), \tag{32}$$

which is the traditional HF potential if the occupation numbers are integers. Lieb[3] proved that a single determinant wave function Φ_0 (integer occupations) will always exist, that is a lower bound to the energy $E[\gamma]$, $E[\gamma] \geq \langle \Phi_0 | \hat{H} | \Phi_0 \rangle$. However, it was showed by Cancés *et al.* in Ref. 24 p. 126 that although solutions with fractional occupation numbers might satisfy the first-order conditions, they never correspond to a (local) minimum. This is basically an extension of the result by Bach *et al.*[13] that in the completely unrestricted case a single determinant always has a finite orbital energy gap between the highest occupied and lowest unoccupied orbital. Therefore, a proper optimization of NOs and occupation numbers with the general constraint $0 \leq n_i \leq 1$ will not lead to fractional occupations in this case.

In the KS system the two-body part of the energy is the exchange-correlation energy E_{xc} plus the classical Coulomb interaction,

$$W^{\mathrm{KS}} \equiv \frac{1}{2} \sum_{r,s} n_r n_s w_{rssr} + E_{xc}[\rho]. \tag{33}$$

We have to keep in mind that W^{KS} should now be regarded as a functional of the density so we cannot take the derivatives directly with respect to the NOs and occupation numbers. Instead, we will use that the density is determined by the orbitals and occupation numbers as

$$\rho(\boldsymbol{x}) = \sum_r n_r |\phi_r(\boldsymbol{x})|^2, \tag{34}$$

so the derivatives can be taken via the chain rule

$$W_{kl}^{\mathrm{KS}} = \int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{x}' \frac{\delta W^{\mathrm{KS}}}{\delta \rho(\boldsymbol{x}')} \frac{\partial \rho(\boldsymbol{x}')}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) = n_k v_{kl}^{Hxc}, \tag{35a}$$

$$\frac{\partial W^{\mathrm{KS}}}{\partial n_k} = \int \mathrm{d}\boldsymbol{x} \frac{\delta W^{\mathrm{KS}}}{\delta \rho(\boldsymbol{x})} \frac{\partial \rho(\boldsymbol{x})}{\partial n_k} = v_{kk}^{Hxc}, \tag{35b}$$

where we used the matrix representation of the Hartree-exchange-correlation potential, which is defined as the functional derivative of W^{KS} with respect to the density

$$v^{Hxc}(\boldsymbol{x}) \equiv \frac{\delta W^{\mathrm{KS}}}{\delta \rho(\boldsymbol{x})}. \tag{36}$$

The Hartree-exchange-correlation potential is equal to the sum of the more commonly used Hartree potential and the exchange-correlation potential, $v^{Hxc}(\boldsymbol{x}) = v_H(\boldsymbol{x}) + v_{xc}(\boldsymbol{x})$. Using these results for the effective potential, we find that the effective potential is equal to the Hartree-exchange-correlation potential,

$$v_{kl}^{\mathrm{eff:KS}} = v_{kl}^{Hxc}. \tag{37}$$

Note that in the KS system fractional occupations are formally allowed.[4,17,18,25,26] It was proven that for interacting electron systems, densities may exist which in the noninteracting system are not V-representable by a pure state (single determinant, integer occupations) but which may be noninteracting ensemble V-representable (and are described with fractional occupation numbers).[4] This is not only a formal mathematical point: It was shown that in strongly correlated systems (with an essentially multideterminant ground state wave function), such ensembles are necessary in the KS system in order to describe the interacting ground state density.[5] The one-electron orbitals with fractional occupations are degenerate in that case. The weights of the determinants in the ensemble are not arbitrary; they are fixed by the requirement of reproduction of the true interacting density.

For DMFT one actually would not need to use the chain rule since the NOs and occupation numbers just constitute some particular representation of the 1RDM. However, using the chain rule, we can remove the division by $(n_l - n_k)$. For the derivatives we have

$$W_{kl}^{\mathrm{DMFT}} = \int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{x}' \int \mathrm{d}\boldsymbol{x}'' \frac{\delta W^{\mathrm{DMFT}}}{\delta \gamma(\boldsymbol{x}', \boldsymbol{x}'')} \frac{\partial \gamma(\boldsymbol{x}', \boldsymbol{x}'')}{\partial \phi_k(\boldsymbol{x})} \phi_l(\boldsymbol{x}) = n_k v_{kl}^{\mathrm{DMFT}}, \tag{38a}$$

