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Variational calculation with general density functional to solve the electronic Schrödinger equation directly for ground state: a recipe for self-consistent field solution

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Abstract

Using orbital-free framework, a simple numerical optimization of the density functional for ground state electronic energy is described for any type of functional approximation, demonstrated via the example of linear combinations of homogeneous functionals of the density. The numerical recipe is given and analyzed for solution: Originating from the linear dependence of nuclear-electron attraction functional on one-electron density ($V_{ne}[\rho_0(\mathbf{r}_1)] = -\Sigma_{A\,=\,1,\ldots,M}$ $Z_A\int\rho_0(\mathbf{r}_1)r_{A1}^{-1}d\mathbf{r}_1$), and a quadratic LCAO approximation for ρ_0, the optimization can be done with iterative use of linsolver. This quadratic approximation, as simplest educated choice for ρ_0, is compared and analyzed algebraically to the HF-SCF one in the Appendices. We call the attention that the introduction of a self-consistent field optimization of non-linear density functional is a new element in this part of the related, general theory.

Keywords: One-electron density; Ground state total electronic energy; Self-consistent field solution of density functional

Introduction

The Lagrangian for ground state electronic energy in density functional formalism

The non-relativistic spinless fixed nuclear coordinate electronic Schrodinger equation (SE) [1,2] in free space is capable to describe the electronic motion in N-electron molecular systems providing the anti-symmetric wavefunction and electronic energy $E_{\text{total-electr}} = E_{\text{electr}}(\{\mathbf{R}_A,Z_A\}) + V_{nn}$ of ground and excited states. The $\mathbf{R}_A$'s and $\mathbf{r}_1$ are the spatial nuclear and electron coordinates, respectively, Z_A's are the nuclear charges, and V_{nn} is the nuclear-nuclear repulsion energy. The spatial dimensionality of SE is $3N$, which increases to $4N$ by the spin coordinates, and its ultimate reduction to three spatial dimensions is a long desired task. In density functional theory (DFT) for ground state electronic energy, the second Hohenberg-Kohn (HK) theorem [2,3] referring to the energy variation principle demands the true electronic functional to satisfy the relation $E_{\text{electr},0}[\rho_0] \leq E_{\text{electr},0}[\rho_{0,\text{trial}}]$ for a trial, N-normalized,

everywhere positive density $\rho_{0,\text{trial}}(\mathbf{r}_1)$, where ρ_0 is the true solution, and the N-norm is

$$\int \rho_0(\mathbf{r}_1)d\mathbf{r}_1 = \int \rho_{0,\text{trial}}(\mathbf{r}_1)d\mathbf{r}_1 = \text{N}. \qquad (1)$$

The 'Lagrange's method of undetermined multiplier' for the second HK theorem [4] minimizes the functional $L^* = E_{\text{electr},0}[\rho_0] - \lambda(\int\rho_0(\mathbf{r}_1)d\mathbf{r}_1 - N)$ with respect to ground state one-electron density, ρ_0, where we emphasize the ground state with subscript zero. The λ is the Lagrange multiplier, provided that the density is normalized to N electrons as constrain, theoretically a routine variational procedure. It takes the form in more detail as

$$L^* = \text{T}[\rho_0(\mathbf{r}_1) + \text{V}_{ee}\rho_0(\mathbf{r}_1)] + \text{V}_{ne}[\rho_0(\mathbf{r}_1)] \qquad (2)$$
$$-\lambda\left(\int \rho_0(\mathbf{r}_1)d\mathbf{r}_1 - N\right),$$

where T is the kinetic energy, V_{ee}, is the electron–electron repulsion, and V_{ne} is the nuclear-electron attraction energy, and if other external forces (electric, magnetic, etc.) apply, their energy functionals are also included. In Hartree-Fock Self Consistent Field (HF-SCF) method [1,2]

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or Kohn-Sham (KS) formulation [2,5], there are constrains for all pairs of molecular orbitals (MOs) to get them ortonormalized to unity. Here, we have only one constraint: the N-normalization of ρ_0. The former two use the kinetic operator from the electronic Hamiltonian ($T^{op} = -\frac{1}{2}\Sigma_{i\ =\ 1...N}\nabla_i^2$), and the latter uses the kinetic energy functional $T[\rho(\mathbf{r}_1)]$ to calculate the kinetic energy (T) in the related formalism. To be more precise, we also need to force the density to be non-negative, e.g., by writing it as the square of some other function, see a particular choice in Equation 6 below. The mathematical variable Lagrange multiplier, λ, bears the role of chemical potential in physical sense, and it relates to the ground state electronic energy as $\lambda \equiv E_{electr,0}(\{\mathbf{R}_A,Z_A\})/N$.

While the DFT formula for the nuclear-electron energy term with the so called external potential, $v(\mathbf{r}_1) \equiv -\Sigma_{A\ =\ 1,...,M}Z_A r_{A1}^{-1}$,

$$V_{ne}[\rho(\mathbf{r}_1)] = -\sum_{A=1,...,M}Z_A\int\rho(\mathbf{r}_1)r_{A1}^{-1}d\mathbf{r}_1$$
$$= \int\rho(\mathbf{r}_1)v(\mathbf{r}_1)d\mathbf{r}_1, \qquad (3)$$

is extremely simple and analytically 100% accurate, the other two are very difficult algebraically, and only approximations are known today. More exactly, Equation 3 is simply the energy of a charge distribution interacting with M point nuclei, giving accurate nuclear-electron energy if accurate ground or excited state density is used. Parr et al. reported a power series [6] based on the rules of density scaling [2] for the other two terms: for kinetic energy, the series of coordinate homogeneous functional of degree two is

$$T[\rho(\mathbf{r}_1)] = \sum_{j=1,...n}A_j\left[\int\rho^{[1+2/(3j)]}d\mathbf{r}_1\right]^j \quad \text{and } n\to\infty,$$
$$(4)$$

while for the electron–electron repulsion energy term, the functional of degree one is

$$V_{ee}[\rho(\mathbf{r}_1)] = \sum_{j=1,...n}B_j\left[\int\rho^{[1+1/(3j)]}d\mathbf{r}_1\right]^j \quad \text{and } n\to\infty.$$
$$(5)$$

The term $j = 1$ in Equation 4 provides the classical Thomas-Fermi formula ($T \approx A_1\int\rho^{5/3}d\mathbf{r}_1$) as the main term for T with constant $c_F = (3/10)(3\pi^2)^{2/3} = 2.871234 \approx A_1$ (remarkable for magnitude but inadequate to account for chemical bond by alone), and the term $j = 1$ in Equation 5 gives the main term as $V_{ee} \approx B_1\int\rho^{4/3}d\mathbf{r}_1$ with $B_1 \approx 2^{-1/3}(N-1)^{2/3}$ [2]. There are many other approximate DFT functionals [2,4,7-9] for T and V_{ee}, as counterparts for Equations 4 and 5. We even do not want to summarize those here, but we make some remarks below. The

method described here works for any case of approximate functionals, even when spin separation is necessary in the algebraic form of functionals as $\rho_0 = \rho_0^\alpha + \rho_0^\beta$; the only requirement we need is the existence of derivatives with respect to ρ_0. The straightforward extra Lagrangian constrain is necessary for spin-separated cases beside the one containing λ: $-\sigma(\rho_0 - (\rho_0^\alpha + \rho_0^\beta))$ with non-negative ρ_0^α and ρ_0^β. The only reason we have picked the linear combinations of homogeneous functionals of the density (LCHFD) in Equations 4 and 5 [6,10] for demonstration in our discussion, i.e., power series in mathematical sense, is the central role of power series in a description. That is, with proper condition, any function or functional can be approximated with it, and it is very simple to handle algebraically. One serious drawback of LCHFD, or in the sense of physics, less special but mathematically the more general moment functionals [10-15], is their slow convergence. Particularly, in Equations 4 and 5, the power series should go up to at least $n = 4$ in the truncation to accurately describe the shell structure, ground state electronic energy ($E_{electr,0}$), and ground state one-electron density ($\rho_0(\mathbf{r}_1)$), as a function of nuclear frame ($\{\mathbf{R}_A,Z_A\}$) and number of electrons (N), concluded in [6] for correction (correlation calculation).

An important point is the form of approximate functional for T. It can be expressed using ρ_0 only (see, e.g., Equation 4), in contrast to Hamiltonian, HF-SCF, or KS kinetic operator (T^{op}, acting on wavefunction, HF-SCF, or KS orbitals, respectively; among which, the first one is exact, the other two are approximate), making a desirable reduction in the dimensionality of the algorithm from $4N$ to 3. The DFT functionals for T and V_{ee} are generally not linear, like for example typically, the LCHFD in Equations 4 and 5 or the various exchange-correlation functionals in KS formalism, and need numerical integration (popular methods are cited in [5,16,17]). There are some non-conventional DFT methods [18], wherein analytical integration is possible because linearity is used in special ways.

