Symmetry preserving optimised effective potential theory (application to atoms)

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Abstract. In this paper, general symmetry properties of physical systems are used in order to produce a mapping of the external potential of a many electron system to its optimized effective potential (OEP). The so derived effective potential is used to calculate the OEP ground state energies and spin orbitals. Applications are made to atoms and ions and the results are compared to those of the exact Hartree-Fock approximation. The relative deviations from the exact HF theory ($\Delta E/E$) are of the order of $10^{-4}$. The same holds for molecules. One of the features of the present theory is that the many electron wave functions derived by the present method, transform according to the irreducible representations of the exact states.

1. Introduction

Symmetry is important in the many-electron problem as it gives the main features of the many-electron wave function, or in more technical terms, the energy eigenstates of the physical system under consideration, transform according to the irreducible representations (Irreps) of the symmetry group of the Hamiltonian. For this reason, it is an advantage for a perturbation theory to conform to this requirement. This means that the approximate Hamiltonian should be invariant under the same symmetry group as the exact one. Nevertheless, this fundamental aspect is ignored in most approximation theories. In fact, there is a good reason for this symmetry breaking: The approximate ground state energy is lower when symmetry breaking is allowed. We shall deal with this matter in more detail.

Among the most popular approximations for electronic structure calculations of atoms, molecules and solids are the Hartree-Fock approximation (HF) and Density Functional Theory (DFT) in its Kohn and Sham (KS) formulation. The first one, HF, is based on a well known variational principle and gives approximate solutions and energies, whereas the second one, DFT, in principle gives the exact ground state energy and density. The first method is a standard topic in Quantum Mechanics books, whereas on the second, there are already many special textbooks[1]. The advantage of the KS theory over HF is that it includes only local terms, whereas in HF the exchange operator is nonlocal. However, as recent calculations have shown, the optimized effective potential approximation (OEP) to HF gives states and energies very close to those of the exact HF. The advantage of OEP is that it involves only local potentials. The difficulty with this approximation is that the effective potential $V_{OEP}(r)$ of this theory cannot be found in a direct way. In fact one puts the constraint that the N-electron Slater determinant $|\Phi\rangle = |\phi_1,...,\phi_N\rangle$ is constructed by spin orbitals $|\phi_i\rangle$ obeying a Schroedinger type equation with
effective potential $V_{\text{eff}}(\mathbf{r})$ and therefore $|\Phi\rangle = |\Phi_{\text{veff}}\rangle$. Then one has to find the minimum of $E(V_{\text{eff}}) = \langle \Phi_{\text{veff}} | H | \Phi_{\text{veff}} \rangle$ with respect to $V_{\text{eff}}$. This procedure however is time consuming.

The original DFT theory was developed for ground state calculations by Kohn and his coworkers\cite{2,3}, but it was later extended to include excited states\cite{4,5,6,7} and time-dependent (TDFT) problems\cite{8}. Other recent developments in this field, especially in the context of the Optimized Effective Potential method (OEP)\cite{9} increased the accuracy and speed of DFT calculations. However, the accuracy of DFT is still limited, because the explicit form of the exchange and correlation energy as functional of the density are sufficiently accurate, although a lot of research work has been done in this field.

In both theories the Hamiltonian involves terms expressed as mappings of the electron density $\rho_\Phi(\mathbf{r}) = \langle \Phi | \hat{\rho}(\mathbf{r}) | \Phi \rangle$ and the density matrix $\rho_\Phi(\mathbf{r}, \mathbf{r}') = \langle \Phi | \hat{\rho}(\mathbf{r}, \mathbf{r}') | \Phi \rangle$, where $|\Phi\rangle$ is the lower energy eigenstate of the Hartree-Fock (see Appendix 1 for details) and KS theory (see Section 2). But electron densities and density matrices are bilinear forms of the wavefunction $|\Phi\rangle$ and therefore if one takes $|\Phi\rangle$ to belong to a multidimensional Irrep of the symmetry group $G$ of the exact Hamiltonian, then $\rho_\Phi(\mathbf{r})$ and $\rho_\Phi(\mathbf{r}, \mathbf{r}')$ in general, do not have the symmetry of the external potential $V(\mathbf{r})$ and neither does the effective Hamiltonian. This is obvious for the HF theory as the Hartree potential, $V_H(\mathbf{r})$, $V_H(\mathbf{r}; \Phi) = \int d^3 \mathbf{r}' \rho_\Phi(\mathbf{r}') \frac{1}{|\mathbf{r}' - \mathbf{r}|}$ (1)

is a linear mapping of the density whereas the exchange operator $\hat{V}_{xc}(\Phi)$ is a linear mapping of the density matrix. Thus, all asymmetries of the densities are transferred to those of the potentials.