$$\frac{\partial W^{\mathrm{DMFT}}}{\partial n_k} = \int \mathrm{d}\boldsymbol{x} \int \mathrm{d}\boldsymbol{x}' \frac{\delta W^{\mathrm{DMFT}}}{\delta \gamma(\boldsymbol{x}', \boldsymbol{x}'')} \frac{\partial \gamma(\boldsymbol{x}', \boldsymbol{x}'')}{\partial n_k} = v_{kk}^{\mathrm{DMFT}}, \tag{38b}$$

where v_{kl}^{DMFT} are the matrix elements of the DMFT potential in the one-electron equations for the NOs derived originally by Gilbert,[6] which is defined in spin-coordinate space as

$$v^{\mathrm{DMFT}}(\boldsymbol{x}, \boldsymbol{x}') \equiv \frac{\delta W^{\mathrm{DFMT}}}{\delta \gamma(\boldsymbol{x}', \boldsymbol{x})}. \tag{39}$$

So we find that the effective potential of Eq. (30) in the DMFT case is equal to Gilbert's v^{DMFT} of Eq. (39),

$$v_{kl}^{\mathrm{eff:DMFT}} = v_{kl}^{\mathrm{DMFT}}. \tag{40}$$

Gilbert already found that all fractionally occupied NOs should have the same one-electron energy. In the DMFT case, this degeneracy usually extends to all NOs since in practice, all NOs have fractional occupation numbers. The occurrence of integer occupations is—except for incidental occurrence of a zero occupation[27]—not established. The explicit form $\delta W^{\mathrm{DFMT}} / \delta \gamma(\boldsymbol{x}', \boldsymbol{x})$ of the effective potential will be rarely used in DMFT since most approximations are de-

fined in terms of the NOs and their occupation numbers.[28–43] The expression for the effective potential in Eq. (30) can then be used directly.

IV. SUMMARY

We have shown that Aufbau does not have to be assumed when solving the equations of the main one-electron models of electronic structure theory, HF, KS, and NO theories. They can be derived straightforwardly from the minimum energy condition. Allowing for fractional occupations in the HF functional, we were able to treat the optimization procedure in HF, KS-DFT, and DMFT on the same footing. Effective one-electron equations are obtained in all cases, which can be identified with the HF, KS, and Gilbert equations in the cases of HF, KS, and DMFT, respectively. Utilizing the KKT conditions, the constraints that the occupation numbers should be between zero and one, $0 \leq n_k \leq 1$, could be directly enforced with Lagrange multipliers. For the fractionally occupied orbitals these constraints are not binding and they have orbital energy equal to the Lagrange multiplier for the $\Sigma_k n_k = N$ constraint. The orbital energies for the fully occupied orbitals are $\epsilon - \epsilon_i^1$, with ϵ_i^1 being the Lagrange multiplier for the $n_i \leq 1$ constraint. The orbital energies for the unoccupied orbitals are $\epsilon + \epsilon_a^0$ with ϵ_a^0 the Lagrange multipliers for the $n_a \geq 0$ constraint. The derivation leads to the Aufbau solution, with fractionally occupied orbitals at the degenerate energy ϵ, all fully occupied orbitals are below ϵ and all empty orbitals are above ϵ, for HF, DFT, and DMFT. The difference is in the nature of the orbital spectrum: In the DMFT case (almost) all orbitals are fractionally occupied and degenerate at ϵ, in the KS case a limited number of orbitals may be fractionally occupied and degenerate, and in the HF case no orbitals will ever be fractionally occupied.

We note that the derivation shows that in all cases the orbital energy is equal to the derivative of the energy with respect to the occupation number, $\epsilon_k = \partial E / \partial n_k$. The magnitude of the Lagrange multiplier indicates how strongly the constraining force has to act in order to enforce the constraint (the multiplier is precisely this force when the derivative of the constraint function is + or −1, like in our case). For instance, if the energy gain upon increasing the occupation of a specific orbital would be large ($\partial E / \partial n_k$ is large and negative), as holds, e.g., for a core orbital, the corresponding Lagrange multiplier ϵ_i^1 has to be large in order to balance this "force." The orbital energy $\epsilon - \epsilon_i^1$ therefore becomes large and negative.

ACKNOWLEDGMENTS

This work was supported by the NWO (The Netherlands) and by the World Class University (WCU) program through the Korea Science and Engineering Foundation funded by the Ministry of Education, Science and Technology (Project No. R32-2008-000-10180-0).

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