The density can be expanded as a linear combination of atomic orbitals (LCAO), where the basis set, $\{b_k(\mathbf{r}_1)\}_{k\ =\ 1...L}$, is e.g. L Cartesian, $x^a y^b z^c \exp(-\alpha r_{A1}^i)$ Slaterian-type orbital (STO, $i = 1$) or Gaussian type orbital (GTO, $i = 2$) functions (or contracted functions), a wisely chosen bunch, grouped, and centered on each nucleus (as in HF-SCF or KS methods for MOs). A good algebraic choice is

$$\rho_0(\mathbf{r}_1) \approx \left(\sum_{k=1...L}d_k b_k(\mathbf{r}_1)\right)^2, \qquad (6)$$

a function which is positive everywhere, as required by the second HK. If L is large enough and the basis set is wisely chosen, the true ρ_0 will be approximated correctly. One must consider the concept of 'minimal basis' [1], at least. Recall the form of HF-SCF or KS one-electron density

[1,2] written with the use of $N/2$ (>1, e.g., closed shell) orthonormal MOs as $\rho_0(\mathbf{r}_1) \approx 2\Sigma_{i=1...N/2}[\Sigma_{k=1...L1}c_{ik}b_k(\mathbf{r}_1)]^2 \geq 0$, wherein the $\{c_{ik}\}$ set is also called LCAO coefficients. It contains $L_1(N/2)$ elements, and the square brackets contain the ith spatial MO square normalized to unity. Though there are only L_1 square terms in it, the $(2\Sigma_i c_{ik}^2)b_k^2$ terms, running via index k and the $2\Sigma_i c_{ik}^2$ correspond to d_k^2, but more cross terms, $b_k b_j$, if $L = L_1$, in comparison to Equation 6. However, if L ($\geq L_1$) is large enough, Equation 6 is a good approximation. Some other properties are described in Appendix 1 to convince us further about preventing orbital-free DFT methods based on the squared sum (e.g., Equation 6) representation for the electron density from tending to be ill conditioned.

Taking the derivatives with respect to d_k and λ, Equation 2 is reformulated as

$$
\begin{aligned}
0 &= \partial L^*/\partial d_i \\
&= \partial T[\rho_0(\mathbf{r}_1)]/\partial d_i + \partial V_{ee}[\rho_0(\mathbf{r}_1)]/\partial d_i \\
&\quad + \int (v(\mathbf{r}_1)-l)\rho_{0i}d\mathbf{r}_1
\end{aligned}
\tag{7}
$$

$$
0 = \partial L^*/\partial \lambda = N - \int \rho_0(\mathbf{r}_1)d\mathbf{r}_1,
\tag{8}
$$

for $i = 1...L$, where for example, one can use Equations 4 and 5 yielding

$$
\partial T[\rho_0(\mathbf{r}_1)]/\partial d_i = \sum_{j=1,...n}(1+2/(3j))jA_j\left[\int \rho_0^{[1+2/(3j)]}d\mathbf{r}_1\right]^{j-1} \\
\int \rho_0^{2/(3j)}\rho_{0i}d\mathbf{r}_1
\tag{9}
$$

$$
\partial V_{ee}[\rho_0(\mathbf{r}_1)]/\partial d_i = \sum_{j=1,...n}(1+1/(3j))jB_j\left[\int \rho_0^{[1+1/(3j)]}d\mathbf{r}_1\right]^{j-1} \\
\int \rho_0^{1/(3j)}\rho_{0i}d\mathbf{r}_1.
\tag{10}
$$

Equation 6 provides the partial derivatives (marked in the second and third indices) entering in any case of approximate functional via Equation 7 as

$$
\rho_{0i} \equiv \partial \rho_0(\mathbf{r}_1)/\partial d_i = 2b_i(\mathbf{r}_1)\left(\sum_{k=1...L}d_k b_k(\mathbf{r}_1)\right),
$$
$$
\text{and } \rho_{0im} \equiv \partial^2 \rho_0(\mathbf{r}_1)/\partial d_i \partial d_m = 2\,b_i(\mathbf{r}_1)b_m(\mathbf{r}_1).
\tag{11}
$$

Equations 9 and 10 are particular choices for demonstration. Notice that Equation 8 just recovers or constrains the normalization required by Equation 1. We call the attention to an important property coming from Equation 6: the third term in Equation 7 containing the

nuclear-electron energy term is linear with respect to LCAO coefficients $\{d_k\}$; recall Equation 11. We will use this property in the iterative solution introduced below. The system in Equations 7, 8, 9, 10, 11 is non-linear, so e.g., the 'steepest descent (gradient)' or 'Newton slope' methods can be employed, needing the $(L+1)^2$ dimensional straightforward Jacobian matrix $\{\partial^2 L^*/(\partial d_i \partial d_m)\}_{i,m=1,...,L+1}$, where $d_{L+1} \equiv \lambda$. The ρ_{0im}'s enter at the point of Jacobian only, not in Equations 7, 8, 9, 10. The Jacobian matrix (W_{im}) with indices i for rows and m for columns using, for example, Equations 4 and 5, is described in Appendix 2 along with some immediate properties. However, most importantly, considering for example only minimal basis, there is at least one STO basis function for each electron (e.g., one STO for *1* s-like orbital of a H atom in a molecule), so the W_{im} using Equations 4 and 5 or any alternative functional generates at least $(N+1)^2$-size Jacobian, which increases rapidly if GTO (e.g., the small STO-3G or larger and non-minimal) basis set is used. By this reason, namely, the N is large in molecular systems, it would be useful to reduce the problem from size $(L+1)^2$ to $N+1 \leq L+1$, as will be shown below, the main point in this work.

Self-consistent field numerical solution of non-linear energy functional for ground state electronic energy and density using lin-solver

The system in Equations 6, 7, 8 solves the problem for ρ_0 and $E_{electr,0} = N\lambda$; however, the question is how to solve effectively. As analyzed above, via the Jacobian, i.e., the second derivatives $\partial^2 L^*/(\partial d_i \partial d_m)$, the dimensionality of the calculation is very large, $(L+1)^2$ with $L \geq N$, and iterative. Now, we describe an algorithm, which is also iterative, but its dimensionality is only $(L+1)$, that is, one needs only the first derivatives $\partial L^*/\partial d_i$.

An important property for the algorithm is that the absolute values of the first three terms in Equation 2 are in about the same magnitude. This comes from the virial theorem for stationary systems (atoms (where $V_{nn} = 0$), and equilibrium geometry or transition state molecules (where $V_{nn} > 0$)), for which the ratio $(V_{ee} + V_{ne} + V_{nn})/T = -2$ holds. For non-stationary geometry, the expression [2] is a bit more complex, but it has the same message in this respect. For example, for H($Z = N = 1$) atom, $E_{electr,0} = T + V_{ee} + V_{ne} = 0.5 + 0 - 1 = -0.5$ hartree, or for the much larger Ar($Z = N = 18$) atom, $E_{electr,0} = (0.527544 + 0.264456 - 1.319544) \times 10^3 = -527.544$ hartree. Furthermore, generally the abs(V_{ne}) term is the largest among the three. Another, although much weaker reasoning is that in Equations 4 to 5, the $\int \rho^{[1+a/(3j)]}d\mathbf{r}_1 \approx G(x \equiv 1 + a/(3j), N) = N^x/5$ approximation can be used, which originates from the crude $\int \rho^{[1+a/(3j)]}d\mathbf{r}_1 \approx (\int \rho d\mathbf{r}_1)^{[1+a/(3j)]} = N^x$, and one can find more detailed discussion and more forms in [4] for G. One must be very careful with this crude

approximation; it weakly holds for near neutral systems ($\Sigma Z_A - N = 0$ or ± 1) because, e.g., for one-electron atoms – $E_{\text{electr},0} = T = Z_A^2/2$ is far from 1^x. G depends only on x and N, but invariant on molecular ρ or molecular frame ($v(\mathbf{r}_1)$); however, this latter invariance on the molecular property we want to use is far not rigorously true. Molecular ρ means mathematically that it can be well approximated with linear combination of GTO or STO functions centered on nuclei. Substituting G into Equations 4 and 5 and truncating at $n = 1$, one finds that $T_{\text{approx}}(G(x = 1 + 2/(3j),N) \approx c_F N^{5/3}/5$ and $V_{\text{ee,approx}}(G(x = 1 + 1/(3j),N) \approx B_1 N^{4/3}/5$, i.e., these crude approximants do not depend on nuclear frame, more exactly on one-electron density (ρ_0), that is, $\partial T(N)/\partial \rho_0$ and $\partial V_{\text{ee}}(N)/\partial \rho_0$ are smaller values for Equation 7 in comparison with the third term. We emphasize that we will not need to use the particular expressions for G, of which accuracy is far below the chemical accuracy; we need only to set up initial values as one choice for iteration. We mention that this reasoning with G for T and V_{ee} via Equations 4 and 5 cannot be done for Equation 3, since that contains the function $v(\mathbf{r}_1)$. In fact, this is in accord with the first HK theorem such that the nuclear frame determines the one-electron density and vice versa, as well as with the fact that in the electronic Hamiltonian, the kinetic and electron–electron repulsion operators show only information on N, while the nuclear-electron operator contains the information on the nuclear frame and N. To be precise, first, in physical sense, T and V_{ee} do contain information on nuclear frame, $v(\mathbf{r}_1)$, via ρ_0, and indeed ρ_0 is in the argument of their DFT functionals. Second, in analytical sense, T and V_{ee} have stronger dependence on N than on $v(\mathbf{r}_1)$.