We shall prove in Appendix 1 Theorem 1: There are no eigenstates of the Kohn and Sham (KS) and Hartree-Fock (HF) operators belonging to the multidimensional Irreps of the symmetry group of the Hamiltonian.

From the above theorem we conclude that the lower energy states of these approximation theories cannot have the proper transformation properties. Thus, formally we can make the statement that symmetry breaking lowers the ground state energy of the HF and KS theories. However, one can restrict the search for the energy minimum in the space of Slater determinants (Sladets) belonging to an Irrep $\Gamma$ of the symmetry group $G$ of the external potential\cite{4,5}. Thus, in the case of degenerate states one can talk about a minimizing subspace and not a single state. For this reason it is necessary to apply the corresponding subspace DFT theory\cite{4,5}, in which the various functionals are defined as traces in a subspace of certain dimension. In this case the subspace density is

$$\rho_\Gamma(\mathbf{r}) = \frac{1}{M_\Gamma} \sum_{m=1}^{M_\Gamma} \langle \Phi_m^\Gamma | \hat{\rho}(\mathbf{r}) | \Phi_m^\Gamma \rangle$$

where the summation is over the orthonormal basis of Irrep $\Gamma$. Note, that a change of the orthonormal basis of the subspace $M_\Gamma$ does not affect the left hand side\cite{10} as the above expression is the Trace of the density operator $\hat{\rho}(\mathbf{r})$ divided by the dimension of the subspace. Thus,

$$\rho_\Gamma(\mathbf{r}) = \frac{1}{M_\Gamma} Tr\{\hat{\rho}(\mathbf{r}), S_\Gamma\}$$

and as the trace is a mapping which depends only on the subspace, the density is invariant under transformations which map the subspace $S_\Gamma$ to itself, i.e., the above density belongs to the Identity Irrep of the symmetry group of the external potential. Thus the effective KS potential in this case will have the symmetry of the external potential and therefore one can develop HF and DFT theories where the effective potential preserves symmetry. The advantage is that the
minimizing states that one gets have the same transformation properties as the exact eigenstates of the physical system. One would argue that the problem of degeneracy can be overcome, by applying a small symmetry breaking perturbation. In this way the conventional ground state DFT is applicable and one can take the limit when the perturbation tends to zero. This means that one cannot use anymore only the symmetric part of the density in order to determine the effective potential. Then, the problem becomes extremely difficult for the numerical calculations as the perturbed effective potential does not regain its symmetry when the perturbation tends to zero. This is a consequence of the fact that the single state density does not tend to a density having the symmetry of the external potential. For this reason, in atoms, the practice was to use spherically symmetric potentials for both the HF and KS theories, long before the subspace theory was developed.

Another reason justifying the need of a symmetry preserving theory is that in order to use the HK or KS many electron states for higher order corrections, it is essential for the approximate states to have the same symmetry i.e. to belong to the same Irrep as the exact states, otherwise, many selection rules and other simplifications resulting from symmetry, like e.g. the Wigner-Eckhardt theorem \[11\], are not applicable.

Recently, we developed a symmetry preserving DFT theory where the KS potential is given as a direct mapping of the external potential \[12, 13\]. The same is true for the OEP theory. In fact the first order approximations of these theories coincide. The direct mapping theory was applied to molecules where the eigenstate energies obtained were very close to those of the exact HF as the relative deviation from HF \((\Delta E/E)\) was of the order of \(10^{-4}\). In this paper we shall apply this theory to atoms. An advantage of this theory is that the input KS potential in the calculations is known, whereas in standard DFT, it is expressed as a mapping of the electron density, which has to be determined self-consistently. In the present state of the theory, the parameters of the mapping of the external potential to the KS potential were determined variationally. Thus in a certain sense our method in its present implementation is closely related to the optimized effective potential approximation.