By these numerical properties above, rearrange Equation 7 with the help of Equation 11, yielding Equation 15 below for $i = 1,...,L$. Via Equations 6 and 8, one has one more equation: $\int(\Sigma_{k = 1...L}d_k b_k(\mathbf{r}_1))^2 d\mathbf{r}_1 = N$. These constitute a second-order algebraic equation system for d_k ($k = 1...L$) and λ (in comparison to the about $(2n + 1)$th-order semi-polynomial system that is detailed in Appendix 2). Here, we need the first derivatives only ($\partial/\partial d_i$), not the second ones ($\partial^2/\partial d_i \partial d_m$). Although many cross terms have zero coefficients and do not show up (e.g., no $d_1 d_2$ in the first one, no λ in the last one, etc.), and there is standard algorithm for solving this in every iteration (with the help of eigen-solver and lin-solver), there is a simpler way to obtain the LCAO parameters d_k ($k = 1...L$) and chemical potential λ. We show this with the simpler algorithm next, wherein we use the fact that the first L equation in the system is a linear equation system for d_k ($k = 1,...,L$), originating from Equations 3 and 6. That is, Equation 3 having linear dependence on ρ and Equation 6 having quadratic dependence on d_k result in a linear block for d_k's in the third term in Equation 7, which

contains the first derivative, ρ_{0i}, only, as expressed in Equation 11.

Start with a wisely chosen basis set and initial values of LCAO parameters, that is, all $d_k^{\text{iter } 0} = 1$ for $k = 1,...,L$ in case of a minimal STO basis, for example. If larger basis set is used, in which for example, there is one-one GTO for 1s- and 2p-like molecule orbitals for a H atom in the system, let the LCAO parameters be 1.0 for 1s and 0.0 for 2p, etc., but more simply, all can be 1.0 also. A much weaker choice for approximating initial value is the use of function $G(x,N)$ based on Equations 4 and 5. For the starting value of $\lambda^{\text{iter } 0} \equiv E_{\text{electr},0}^{\text{iter } 0}/N$, one can choose 0.0, but since λ is the simple average for ground state electronic energy by N, its final value which is what we are looking for is between [16] the lower boundary (that is, the H-like atom 1s state energy of the heaviest element, $-(\max Z_A)^2/2)$ and the upper boundary (that is, the lightest element, $-(\min Z_A)^2/(2\,n_{\text{shell}}^2)$ in the system, where n_{shell} is the neutral atomic HOMO main quantum number, e.g. 1 for hydrogen, 2 for carbon, oxygen, etc.). For example, in the presence of hydrogen in the system, the latter is -0.5 hartree for a general iterative algorithm; however, for our iteration here, we do not need $\lambda^{\text{iter } 0}$ in this way. Instead, see Equation 14 below. Another choice for the magnitude of $E_{\text{electr},0}^{\text{iter } 0}$ [16], for example, for close to neutral systems, is the sum of neutral atomic energies in free space for all atoms in the molecule, known for all elements in the periodic table. The starting point of Harris initial LCAO values [19,20] of iteration for HF-SCF algorithm is effectively used in, e.g., Gaussian 98 [21] and higher codes. The simple conversion is described in Equation 20 of Appendix 1. Let us suppose that we have the mth (≥ 0th) iteration for all LCAO parameters $d_k^{\text{iter } m}$. For the $(m + 1)$th iteration,

$\rho_0^{\text{iter } m}$ can be calculated for any $\mathbf{r}_1$ by Equation 6

$$(12)$$

$\rho_0^{\text{iter } m}$ must be normalized to N via Equation 1 or 8.

$$(13)$$

In the latter step, the normalization means that all $d_k^{\text{iter } m}$ will be divided with a proper constant and overwrite as a standard normalization trick, that is, if the integral in Equation 8 via Equation 6 yields a value c, not necessarily N, then $d_k^{\text{iter } m} := d_k^{\text{iter } m} \text{sqrt}(N/c)$. Based on Equation 2, calculate the mth iteration ground state electronic energy and chemical potential

$$\lambda^{\text{iter } m} \equiv E_{\text{electr},0}^{\text{iter } m}/N = \left(T[\rho_0^{\text{iter } m}(\mathbf{r}_1) + V_{\text{ee}}\rho_0^{\text{iter } m}(\mathbf{r}_1)] + \int v(\mathbf{r}_1)\rho_0^{\text{iter } m}(\mathbf{r}_1)d\mathbf{r}_1 \right)/N$$

$$(14)$$

using the chosen DFT functionals for T and V_{ee}, see e.g., Equations 4 and 5, where n is also an input at the

beginning, specified before the iteration starts. Using Equation 11, the rearrangement of Equation 7 yields

$$\sum_{k=1...L} d_k^{\text{iter } m+1} \int \left(v(\mathbf{r}_1) - \lambda^{\text{iter } m}\right) b_i(\mathbf{r}_1) b_k(\mathbf{r}_1) d\mathbf{r}_1$$
$$= -(1/2)\partial T\left[\rho_0^{\text{iter } m}(\mathbf{r}_1)\right]/\partial d_i - (1/2)\partial V_{ee}\left[\rho_0^{\text{iter } m}(\mathbf{r}_1)\right]/\partial d_i \tag{15}$$

for $i = 1,...,L$, where the left-hand side of Equation 9 and 10 comes from the particular DFT functionals used, and the right-hand side is a demonstration if e.g. Equations 4 and 5 are chosen for functional approximation. Equation 15 can be set up for lin-solver using the iteration $\rho_0^{\text{iter } m}$ for the right-hand side and the value $\lambda^{\text{iter } m}$ in the left-hand side. Notice that in the left-hand side, $d_k^{\text{iter } m+1}$ enters instead of $d_k^{\text{iter } m}$. Equation 15 is a linear equation system for $d_k^{\text{iter } m+1}$ for $k = 1,...,L$, with matrix $[\int(v(\mathbf{r}_1) - \lambda^{\text{iter } m})b_i(\mathbf{r}_1)b_k(\mathbf{r}_1)d\mathbf{r}_1]_{i,k}$ and parameter column vector $[-(1/2)\partial T[\rho_0^{\text{iter } m}(\mathbf{r}_1)]/\partial d_i - (1/2)\partial V_{ee}[\rho_0^{\text{iter } m}(\mathbf{r}_1)]/\partial d_i]_i$. Equation 15 is not linear with respect to $d_k^{\text{iter } m}$ for $k = 1,...,L$ because the algebraic form of ρ_0-nonlinear functionals $T[\rho_0]$ and $V_{ee}[\rho_0]$, but their values are known from the previous cycle. A simple lin-solver yields the $(m+1)$th iteration for LCAO parameters $d_k^{\text{iter } m+1}$. In the programming algorithm, replace the old $d_k^{\text{iter } m}$'s by this $(m+1)$th iteration of $d_k^{\text{iter } m+1}$'s, and the next cycle can be done by proceeding again from Equation 12. The algorithm can be stopped if $|E_{\text{electr},0}^{\text{iter } m} - E_{\text{electr},0}^{\text{iter } m-1}|$ is smaller than a threshold value, presumably less than the chemical accuracy 1 kcal/mol, or if stationary LCAO parameter set is reached, that is, $|d_k^{\text{iter } m+1} - d_k^{\text{iter } m}| < \varepsilon_{\text{threshold}}$ for all k's. We mention that the trick with re-normalization as in Equation 13 during another kind of iteration was tested and analyzed in [16] for $n = 1$ in Equations 4 and 5. An additional reason which supports the core of iteration in Equation 15 is that the left-hand side is the direct calculation for V_{ne} (the block containing $v(\mathbf{r}_1)$) which is close to the real value if one starts with reasonable LCAO parameters, and, as mentioned above, V_{ne} constitutes the large part of $E_{\text{electr},0}$, provided by the virial theorem, that is, simple and reasonable initial LCAO parameters put the iteration on a right track. Figure 1 shows the step-by-step algorithm described above as recipe: how the numbered list of equations/algorithms to be solved. It allows the interested reader to quickly extract the key ideas and build a prototype of the method.

Another alternative of Equation 15 is when the branch containing $d_k^{\text{iter } m+1}\lambda^{\text{iter } m}$ on the left-hand side is pulled to the right-hand side, but with using the previous iteration, $d_k^{\text{iter } m}\lambda^{\text{iter } m}$, to have values in hand for all variables on the right-hand side, the lin-solver must be applied accordingly. A few particular comments for the integration follows: the right-hand side of Equation 15 and the linear equation system for d_k's must be

evaluated and solved, respectively, in every cycle. But in the left-hand side, the L^2 pieces of the integrals $\int v(\mathbf{r}_1)b_i(\mathbf{r}_1)b_k(\mathbf{r}_1)d\mathbf{r}_1$ and $\int b_i(\mathbf{r}_1)b_k(\mathbf{r}_1)d\mathbf{r}_1$ must be evaluated at the beginning only. The cross terms $b_i(\mathbf{r}_1)b_k(\mathbf{r}_1)$ for $i,k = 1,...,L$ of the basis functions map the nuclear frame *ala* linear algebra. Notice that we did not need eigensolver for this algorithm, only lin-solver as opposed to HF-SCF or KS algorithms. Up to this point, if one uses Equations 4 and 5, that is, using the right-hand side of Equations 9 and 10, or any existing functional approximation (to the knowledge of the author), the integrals on the right-hand side of Equation 15 can be solved only numerically for both GTO and STO basis sets (until special tricks and forms of functionals are worked out), the left-hand side can be solved numerically and analytically for GTO basis sets, and numerically only for STO basis sets. The opportunity for analytical evaluation for GTO basis sets is based on the fact that multiplication of GTO functions yields GTO functions, the standard usage in HF-SCF-based algorithms. Equation 6 can be evaluated numerically and analytically for GTO basis sets, and numerically only for STO basis sets. Generally, the GTO functions provide the opportunity for analytical integration in DFT and HF-SCF-based algorithm (e.g., KS) in many, but not all cases; however, on the other hand, the STO functions also make analytical integration possible in some cases, although these are not in practice in that extent as the GTO functions. The STO basis sets provide faster convergence and smaller L values by the known fact that the exact atomic wavefunctions are STO-type functions, as well as for example, the simplest mimic of STO is its approximations by these GTO functions (recall the STO-3G basis set).