It is useful here to give a brief outline of DFT. The basic theorem of DFT, put forward by Hohenberg and Kohn \[2\], states that the ground state density of any system, \(\rho(r)\), determines uniquely the external potential \(V(r)\) and consequently the ground state \(|\Psi_0\rangle\), provided that no degeneracy is present. A direct consequence of this fundamental theorem is that we can, in principle, express the total energy as a functional of \(\rho(r)\) and find its minimum, bypassing the solution of the many-particle Schroedinger equation. A difficulty of this approach is that the space of densities is not well defined and for finding the energy minimum, it is essential to define the space where these minima are sought. A further difficulty was the derivation of sufficiently accurate density functionals and in particular that of the kinetic energy. All efforts for this functional had limited success \[15, 16\]. This difficulty was overcome by Kohn and Sham \[3\] who, instead of energy density functionals, considered the energy as a functional of a noninteracting state having the same electronic density as that of the ground state of the real interacting system. The minimization of this functional leads to a set of one-particle Schroedinger equations, the KS equations, with potential: \(V_{KS}(r) = V(r) + V_K(r)\), where \(V_K(r)\), to be referred to as the Kohn potential, is a function of the electronic density. Still, this theory needs a better explicit form of the exchange and correlation functional, \(E_{xc}\). Although, considerable effort was put in this field \[17\], there are not yet any such functionals which provide sufficient accuracy.

Closely related to the present theory is the work of the model potential for atoms developed by Green and coworkers \[18\] which was done in relation to the HF approximation. However, the attempts for parametrized model potentials was restricted to atoms and not general mappings were sought. Some applications concerning molecules were also attempted, but to our knowledge they had no continuation \[19\]. The essential difference with previous work is that we search for a general mapping of the external potential \(V\) to the effective KS potential \(V_{KS}\) or to the optimized...
effective potential $V_{OEP}$ and not one limited to a single point charge. In fact the initial scope of applicability of the independent particle model was more ambitious as it aimed to include not only energy eigenstates but also scattering states.

In section 2 we give an outline of an alternative formulation of DFT [20] valid also for degenerate states. (The first attempts for this formulation appeared in [21]). The advantage of this formulation is that all densities involved are single state representable and no functional derivatives are needed.

In Section 3, we derive a first approximation of the effective potential as a mapping of the external potential. This mapping is based on symmetry properties and on some physical considerations regarding some simple many electron systems, like atoms, molecules and the finite radius jellium model.

In Section 4, we implement our proposed method to the lower energy states of atoms of the three first rows of the periodic table ($Z=2$ to $Z=18$). Some ionization energies are also given. A brief discussion about the accuracy of the present method is given.

2. The Formulation of DFT without the use of functional derivatives

The Hamiltonian considered is the N-electron Hamiltonian

$$H = T + H_{int} + \hat{V},$$

where $T$ is the kinetic energy operator

$$T = \frac{1}{2} \int d^3 r \sum_s \nabla \psi^s \dagger (r) \nabla \psi^s (r),$$

$H_{int}$ is the interaction energy,

$$H_{int} = \frac{1}{2} \int d^3 r \int d^3 r' \sum_{st} \psi^s \dagger (r) \psi^t \dagger (r') \psi^t (r') \psi^s (r) \frac{1}{|r - r'|},$$

$$\hat{V} = \int d^3 r \hat{\rho} (r) V(r)$$

$\hat{\rho} (r)$ is the density operator

$$\hat{\rho} (r) = \sum_s \psi^s \dagger (r) \psi^s (r)$$

and $\psi^s \dagger (r) , \psi^s (r)$ are the fermion field creation and annihilation operators. The summation over $s$ and $t$ indicates summation with respect to the spin indices.

As the initial DFT theory uses functional derivatives, the existence of which recently has been questioned, we shall give a brief summary of a different formulation of the KS theory in terms of a minimum principle [20], in which no use is made of functional derivatives and the Hohenberg and Kohn theorem, i.e. the one to one correspondence between states and densities [2] is not needed. Further, instead of the energy minimum, in our formulation one has to determine the minima of a new functional denoted by $G(\Psi)$, the definition of which will be given below.

We define first the space $S_\Phi$ as the space of all states $|\Phi\rangle$ having the same density as the state $|\Psi\rangle$. The following functionals are well defined for any state $|\Psi\rangle \in \mathcal{H}$, where $\mathcal{H}$ is the Hilbert space of the N-electron wave functions having finite kinetic energy and normalized to unity.

$$K(\Psi) = \min \{ \langle \Phi | T | \Phi \rangle : \rho_\Phi (r) = \rho_\Psi (r) \}$$

This functional assigns a kinetic energy to every state $|\Psi\rangle$ belonging to the Hilbert space $\mathcal{H}$. However the kinetic energy is not that of $|\Psi\rangle$, but of the state $|\Phi\rangle$ which has the minimum
kinetic energy in the space $S_{\Phi}$. Note that the value of this functional is the same in the whole space $S_{\Phi}$, so in fact its value depends on the density. We next define the functional

$$L(\Psi) = \min\{\langle\Phi|T + H_{\text{int}}|\Phi\rangle : \rho_{\Phi}(r) = \rho_{\Psi}(r)\}$$  \hspace{1cm} (8)

This functional is related to the kinetic plus interaction energy and its value is the same for all states with the same density. Finally we define

$$G(\Psi; V) = L(\Psi) + \langle\Psi|T|\Psi\rangle - K(\Psi) + \int d^3 r \rho_{\phi}(r) > V(r)$$  \hspace{1cm} (9)

Note that all these functional are defined for the whole Hilbert space of the $N$-particle states $|\Psi\rangle$ and not in the space of densities, although densities play a significant role in these definitions. In [20] we proved

**Theorem 2.** The ground state energy $E(V)$ for given potential $V$ is

$$E(V) = \min G(\Psi; V) = G(\Phi; V)$$  \hspace{1cm} (10)

We note here that since $\langle\Psi|T|\Psi\rangle - K(\Psi) \geq 0$ it follows that the minimum of $G(\Psi; V)$ is obtained when equality holds, i.e. when the minimising $|\Phi\rangle$ gives the minimum of the kinetic energy under the condition that $\rho_{\Phi}(r) = \rho_{\Phi}(r)$, where here $|\Theta\rangle$ is the exact ground state. This implies that there is an effective potential $V_{\text{eff}}(r)$ such that the noninteracting state obeys the KS equation

$$T|\Phi\rangle + \hat{V}_{\text{eff}}|\Phi\rangle = E|\Phi\rangle$$  \hspace{1cm} (11)

for some effective potential $V_{\text{eff}}(r) = V(r) + V_K(r)$, where $V_K(r)$ depends on the exact ground state density $\rho_0(r)$. But this implies that the effective potential $V_{\text{eff}}(r)$ is a unique mapping of the external potential $V(r)$, since by the Hohenberg and Kohn theorem there is one to one correspondence between density and external potential. A detailed treatment concerning the existence of this potential is given in [13]. Obviously equation (11) is an equation corresponding to a noninteracting system and therefore $|\Phi\rangle$, to be referred in the following as the KS state, is not restricted to a single Sladet as in the initial KS theory, but a linear combination of such determinants is allowed when demanded by symmetry. Note that the present formulation does not exclude degenerate states as no use is made of the Hohenberg and Kohn theorem. However, for each Irrep, the minimization has to be obtained in the subspace of states transforming according to this Irrep. This means that the Kohn potential will have the symmetry of the external potential, otherwise, no minimization is possible. This is the reason that we use the label eK instead of KS. The spin orbitals (one-particle wave functions) $\phi_i(r)$ of $|\Phi\rangle$ which minimizes $G(\Psi; V)$ satisfy the equation

$$-\frac{1}{2} \nabla^2 \phi_i(r) + V_{\text{eff}}(r)\phi_i(r) = \varepsilon_i \phi_i(r).$$  \hspace{1cm} (12)