Remark on the choice and speed of convergence with different functional approximations

We talk about the speed of convergence in relation to the most important quantity: the accuracy of the energy. With exact (or at least excellent approximate) DFT functional for T and V_{ee}, the algorithm in principle is not restricted to the vicinity of stationary points. So, if the energy is accurate, then the stationary or equilibrium geometry is also accurate, providing excellent potential energy surfaces (PES) for frequency calculation toward excellent prediction of thermodynamic behavior, i.e., to excellently describe molecular motions in general, the ultimate goal in quantum or computation chemistry. To set the first variation of L^* equal to zero in Equation 2 leads to the three spatial dimension integral equations analyzed, for example, with using LCHFD in [4]. The system in Equations 7 and 8 is a substitute for the $4N$ spin-orbit dimension eigenvalue partial differential electronic Schrodinger equation to calculate the ground state electronic energy and density. Equations 7 and 8
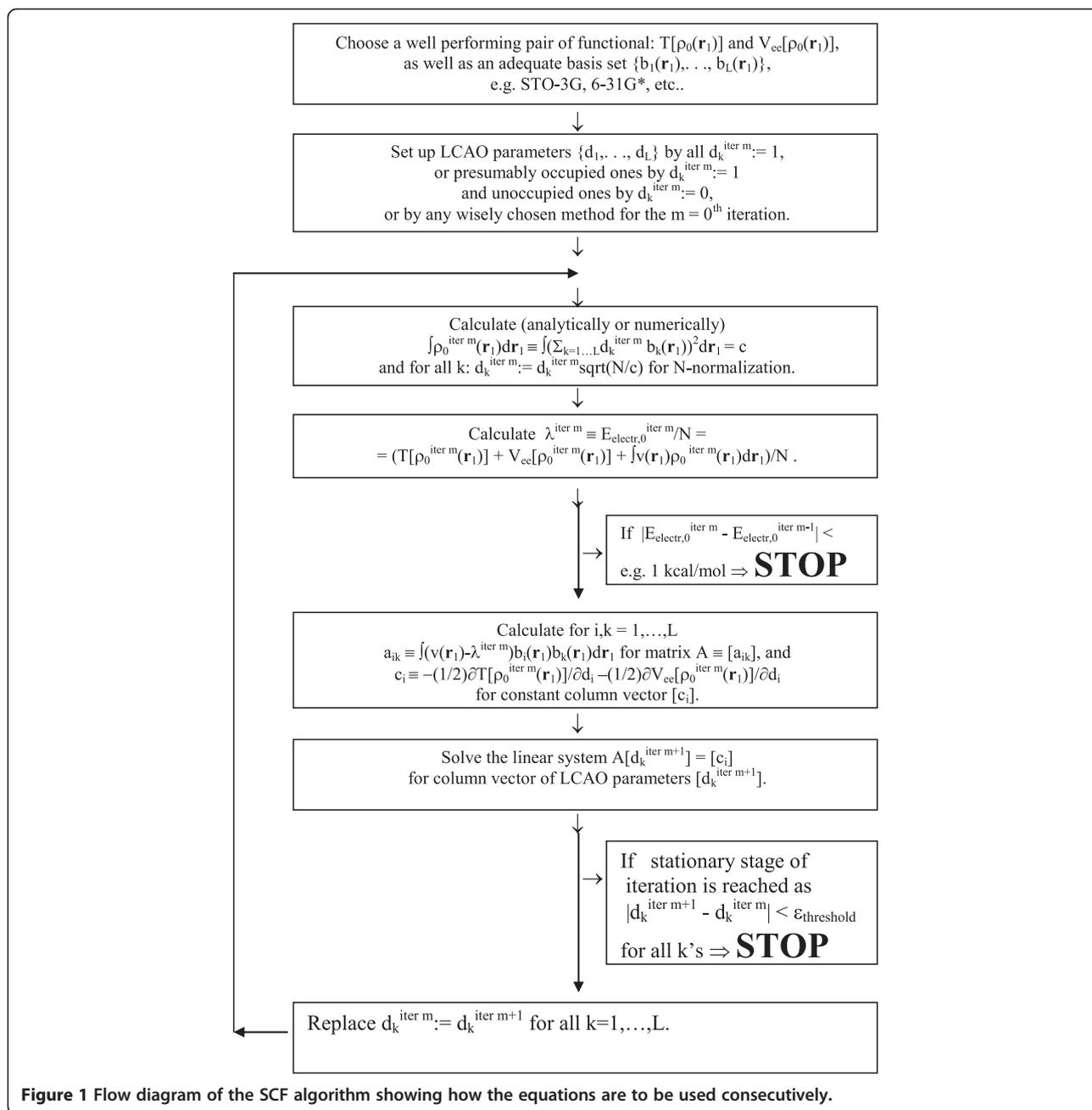
Choose a well performing pair of functional: $T[\rho_0(\mathbf{r}_1)]$ and $V_{ee}[\rho_0(\mathbf{r}_1)]$,
as well as an adequate basis set $\{b_1(\mathbf{r}_1),\ldots, b_L(\mathbf{r}_1)\}$,
e.g. STO-3G, 6-31G*, etc..

$\downarrow$

Set up LCAO parameters $\{d_1,\ldots, d_L\}$ by all $d_k^{\text{iter m}} := 1$,
or presumably occupied ones by $d_k^{\text{iter m}} := 1$
and unoccupied ones by $d_k^{\text{iter m}} := 0$,
or by any wisely chosen method for the $m = 0^{\text{th}}$ iteration.

$\downarrow$

Calculate (analytically or numerically)
$\int \rho_0^{\text{iter m}}(\mathbf{r}_1)d\mathbf{r}_1 \equiv \int (\Sigma_{k=1\ldots L} d_k^{\text{iter m}} b_k(\mathbf{r}_1))^2 d\mathbf{r}_1 = c$
and for all k: $d_k^{\text{iter m}} := d_k^{\text{iter m}} \sqrt{N/c}$ for N-normalization.

$\downarrow$

Calculate $\lambda^{\text{iter m}} \equiv E_{\text{electr},0}^{\text{iter m}}/N =$
$= (T[\rho_0^{\text{iter m}}(\mathbf{r}_1)] + V_{ee}[\rho_0^{\text{iter m}}(\mathbf{r}_1)] + \int v(\mathbf{r}_1)\rho_0^{\text{iter m}}(\mathbf{r}_1)d\mathbf{r}_1)/N$.

$\rightarrow$ If $|E_{\text{electr},0}^{\text{iter m}} - E_{\text{electr},0}^{\text{iter m-1}}| <$
e.g. 1 kcal/mol $\Rightarrow$ **STOP**

Calculate for $i,k = 1,\ldots,L$
$a_{ik} \equiv \int (v(\mathbf{r}_1)-\lambda^{\text{iter m}})b_i(\mathbf{r}_1)b_k(\mathbf{r}_1)d\mathbf{r}_1$ for matrix $A \equiv [a_{ik}]$, and
$c_i \equiv -(1/2)\partial T[\rho_0^{\text{iter m}}(\mathbf{r}_1)]/\partial d_i -(1/2)\partial V_{ee}[\rho_0^{\text{iter m}}(\mathbf{r}_1)]/\partial d_i$
for constant column vector $[c_i]$.

$\downarrow$

Solve the linear system $A[d_k^{\text{iter m+1}}] = [c_i]$
for column vector of LCAO parameters $[d_k^{\text{iter m+1}}]$.

$\rightarrow$ If stationary stage of
iteration is reached as
$|d_k^{\text{iter m+1}} - d_k^{\text{iter m}}| < \varepsilon_{\text{threshold}}$
for all k's $\Rightarrow$ **STOP**

Replace $d_k^{\text{iter m}} := d_k^{\text{iter m+1}}$ for all $k=1,\ldots,L$.

Figure 1 Flow diagram of the SCF algorithm showing how the equations are to be used consecutively.

solve the single Euler equation, which follows from orbital-free DFT; *c.f.*, for example, equation (12) in Wang and Carter's review article [8] or equation (4) of Karasiev et al. [9]. We emphasize that this work here is not a review on functional approximations, like [1] on wavefunction-based methods (HF-SCF, configuration interactions (CI), correlation calculations as MP2, CCSD, etc.) or [2] on general DFT and KS theory, or the review book in [22] summarizing the performance of exchange-correlation functionals in KS formalism. Review article on LCHFD can be found in [4], and the review articles in [8] and [9] are excellent reviews on orbital-free kinetic energy functionals. As we mentioned, the only reason to pick the LCHFD in Equations 4 and 5 is the central role of function series in mathematical approximation; their disadvantages is the slow convergence. In Equations 4 and 5, the first $(j = 1)$ terms can be the approximate main terms for T and V_{ee} energy, respectively, as well as they can serve as main correctional terms only. In [6], Equations 4 and 5 were used as correctional terms; the $n = 4$ truncation was based on this fact. The most thorough test on moment functionals is in [10]; however, it should be noted that Ayers et al. applied moment functionals to the ionization potential [23], and there is a

rather comprehensive test of moment functionals in [24]. Also importantly, Equations 4 and 5 depend only on one-electron density and do not depend, for example, on HF or KS MOs, that is, orbital-free formalism [7-11,25-28], making the reduction of dimensionality to 3 possible. However, the procedure in the simple Equations 4 and 5 is not rigorous because as has been extensively discussed by Liu et al. [29] or Parr et al. [30], the expansion used in Equations 4 and 5 corresponds to a local approximation. As a consequence, using only one-electron density or orbital-free formalism, the non-local approximations provide faster convergence.

We mention that in the KS formalism, beside the main idea of introducing the concept of exchange-correlation in calculating energy V_{ee} (approximating with local, non-local, spin and spinless, gradient corrected and hybrid functionals), the other effective [2] device was to use the kinetic operator (T^{op}) for KS orbitals (as analogues to MOs in the HF-SCF formalism). As a consequence, the derivatives of the KS orbitals in kinetic terms and derivatives of ρ_0 in exchange correlation functionals are included, showing faster convergence in functional approximation. If we switch from the $3N$ (or by spin pairing effect), the $3N/2$ or $3(N+1)/2$ dimensional KS kinetic operator to functionals having three spatial dimensions, for example, the $T[\rho_0(\mathbf{r}_1)] \approx \int [c_F \rho_0^{5/3} + (\lambda/8)|\nabla_1 \rho_0|^2/\rho_0 + \ldots] d\mathbf{r}_1$ form is the so-called Weizsacker gradient correction [2,31]. In the $TF + \lambda W$ theories, the estimation for λ is between 1/9 and 1/5 [2], and a very popular choice, early on, was $\lambda = 1$. On the other hand, as was discussed e.g. in [5,9], the Weizsacker functional

$$T[\rho_0]^W \equiv A_0 \int |\nabla_1 \rho_0|^2/\rho_0 d\mathbf{r}_1 \qquad (16)$$

can be considered as main term as $T[\rho_0(\mathbf{r}_1)] \approx T[\rho_0]^W +$ correction. Particularly, for H-like atoms ($N = M = 1$) or one-electron molecular systems ($N = 1$, $M > 1$) [5], $T[\rho_0(\mathbf{r}_1)] = (1/8)\int |\nabla_1 \rho_0|^2/\rho_0 d\mathbf{r}_1$ holds exactly, and for systems $N > 1$, the correction is fundamental. The operator *nabla* provides faster convergence, and the correction can be via Equation 4, for example. The related modification for $\partial T[\rho_0]/\partial d_i$ in Equation 9 and for $\partial^2 T[\rho_0]/\partial d_i^2$ in Appendix 2 is straightforward, that is, the inclusion of $|\nabla_1 \rho_0|$ for example in the functional approximation for T. The Weizsacker form with one-electron density in Equation 6 as the main kinetic term and the HF-SCF or KS (the latter called non-interacting) as the kinetic energy term with HF-SCF one-electron density are compared in some algebraic respect in Appendix 3, showing strong similarity. The author thinks that this latter can be a crucial point in the convergence of orbital-free formalism based on Equations 2, 6, 7, and 8, as the other and already known property described in the next paragraph.

In the literature, there is an opinion that it is difficult to expand the Coulomb energy in terms of LCHFD or moment functionals. Recall what KS uses with classical Coulomb term [2,4,6],

$$J[\rho_0] \equiv (1/2) \int \rho_0(\mathbf{r}_1)\rho_0(\mathbf{r}_2) r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2, \qquad (17)$$

and $V_{ee} \approx J[\rho_0] + \int \varepsilon_{xc} \rho_0 d\mathbf{r}_1$, the origin of the huge literature on exchange-correlation energy. By this reason, instead of Equation 5, the alternative form is $V_{ee}[\rho_0(\mathbf{r}_1)] \approx J[\rho_0] +$ correction, and, for example, the correction can be via Equation 5 [6] or else [2,22]. The classical Coulomb term is the major one, and in e.g. the LCHFD formalism, the entire set of coefficients B falls into correction terms. The related modification for $\partial V_{ee}[\rho_0]/\partial d_i$ in Equation 10 and for $\partial^2 V_{ee}[\rho_0]/\partial d_i^2$ in Appendix 2 is straightforward. For example, for the former, the additional term entering to Equation 10, by adding J as main term into Equation 5, is $\int \rho_0(\mathbf{r}_2)(\partial \rho_0(\mathbf{r}_1)/\partial d_i) r_{12}^{-1} d\mathbf{r}_2 d\mathbf{r}_1$. A famous correction to J is the Dirac exchange functional approximation [2,32] $B_{Dirac} \int \rho_0^{4/3} d\mathbf{r}_1$, i.e., the first term in Equation 5 with different values for the constant than the one written after Equation 5. The known, relatively good long-range behavior of this non-local functional J as major term is well established in contrast to the local functional in Equation 5. Mathematically speaking, the threshold value of n is smaller in Equation 5 if J is present. In [6] and references therein, the approximation $J[\rho_0] \approx C_J[\int \rho_0^{6/5} d\mathbf{r}_1]^{5/3}$ is also discussed (see some more remarks in 'Some numerical illustration' section and Appendix 4) which, similar to Equation 5 as mentioned, allows numerical integration for GTO and STO basis sets as well, while $J[\rho_0]$ is traditionally evaluated effectively and analytically with GTO basis sets. The numerical restriction coming up using the classical Coulombic term in Equation 7 as the main part of V_{ee} is that the GTO basis set must be used for all terms in the corresponding expression to Equation 10. So, the entire algorithm, as well as the numerical integration, cannot be used for this term (coming from the presence of r_{12}^{-1}), only the above mentioned analytical one. But of course, the other terms (non-linear parts of functional approximations) can be evaluated only numerically. However, it must be emphasized that up today, the most accurate correction to $J[\rho_0]$ in relation to chemical accuracy for the different molecular systems is the exchange-correlation functionals in the huge literature on KS formalism. In this way, the correction can be achieved via the good performing and broadly tested exchange-correlation functionals to describe the so called Coulomb and Fermi holes caused by $J[\rho_0]$ in the HF-SCF or KS formalism, and since these are functions of ρ_0 in the integrand, the expressions change accordingly as counterparts of Equation 10. We emphasize that the exchange-correlation functionals as correction to term $J[\rho_0]$ are worked out in the formalism or framework

of KS eigenvalue differential equation system [2], see e.g., equations (5–13) and (14) in [22], so their conversion for V_{ee} in the formalism in Equation 2 or 7 needs to be done carefully: (1) these good approximate corrections relate somehow to (or acts beside) the kinetic term chosen in the KS formalism, that is, these sum to T^{op} in KS formalism and not to $T[\rho]$ in Equation 2. (2) These are parameterized and optimized for the KS equation system and not for Equations 7 and 8. (3) The HF-SCF approximation of ρ is used with KS orbitals and not Equation 6.

Even more importantly, Equations 14 and 15 reveal that for T and V_{ee}, any form of accurate and fast convergent approximation of density functional can be used as a substitute of Equations 4 and 5, making the SCF algorithm described above general. Up today, the $3N$ (more exactly $3N/2$ or $3(N+1)/2$) spatial dimension post-HF-SCF and KS methods have survived for direct calculations on molecular systems (to avoid the expensive few kind of CI ones). The three spatial dimension non-KS DFT methods described in Equation 2 are not direct routines yet, but only tests for different functional approximations for Equation 2 how it recovers the ground state electronic energy with using for example HF-SCF one-electron densities, i.e., these are still on theoretical ground only and not qualified yet for direct use in practice.