As in the present formulation linear combinations of Sladets are allowed, the number of spin orbitals needed in some cases is larger than the number of particles $N$. Although according to Harriman and Gilbert [22], for each density, one can find a single Sladet having this density, this Sladet may not fulfill at all the symmetry requirements. Such an example is the density of the $S = 0$, $l = 2$, $m = 1$ state $|\Phi_2^l\rangle = \frac{1}{\sqrt{2}}(|\phi_0^{11}, \phi_0^{11}) + |\phi_1^{11}, \phi_0^{11})$. The density of this state is the same as that of the Sladet $|\phi_0^{11}, \phi_0^{11})$, or $|\phi_1^{11}, \phi_0^{11})$ but the spin symmetry is lost, as this is not anymore an eigenstate of $S^z$. One might argue that either of the above could represent $|\Phi_2^l\rangle$, but then this could represent equally well the state $|\Phi_1^l\rangle = \frac{1}{\sqrt{2}}(|\phi_0^{11}, \phi_1^{11}) - |\phi_1^{11}, \phi_0^{11})$ which is again an $S = 0$ state, with $l = 1$, $m = 1$. The exact eigenstates of an atom corresponding to the above quantum numbers correspond to very different energies and densities. Further, the state
\[ |\Phi_1^\prime\rangle = |\phi_0^\dagger, \phi_1^\dagger\rangle \] has the same density as \[ |\Phi_2^\prime\rangle \] but its spin eigenvalues are \( S = 1, S_z = 1 \). Thus if one neglects symmetry, one can have many states having the same density but as our examples show, it is not clear to which exact eigenstate they are assigned.

We conclude that in the present formulation one is not forced to use a single Sladet as in the initial formulation of Kohn and Sham. The basic philosophy of the present DFT theory is that the noninteracting state, must have the same symmetry (transform according to the same Irrep) as the exact ground state. The present formulation allows linear combinations of Sladets until the proper symmetry is obtained. This implies that there are many Sladets, built from orbitals satisfying equation (12), satisfying the noninteracting state equation (11). However, in order to get the correct Irrep state, one may have to use linear combinations of such determinants.

As we discussed in the introduction there are many advantages when we express the effective potential \( V_{\text{eff}} \) of the present theory as a mapping of the external potential. This mapping is much more convenient since one maps a physical quantity to another one with the same symmetry and of the same physical nature. In this formulation the total energy is also a functional of the density, because the Hohenberg and Kohn theorem is also valid, but the noninteracting system equations are not derived by minimizing this functional and thus no functional derivatives are used. Beyond the symmetry considerations, the new methodology, has the advantage that one can determine the self-consistent \( eK \) potential at the first stage of the calculations as the external potential of a physical system is a function that one knows, whereas in conventional DFT, one has to perform a series of iterations to find the self-consistent density in terms of which the self-consistent KS potential is determined. Thus, finally one expects a significant increase of the speed of calculations. In our present treatment we preferred to calculate the ground state energy in terms of the Hartree-Fock energy using the KS state in place of the HF one and adding a correlation term, i.e. we used the formula

\[
E[\Phi_{\text{KS}}] = \langle \Phi_{\text{KS}} | T | \Phi_{\text{KS}} \rangle + \int d^3r \rho(\mathbf{r}) \rho(\mathbf{r}) V(\mathbf{r}) + \frac{1}{2} \int d^3rd^3r' \rho(\mathbf{r}) \rho(\mathbf{r'}) - \sum_s \rho_s(\mathbf{r}, \mathbf{r'}) \rho_s(\mathbf{r'}, \mathbf{r}) \frac{1}{| \mathbf{r} - \mathbf{r'} |} \] (13)

where \( \rho_s(\mathbf{r}, \mathbf{r'}) = \langle \Phi_{\text{KS}} | \psi^s(\mathbf{r}) \psi^s(\mathbf{r'}) | \Phi_{\text{KS}} \rangle \) and as usually, the successive terms in the second side of the equation stand for the kinetic, the potential, the Coulomb (Hartree) and the exchange energy, respectively. Finally the correlation energy \( E_c[\Phi_{\text{KS}}] \) is the only term about which there is no exact functional form. Note that \( E_c[\Phi_{\text{KS}}] \) does not coincide with the one corresponding to Hartree-Fock, as \( |\Phi_{\text{KS}}\rangle \) and \( |\Phi_{\text{HF}}\rangle \) do not coincide. In practice we found that, for atoms and molecules that we tried up to now, they are not very different.

So far we refer to the KS theory, but the mapping of the external potential to the effective potential is also valid for the Optimized Effective Potential Theory.