Some numerical illustration

We mention that in the step from Equation 2 to the practical Equations 7 and 8, in fact, there is an important theoretical point to stop [4] for considering the first variation δL^{*} $[\rho_0(\mathbf{r}_1)] = [\partial T[\rho_0]/\partial \rho_0 + \partial V_{ee}[\rho_0]/\partial \rho_0]\delta \rho_0 + \int(v(\mathbf{r}_1) - \lambda)\ \delta \rho_0\ d\mathbf{r}_1$ from Equation 2. If Equation 6 or other adequate form is used to expand ρ_0, one is able to switch from variable $\rho_0(\mathbf{r}_1)$ to (e.g., LCAO) parameter space $\{d_k\}$ belonging to an adequate basis set, and the minimization can be done via Equations 7 and 8. It is less practical, but theoretically important if one keeps the $\rho_0(\mathbf{r}_1)$ as variable. In some cases, the functionals can be written in the form $T[\rho_0(\mathbf{r}_1)] = \int t(\rho_0)d\mathbf{r}_1$ and $V_{ee}[\rho_0(\mathbf{r}_1)] = \int v_{ee}(\rho_0)d\mathbf{r}_1$, for example, the approximate functionals T^W and J in Equations 16 and 17 belong to this category with $t^W(\rho_0) \equiv A_0|\nabla_1\rho_0|^2/\rho_0$ and $j(\rho_0) \equiv (1/2)\rho_0$ $(\mathbf{r}_1)\int\rho_0(\mathbf{r}_2)r_{12}^{-1}d\mathbf{r}_2$, respectively, as well as the exact functional V_{ne} in Equation 3. However, the LCHFD in the right-hand sides of Equations 4 and 5 do not fall in this category for $n > 1$, but they do for $n = 1$, e.g., $t^{TF}(\rho_0) \equiv c_F\ \rho_0^{5/3}$. In this way, the variation is $\delta L^{*}[\rho_0(\mathbf{r}_1)] = \int(\partial t$ $(\rho_0)/\partial \rho_0 + \partial v_{ee}(\rho_0)/\partial \rho_0 + v(\mathbf{r}_1) - \lambda)\ \delta \rho_0\ d\mathbf{r}_1$, and since the $\delta \rho_0$ is arbitrary, it follows that the quantity in the brackets must be zero, yielding

$$\partial t(\rho_0)/\partial \rho_0 + \partial v_{ee}(\rho_0)/\partial \rho_0 + v(\mathbf{r}_1) = \lambda. \quad (18)$$

One must solve Equation 18 for $\rho_0(\mathbf{r}_1,\lambda) \geq 0$ and choose that λ for which Equation 1 normalizes ρ_0 to N.

That ρ_0 is what we are looking for, and $E_{electr,0} = N\lambda$. $E_{electr,0}$ can also be obtained from L^{*} if this normalized ρ_0 is substituted in Equation 2 (the fourth term drops). Equation 18 is an exact substitute of the electronic SE if $t(\rho_0)$ and $v_{ee}(\rho_0)$ are known exactly, but only approximate functions are in hand yet with the even more problematic algebraic forms and their problematic analytic or numerical way to the solution. Equation 18 has been analyzed for LCHFD in [4]; this can be called the 'minimize and solve' way. Technically, if e.g. Equation 16 is used in approximating Equation 18, the t includes (or function of) the derivative $\partial\rho_0/\partial x$, etc., and one needs to evaluate $\partial t/\partial\rho_0$. As a consequence, e.g. the term $(\partial/\partial\rho_0)$ $(\partial\rho_0/\partial x)$ comes up. These types of terms can be evaluated with the straightforward, but not trivial $(\partial/\partial\rho_0)(\partial\rho_0/\partial x) = (\partial/\partial\rho_0)(\partial x/\partial\rho_0)^{-1} = -(\partial\rho_0/\partial x)^2(\partial^2 x/\partial\rho_0^2)$, i.e., using the derivative of reciprocal function, wherein the inverse function $x(\rho_0)$ is also necessary, the latter indicates the algebraic complexity involved in Equation 18.

Another, called the 'solve and minimize' way is the counterpart of Equation 18, that is when the electronic SE is multiplied from left by the complex conjugate of wavefunction (Ψ_k^{*}) and integrated such as keeping the N-normalized variable $\rho_0(\mathbf{r}_1)$ [4,5,16], yielding integrand equation $t(\rho_k) + v_{ee}(\rho_k) + (v(\mathbf{r}_1) - E_{electr,k})\ \rho_k = 0$ and integral equations $\int(t(\rho_k) + v_{ee}(\rho_k) + v(\mathbf{r}_1)\rho_k - E_{electr,k}\ \rho_k)d\mathbf{r}_1 = \int(t(\rho_k) + v_{ee}(\rho_k) + v(\mathbf{r}_1)\rho_k)d\mathbf{r}_1 - NE_{electr,k} = 0$ for the kth excited state, both are arranged to have zero on the right-hand side. Solve the integrand equation for $\rho_0(\mathbf{r}_1,E_{electr,0})$ considering $E_{electr,0}$ as variable, and multiply it with a constant to normalize it to N via Equation 1. This constant is 1 if the functionals are exact. Next, find that $E_{electr,0}$, where the energy integral $E(E_{electr,0}) \equiv (1/N)\int(t(\rho_0(\mathbf{r}_1,E_{electr,0})) + v_{ee}$ $(\rho_0(\mathbf{r}_1,E_{electr,0})) + v(\mathbf{r}_1)\ \rho_0(\mathbf{r}_1,E_{electr,0}))d\mathbf{r}_1$ has its minimal value (via analytically or numerically solving $\partial E(E_{electr,0})/\partial E_{electr,0} = 0$), that is, the $E_{electr,0}$ we are looking for [16]. E $(E_{electr,0}) = E_{electr,0}$ if the functionals are exact [16]. Notice that in the latter formalism, the correspondence to the above notations is $t/N \rightarrow t$, $v_{ee}/N \rightarrow v_{ee}$ and $v/N \rightarrow v$. Coming from that, the wavefunction is normalized to 1, while the ρ_0 is normalized to N, as well as the way how the DFT forms in Equations 2 and 3 as defined in the literature. This latter fact is also a proof for the relationship $E_{electr,0} = N\lambda$. The user must be very careful when manipulating with t and $\int t$ or v_{ee} and $\int v_{ee}$ in these algorithms, see note under (21) of Appendix 1.

The interesting property of approximation in Equation 16 is discussed in Appendix 3, that is, similar algebraic form acts as of the HF-SCF and KS kinetic energy, and on other hand, the 'milestone' status of approximation in Equation 17 is well known with all of its advantages and disadvantages. If the exact Equation 3 and the approximate Equations 16 and 17 are chosen for L^{*} in Equation 2 along with the expansion in Equation 6, the

approximation of L^* comes out as a pure polynomial of multi variable LCAO parameters $\{d_k\}$. This polynomial is a linear combination of integer powers such as the second-order terms $(d_k^2, d_k d_{k'})$ via Equations 3, 16, and 25 of Appendix 3, fourth-order terms $(d_k^4, d_k^3 d_{k'}, d_k^2 d_{k'}^2, d_k^2 d_{k'} d_{k''}, d_k d_{k'} d_{k''} d_{k'''})$ via Equation 17, as well as the fourth term in Equation 2 which yields third-order terms $(\lambda d_k^2, \lambda d_k d_{k'})$ and the single particular first-order term λN. The coefficients of this polynomial can be calculated analytically in a standard way if GTO basis set $\{b_k(\mathbf{r}_1)\}$ is used for evaluating the integrals. In the space of independent variables $\{d_k\}$, the polynomial degree of this approximate L^* is 4, of the system $\partial L^*/\partial d_i$ and $\partial L^*/\partial \lambda$ in Equations 7 and 8 is 3, and of W_{im} is 2; compare the latter to the messy form seeded by LCHFD in Appendix 2. The idea that many powers are missing in this polynomial of total order of 4 (e.g., no d_k^3 or λ^4 alone, etc.) is minor. But it is very important to note that when this polynomial approximation is chosen for the system in Equation 15, the integrals in its right-hand side do not have to be evaluated again and again in every cycle of iteration (e.g., numerically by a non-linear property as it can be the case in the general DFT functionals). However, one needs to evaluate the linear combinations with better values of $\{d_k^{\text{iter } m}\}$ only; the coefficients (the integrals on functions $\{b_k(\mathbf{r}_1)\}$ and $v(\mathbf{r}_1)$ of polynomial) have to be evaluated at the beginning only as the case for the left-hand side in Equation 15.

Some researchers are skeptical that orbital-free DFT will ever work (at least in the sense of being a competitor to conventional DFT calculations). But it does offer the prospect of treating truly massive systems (e.g., microscopic hunks of metal), and its niche is orthogonal

to conventional Kohn-Sham DFT for this reason. One of the biggest issues with orbital-free DFT is that the usual algorithms for converging the equations, while robust in principle, converge very slowly in practice. Also, good scaling is irrelevant if conditioning is poor (leading to a large prefactor).