3. A first approximation of the mapping of the external potential \( V(\mathbf{r}) \) to the effective potential \( V_{\text{eff}}(\mathbf{r}) \)

According to the previous section, the external plus Kohn potential of the present KS theory, as well as the optimized effective potential \( V_{\text{OEP}} \), which in the following will both be denoted by \( V_{\text{eff}} \), must be invariant under the symmetry group \( G \) of the external potential \( V \). This will be a consequence of covariance. This means that, if the external potential of a physical system is subject to a rotation or translation all physical properties, like e.g. the density, must be transformed accordingly. Then the mapping of \( V \) to \( V_{\text{eff}} \) must belong to the identity Irrep of \( T_3 \), the group which contains all rotation and translations in the three dimensional Euclidean space. Such a mapping will map the translated potential \( V_0(\mathbf{r}) = V(\mathbf{r} - \mathbf{a}) \) to \( V_{\text{eff},a}(\mathbf{r}) = V_{\text{eff}}(\mathbf{r} - \mathbf{a}) \). Thus e.g. if all nuclei of a molecule in zero external field are translated
by \( \mathbf{a} \), the external potential \( V_a(r) \) becomes \( V(r - \mathbf{a}) \) and then as one expects the relation 
\( V_{KS,a}(r) = V_{KS}(r - \mathbf{a}) \) must hold. This mapping implies that all physical properties of the initial system must be translated by \( \mathbf{a} \) when the external potential is translated. Thus in the case of molecules, where the external potential is due to the Coulomb forces of the atomic nuclei, transformation of all nuclei, imply transformation of all electronic properties and therefore of the effective potential. The same relation must hold for rotations.

The simplest forms compatible with the symmetry requirements are:

(a) \( V_{eff}(r) = \lambda(N)V(r) \), (b) \( V_{eff}(r) = \lambda_{2n}(N)\nabla^2 V(r) \), \( n \geq 2 \), or linear combinations of the above. (Note that \( \nabla^2 = \nabla . \nabla \) transforms according to the identity irreducible representation of the \( I^3_3 \) group, i.e. this operator is invariant under all rotations and translations).

These mappings were rejected as they did not comply with the uniform electron density of the finite radius jellium model \([12]\). Note that because of the universality of the mapping, if for a single case it gives unphysical results, it is not acceptable.

The next family of mappings of \( V(r) \) to \( V_{eff}(r) \) complying with covariance includes nonlocal integral forms like:

\[
V_{eff}(r) = \int V(r') Q(\mid r' - r \mid ; N) d^3 r'
\]

As it is shown in the Appendix of \([12]\) we can write this formula in an alternative way by which we can have more physical insight, namely:

\[
V_{eff}(r) = \int d^3 r' \frac{K(\mid r' - r \mid ; N)}{\mid r' - r \mid} \nabla^2 V(r').
\]

Since \( 4\pi \rho^+(r) = -\nabla^2 V(r) \) we have effectively a mapping of the external charge density to the effective potential.

Next, we consider a non extended system, with total charge \( \int \rho^+(r')d^3 r' = Q \) in a finite volume. The asymptotic behavior of the external potential is \( -\frac{Q}{r} \) for \( r \to \infty \) and that of the KS potential should be:

\[
\lim_{r \to \infty} V_{eff}(r) = -\frac{Q - N + 1}{Q}.
\]

It then follows that \( K(r; N) = \frac{Q - N + 1}{Q} \) for \( r \to \infty \).

One can readily verify that this is compatible with the previous demand by considering the case of point charges.

We now consider the positive density \( \rho^+(r) = \frac{1}{4\pi} \sum_k Z_k \delta(r - R_k) \) of a molecule or solid, due to the point charges \( Z_k \) of atomic nuclei at positions \( R_k \). Then, because of the \( \delta \)-functions, the integration of the right hand side of the previous equation can be carried out and we find

\[
V_{eff}(r) = -\sum_k Z_k \frac{K(\mid R_k - r \mid ; N)}{\mid R_k - r \mid}.
\]

The effective potential in the vicinity of \( R_k \), in a generalized Taylor expansion, must not include powers smaller than \( \mid r - R_k \mid^{-1} \), i.e. it must be of the form \( V_{eff}(r) \to Z_k(\frac{1}{r - R_k}) + c_0 + c_1 \mid r - R_k \mid + ... \) for \( r \to R_k \). It then follows that \( K(\mid R_k - r \mid) = \frac{1}{r - R_k} + c_0 + c_1 \mid r - R_k \mid + ... \) when \( r \to R_k \).