A calculation and proof test on atoms and molecules in [16] for $n = 1$ in Equations 4 and 5 has yielded that $A_1 = 0.866027c_F$, and $B_1 = 0.628060$ $(2^{-1/3}(N-1)^{(2/3)})$. Using these, the calculation on ionization potentials of atoms $(A \rightarrow A^+)$ is demonstrated on Figure 2 (with optimized parameters from [16], ordered with increasing atomic number, Z, and number of electrons, N). Equation 4 with $n = 1$ cannot account for chemical bond, so the atoms can be tested only with $n = 1$. The important is the direct calculation for ρ_0 and $E_{\text{electr},0}$, yielding a non-HF-SCF one-electron density (Appendix 1). Another calculation and proof test on atoms was made in [6] for $n = 3$ in Equations 4 and 5; however, they used HF-SCF one-electron density and accurate $E_{\text{electr},0}$ to fit the parameters of Equations 4 and 5, i.e., not a direct calculation for ρ_0 and $E_{\text{electr},0}$, but a fit after an *ab intio* calculation. Another difference is that instead of Equation 5, they [6] used the above mentioned form $V_{ee}[\rho_0(\mathbf{r}_1)] = J[\rho_0] + \Sigma_{j\,=\,1,\ldots n} C_{xj}[\int \rho_0^{[1\,+\,1/(3j)]} d\mathbf{r}_1]^j$ with $J[\rho_0] \approx C_J[\int \rho_0^{6/5} d\mathbf{r}_1]^{5/3}$ and $n \rightarrow \infty$. As it is used in this paper, in Equations 4 and 5, and the corresponding ones, the equalities stand if $n \rightarrow \infty$ and n in the summation means the truncation. In this way, the classical Coulomb repulsion energy $J[\rho_0]$ was modeled [6] ala orbital-free DFT, and Equation 5 was used to estimate the exchange energy, $E_x[\rho_0]$ (recall the Dirac form). Furthermore, we draw attention to the

Figure 2 Ionization potentials of atoms by CI, HF-SCF/6-31G*, and Equations 2 to 5 ($n = 1$).
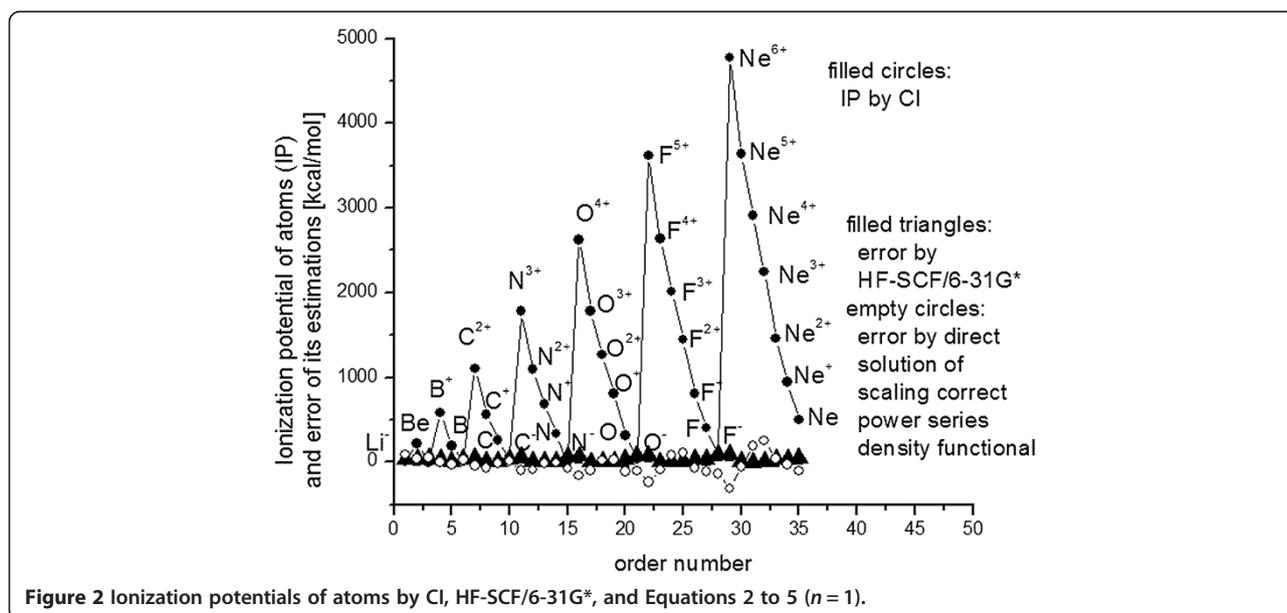
fact that this latter form with estimating J by a term with power 6/5 is also an example for alternative moment functional to Equation 5, as well as Equations 7 and 10 which can again be changed accordingly. Finer fit for the parameters in Equations 4 and 5 can be done as in [16], and the initial guess (with some simple trivial conversion) can be taken from [6]. We will report it in a later work extending with the important more powerful forms of functionals listed in 'Remark on the choice and speed of convergence with different functional approximations' section.

Summary

A self-consistent field numerical procedure has been described for any general and adequate density functional approximation to solve (minimize or optimize) the Lagrangian (Equation 2) of molecular systems accomplished by these functionals for obtaining ground state one-electron density (ρ_0) and electronic energy ($E_{\text{electr},0}$), based on the fact that the nuclear-electron attraction functional ($V_{\text{ne}}[\rho_0]$) *d*epends linearly on quadratic approximate (Equation 6) one-electron density. It is an iterative algorithm using lin-solver in every step. Particularly, the LCHFD was used for algebraic demonstration, but the discussion makes it clear that any approximate functional can be used in this recipe. The HF-SCF, post-HF-SCF and KS methods have been widely used and tested in contrast to the direct solution of DFT energy functionals, and this work tries to be a step forward by providing a tool for solution: to get the answer if direct solution of (non-KS) DFT functionals can compete in speed and accuracy with the HF-SCF-based and KS methods. For this, still accurate and general (molecular frame-independent) parameterization and several tests on different molecular systems must be done in the future.

Appendices

Appendix 1

The HF-SCF one-electron density with orto-normalized $f_1(\mathbf{r}_1), f_2(\mathbf{r}_1),...,f_{N/2}(\mathbf{r}_1)$ MOs, that is $\int f_i f_j d\mathbf{r}_1 = \delta_{ij} \equiv 1$ if $i = j$ and 0 if $i \neq j$, for closed shell (open shell is analogous) is $\rho_{0,\text{HF-SCF}}(\mathbf{r}_1) = 2\Sigma_{i = 1...N/2}[f_i(\mathbf{r}_1)]^2 = 2\Sigma_{i = 1...N/2}[\Sigma_{k = 1...L1}c_{ik}b_k(\mathbf{r}_1)]^2$, and $\int \rho_{0,\text{HF-SCF}}(\mathbf{r}_1)d\mathbf{r}_1 = N$. The integral

$$2\int\left(\sum_{i=1...N/2}f_i\right)^2 d\mathbf{r}_1 = 2\sum_{i=1...N/2}\int f_i^2 d\mathbf{r}_1$$
$$+4\sum_{i=1...N/2}\sum_{j=i+1...N/2}\int f_i f_j d\mathbf{r}_1$$
$$= 2\sum_{i=1...N/2}1 + 0 = N, \quad (19)$$

which says that for integral values, the $\Sigma_{i = 1...N/2}()^2$ and $[\Sigma_{i = 1...N/2}()]^2$ are interchangeable operators in this case, and the integral of square of sum of MOs yields the

number of electrons, N, also. After a HF-SCF algorithm, the LCAO approximation of the ith MO in the basis set $\{b_k(\mathbf{r}_1)\}_{k = 1...L1}$ is $f_i(\mathbf{r}_1) = \Sigma_{k = 1...L1}c_{ik}b_k(\mathbf{r}_1)$, and $\Sigma_{i = 1...N/2}f_i = \Sigma_{i = 1...N/2}\Sigma_{k = 1...L1}c_{ik}b_k(\mathbf{r}_1) = \Sigma_{k = 1...L1}(\Sigma_{i = 1...N/2}c_{ik})b_k(\mathbf{r}_1) = (1/\sqrt{2})\Sigma_{k = 1...L1}d_k b_k(\mathbf{r}_1)$, where we have assigned the value

$$d_k := (\sqrt{2})\sum_{i=1...N/2}c_{ik}. \quad (20)$$

From the evaluation of square of sum and (20), the 2 $(\Sigma_{i = 1...N/2}f_i)^2 = 2\Sigma_{i = 1...N/2}f_i^2 + 4\Sigma_{i = 1...N/2}\Sigma_{j = i + 1...N/2}f_i f_j = (\Sigma_{k = 1...L1}d_k b_k(\mathbf{r}_1))^2$ and from the middle part and right-hand side

$$\rho_{0,\text{HF-SCF}}(\mathbf{r}_1) + 4\sum_{i=1...N/2}\sum_{j=i+1...N/2}f_i(\mathbf{r}_1)f_j(\mathbf{r}_1)$$
$$= \left(\sum_{k=1...L1}d_k b_k(\mathbf{r}_1)\right)^2. \quad (21)$$

A HF-SCF algorithm calculates the LCAO coefficients $\{c_{ik}\}$, while the coefficients $\{d_k\}$ come from the assignment in (20), providing the form in right-hand side of (21), which is the form in Equation 6. Integrating both sides of (21) gives the value of N, again, because the double summation on the left-hand side contains only zeros by the orto-normality. (21) gives the relationship for a HF-SCF one-electron density (containing $L_1(N/2)$ coefficients) how to convert to the form of Equation 6 (containing L_1 coefficients). In the direct solution of DFT energy functional, the iterative algorithm, seeded by Equation 15, calculates the L ($\geq L_1$) coefficients, $\{d_k\}$, for Equation 6.