We can construct an approximate formula of the KS potential by a proper interpolation of these two asymptotic forms. The simplest way to do it is described by the formula:

\[
V_{KS}(r) = -\frac{Z + N - 1}{r} - \frac{(N - 1)}{r} e^{-r/a}.
\]
nucleus relative to the external potential to take into account the flow of charge away from areas of high density, when the repulsive forces between the electrons are switched on. The constant $a$, which could depend on $Z$ and $N$, is expected to be of the order of magnitude of the atomic unit as it is a measure of the extension of the electronic cloud around the nucleus.

We tried this parametric form of $V_{KS}(r)$, equation (17), in many atoms and ions, in combination with equation (13) which gives the total ground state energy. Since in the present state of development of this theory, the parameter $\alpha$ is free, differing from atom to atom, we had to try a series of values of the parameter $a$ in order to find the one leading to the minimum of the energy as mentioned above. The number of values of $\alpha$ for which we had to solve the KS equations was dramatically diminished by plotting $E$ v.s. $a$ and noticing that the graph was a smooth parabolic curve. The results were quite encouraging, although this is the lowest order approximation of the KS potential. The calculation of the total ground state energies for the first two periods of the periodic system gave relative errors between 0.5% and 3% with a tendency to increase with $Z$, while the optimum $a$ was found to vary between 0.3 and 0.6 atomic units, with a tendency to decrease with $Z$.

We now return to the general form of the kernel $K$. By equating the right hand sides of Eqs(16) and (17) for a single point charge at the origin we find

$$K(|r'-r|;N) = 1 - \frac{N-1}{Z} + \frac{N-1}{Z} e^{-|r'-r|/a}. \quad (18)$$

Searching for a better approximation, we tried the two- parameter formula:

$$V_{KS}(r) = \frac{-Z + N - 1 + C}{r} - \frac{N - 1 + C}{r} e^{-r/a} \quad (19)$$

with the second parameter $C$, depending like $a$, on $Z$ and $N$. This time, we had to find the minimum of the function $E = E(a, C)$, varying both $a$ and $C$. The results were very promising, as the relative errors were reduced by one or even two orders of magnitude, as we will see in detail in the next section.

The problem with the above expression is that, introducing the constant $C$, we change the asymptotic behavior of $V_{KS}(r)$ at infinity, since we have $V_{KS}(r \to \infty) = -\frac{Z-N+1-C}{r}$ which deviates from the correct asymptotic form at infinity but preserving that at zero. Although this does not play an essential role in the calculations one can remedy the situation by taking $C$ a function of $r$, which is practically a constant in the vicinity of the nucleus and tends to zero in the asymptotic limit $r \to \infty$. The simplest way to achieve such a behavior is through a Fermi-type function,

$$C(r, Z, N) = \frac{c(Z, N)}{1 + e^{r/b}} \quad (20)$$

Assuming that $b >> 1$, $C(r, Z, N)$ tends to a step function: $C(r, Z, N) = c(Z, N)$ if $r \leq b$ and 0 otherwise.

Then one has to modify the kernel as follows

$$K(|r'-r|;N) = 1 - \frac{N-1}{Q} - \frac{C(|r'-r|;N,Q)}{Q} e^{-|r'-r|/a} \quad (21)$$

where again $Q$ is the total positive charge $Q = -\int d^3r \nabla^2V(r)$.

Then it is easy to verify that our formula for large $N$ gives: $V_{KS}(r) \approx -\frac{Z-r/a}{r} - V_0$, which is the familiar Thomas-Fermi formula for the electronic screening in metals. We made application of our present effective potential to atoms the results of which will be discussed in the next section.
Table 1. The ground state energies of neutral atoms from Z=2 to 18. The percent error of the present result (denoted by $E_{TP}$) is relative to the exact energy $E_{Exact}$. $E_{LDA-SIC}$ denotes the energies obtained by the linear density approximation with the self-interaction correction. $E_{OEP}$ are the results of the Optimised Effective Potential approximation. The parameters a and c are those of the effective potential used as defined in the text.