We also mention that the left-hand side of (21) is another good example for the general property such that the integrand of a functional $F_{\text{quantity}}[\rho] = \int g_a(\rho)d\mathbf{r}_1 = \int g_b(\rho)d\mathbf{r}_1 =$ "value" may not be the same (i.e., $g_a \neq g_b$), but they yield the same value for a certain quantity. It is a simple known property in the theory of Riemann integrals, but interesting in its relation to molecular physics in DFT. The consequence is that when switching the integro-differential DFT equations to density functionals, some terms in the integrand can give zero values, but they have a role to shape the density [4,5,16]. In this case, the functional counting the number of electrons ($\int \rho_{\text{approx}}d\mathbf{r}_1 = N$) for the first term in the left-hand side of (21) as well as for the entire left-hand side falls into this category ($\rho_{0,\text{HF-SCF}} \neq \rho_{0,\text{Eq.6}}$ if $L = L1$, but $\int \rho_{0,\text{HF-SCF}}d\mathbf{r}_1 = \int \rho_{0,\text{Eq.6}}d\mathbf{r}_1 = N$). Another example for kinetic energy operator in this respect is mentioned in [5]: that is based on the interesting property [5] of the one-electron density such as $\int \nabla_1^2 \rho_0(\mathbf{r}_1)d\mathbf{r}_1 = 0$. This latter holds not only for the exact one-electron density but also for any set of optimized (and not-optimized) LCAO parameters for the form in Equation 6 and HF-SCF or KS form of electron

densities. The proof is elementary, only the rule of partial integration must be applied along with the property such as the one-electron density and the MOs vanish at infinite spatial coordinates.

Appendix 2

The elements of the Jacobian matrix (W_{im}) generated by Equations 4 and 5, and 9 and 10 are $W_{im} \equiv \partial^2 L^*/(\partial d_i \partial d_m) =$

$$= \sum_{j=1,\dots n}\left((1+2/(3j))^2\right)j(j-1)A_j\left[\int\rho_0^{[1+2/(3j)]}dr_1\right]^{j-2}$$
$$\int\rho_0^{2/(3j)}\rho_{0i}dr_1\int\rho_0^{2/(3j)}\rho_{0m}dr_1$$
$$+\sum_{j=1,\dots n}(1+2/(3j))jA_j\left[\int\rho_0^{[1+2/(3j)]}dr_1\right]^{j-1}\int((2/(3j))$$
$$\rho_0^{(2/(3j)-1)}\rho_{0i}\rho_{0m}+\rho_0^{2/(3j)}\rho_{0im})dr_1$$
$$+\sum_{j=1,\dots n}\left((1+1/(3j))^2\right)j(j-1)B_j\left[\int\rho_0^{[1+1/(3j)]}dr_1\right]^{j-2}$$
$$\int\rho_0^{1/(3j)}\rho_{0i}dr_1\int\rho_0^{1/(3j)}\rho_{0m}dr_1$$
$$+\sum_{j=1,\dots n}(1+1/(3j))jB_j\left[\int\rho_0^{[1+1/(3j)]}dr_1\right]^{j-1}\int((1/(3j))$$
$$\rho_0^{(1/(3j)-1)}\rho_{0i}\rho_{0m}+\rho_0^{1/(3j)}\rho_{0im})dr_1$$
$$+\int(\nu(r_1)-\lambda)\rho_{0im}dr_1 \; for \; i,m=1,\dots,L$$

$$W_{i,L+1}=W_{L+1,i}\equiv\partial^2L^*/\partial d_i\partial\lambda=-\int\rho_{0i}dr_1 \text{ for } i \qquad (22)$$
$$=1,\dots,L \qquad (23)$$
$$W_{L+1,L+1}\equiv\partial^2L^*/\partial\lambda^2=0. \qquad (24)$$

Some miscellaneous properties of the equations in (22) to (24) are the following: W is symmetric, so to save time in running the program, the lower diagonal should be copied from the upper one or vice versa instead of re-calculating, as well as there are many common multipliers (integrals) in this expression, and of course, each should be calculated only once for all terms to insert. One should also notice that in (22) terms with $[\dots]^{j-1}$ and $[\dots]^{j-2}$ for $j = 1$ and 2, respectively, are unity, so the integral in square bracket should not be calculated to save time, and similarly, for $j = 1$, the terms with factor $(j - 1)$ zero out.

If the LCHFD in Equations 4 and 5 is chosen, Equation 2 with the help of Equation 3 acquires the powers for the defined LCAO parameters (d_k's) via Equation 6. In L^*, the d_k parameters obtain the integer and non-integer power values between 1 and maximum $2(1 + 2/(3n))n = 2(n + 2/3) = 9.333$ for $n = 4$ for example, roughly and generally $2n + 1$. It means that the L^*, that we have to optimize via Equations 7 and 8, is an $L + 1$ dimensional polynomial with 'variable vector' $\{d_k\}_{k=1\dots L+1}$ (which is the 'parameter vector' for ρ_0 in Equation 6) with roughly the degree of about $2n + 1$ if truncation at $j = n$ is taken, and hopefully, the truncation not much larger than $n = 4$ [6] will provide an enough flexible function to calculate the ground state electronic energy and one-electron density for molecular systems. For HF-SCF correction (correlation calculation), $n = 4$ is enough [6] in

Equations 4 and 5 for full T and V_{ee} values $n > 4$ are necessary. The coefficients to d_k come from integrating certain powers of linear combinations of the basis functions $b_k(\mathbf{r}_1)$, see note on the non-integer powers as well as on GTO and STO basis sets in the text.

Appendix 3

The expression $(\partial\rho_0(\mathbf{r}_1)/\partial x)^2/\rho_0(\mathbf{r}_1) = 4(\Sigma_{k=1\dots L}d_k\partial b_k(\mathbf{r}_1)/\partial x)^2$, immediately coming from Equation 6, expands the Weizsacker kinetic energy as

$$T[\rho_0(\mathbf{r}_1)]^W = (1/8)\int|\nabla_1\rho_0|^2/\rho_0\,d\mathbf{r}_1$$
$$= (1/2)\int\left[\left(\sum_{k=1\dots L}d_k\partial b_k(\mathbf{r}_1)/\partial x\right)^2+.+.\right]d\mathbf{r}_1, \qquad (25)$$

where the '+.' means the analogous additional term but with respect to y and z derivative, respectively. Despite the divisor ρ_0, T^W is a second-order algebraic expression with respect to LCAO parameters, d_k's, N-normalized via Equation 6, a relatively simple formula, as well as for example it can be evaluated analytically with using GTO basis set for $\{b_k(\mathbf{r}_1)\}$. We mention the close algebraic relationship to HF-SCF or KS form of kinetic energy, which shows algebraically why the Weizsacker form can be a main term: the (e.g. closed shell) HF-SCF or KS kinetic energy is $T^{HF\text{-}SCF \; or \; KS} = 2\Sigma_{i=1\dots N/2}\int f_i(-\nabla_1^2/2)f_i d\mathbf{r}_1 = \Sigma_{i=1\dots N/2}\int|\nabla_1 f_i|^2 d\mathbf{r}_1 = \Sigma_{i=1\dots N/2}\int[(\partial f_i/\partial x)^2+.+.]d\mathbf{r}_1$, where $f_i \equiv \Sigma_{k=1\dots L1}c_{ik}b_k(\mathbf{r}_1)$ is the ith spatial MO square-normalized to unity. Finally,

$$T^{HF\text{-}SCF \; or \; KS} = \sum_{i=1\dots N/2}\int\left[\left(\sum_{k=1\dots L1}c_{ik}\partial b_k(\mathbf{r}_1)/\partial x\right)^2 +.+.\right]d\mathbf{r}_1, \qquad (26)$$

i.e., both T^W and $T^{HF\text{-}SCF \; or \; KS}$ are expressed with the linear combination of value set $\{\int(\partial b_k(\mathbf{r}_1)/\partial u)(\partial b_{k'}(\mathbf{r}_1)/\partial u)d\mathbf{r}_1\}_{k,k'}$ for $u = x, y$, and z. The argument about L and $L1$ in relation to T is the same as for ρ_0 described immediately after Equation 6, that is, $L > L1$ should be. By this property, we call the attention again that orbital-free DFT (seeding from Equations 2, 7, and 8) can take great advantage of the involvement of Weizsacker term (T^W) and classical Coulomb term (J) as main terms in $T[\rho_0]$ and $V_{ee}[\rho_0]$, respectively, as was broadly experienced via $T^{HF\text{-}SCF \; or \; KS}$ and J in HF-SCF and KS theory.

Appendix 4

The LCHFD expansion in Equations 4 and 5 is not unique, but there are alternatives. Accrediting $j = 1$ as major term or major correctional term, a fit for parameters in Equations 4 and 5 can be performed as in [16], and the initial guess (with some simple trivial conversion) can

be taken from [6]. An emerging task is to calculate the energies within the non-KS approximation using e.g. Equations 4 and 5 or other appropriate ones for at least first- and second-row atoms and selected diatomic molecules constructed from them. Furthermore, it has to be discussed whether or not this procedure leads to a universal functional or whether or not different parameters (e.g., *A*'s, *B*'s in Equations 4 and 5) minimize each particular physical case or group.

Abbreviations

AO: Atomic orbital; CI: Configuration interactions; DFT: Density functional theory; GTO: Gaussian-type (atomic) orbital; HF-SCF: Hartree-Fock self-consistent field; HK: Hohenberg-Kohn; HOMO: Highest occupied MO; KS: Kohn-Sham; LCAO: Linear combination of atomic orbitals; LCHFD: Linear combinations of homogeneous functionals of the density; MO: Molecular orbital; SE: Schrödinger equation; STO: Slaterian-type (atomic) orbital.

Competing interests

The author declares that he has no competing interests.

Authors' information

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