| At. | Z | $-E_{exact}$ | $-E_{LDA-SIC}$ | $-E_{OEP}$ | $-E_{TP}$ | Error(%) | a | c |
|-----|---|--------------|----------------|------------|----------|----------|---|---|
| He  | 2 | 2.904        | 2.920          | 2.903      | 2.903    | 0.03     | 0.500 | 0.000 |
| Li  | 3 | 7.478        | 7.506          | 7.483      | 7.482    | 0.05     | 0.555 | 0.000 |
| Be  | 4 | 14.667       | 14.695         | 14.665     | 14.665   | 0.01     | 0.497 | 0.317 |
| B   | 5 | 24.654       | 24.702         | 24.658     | 24.655   | 0.00     | 0.440 | 0.729 |
| C   | 6 | 37.845       | 37.933         | 37.849     | 37.846   | 0.00     | 0.416 | 0.990 |
| N   | 7 | 54.589       | 54.729         | 54.591     | 54.584   | 0.01     | 0.398 | 1.150 |
| O   | 8 | 75.067       | 75.259         | 75.072     | 75.064   | 0.00     | 0.377 | 1.258 |
| F   | 9 | 99.734       | 99.999         | 99.731     | 99.724   | 0.01     | 0.365 | 1.214 |
| Ne  | 10| 128.939      | 129.287        | 128.921    | 128.914  | 0.02     | 0.348 | 1.200 |
| Na  | 11| 162.257      | 162.672        | 162.256    | 162.208  | 0.03     | 0.366 | 0.752 |
| Mg  | 12| 200.059      | 200.536        | 200.063    | 200.006  | 0.02     | 0.353 | 0.867 |
| Al  | 13| 242.356      | 242.891        | 242.362    | 242.301  | 0.02     | 0.329 | 1.333 |
| Si  | 14| 289.374      | 289.969        | 289.376    | 289.302  | 0.02     | 0.302 | 1.900 |
| P   | 15| 341.272      | 341.930        | 341.273    | 341.195  | 0.02     | 0.291 | 2.303 |
| S   | 16| 398.139      | 398.852        | 398.129    | 398.030  | 0.03     | 0.280 | 2.684 |
| Cl  | 17| 460.196      | 460.967        | 460.129    | 460.043  | 0.03     | 0.270 | 3.055 |
| Ar  | 18| 527.604      | 528.432        | 527.555    | 527.406  | 0.04     | 0.259 | 3.488 |

4. Numerical results and conclusions
The ground state energies of the atoms which were calculated with the present method compare in accuracy with those of the optimized effective potential method and are better than other familiar methods like the local density approximation self-interaction correction LDA-SIC, as one can realize from tables 1 and 2. The relative errors with respect to the exact energies, had a tendency to increase with Z and were smaller than 0.05%, i.e. $\frac{\Delta E}{E} < 5 \cdot 10^{-4}$. Calculations of ground states of ions exhibited the same or even better accuracy than the ones of the corresponding neutral atoms (See table 2). The relative errors were bigger in excited state calculations, with the maximum error, for the first excited state of Helium, being 0.14%. As

Table 2. The energies of several ions are given for the configurations denoted. The notation used is the same as that of Table 1.

| Ion | Z | N | State | -$E_{exact}$ | -$E_{LDA}$ | -$E_{OEP}$ | -$E_{TP}$ | Error(%) | a | c |
|-----|---|---|-------|--------------|------------|------------|----------|----------|---|---|
| O$^{2+}$ | 8 | 6 | $\{1s^22s^22p^2\}^3P$ | 73.224 | 73.319 | 73.219 | 73.218 | 0.01 | 0.303 | 0.700 |
| C$^{4+}$ | 6 | 2 | $\{1s^2\}^3S$ | 32.406 | 32.450 | 32.404 | 32.404 | 0.01 | 0.148 | 0.000 |
| He | 2 | 2 | $\{1s2\}^3S$ | 2.174 | 2.176 | 2.174 | 2.168 | 0.27 | 1.160 | 0.000 |
| C$^{4+}$ | 6 | 2 | $\{1s2\}^3S$ | 21.431 | 21.423 | 21.418 | 21.424 | 0.08 | 0.357 | 0.000 |
| Li | 3 | 3 | $\{1s^22p\}^2P$ | 7.410 | 7.441 | 7.414 | 7.413 | 0.04 | 0.555 | 0.000 |
| Be | 4 | 4 | $\{1s^22s2p\}^3P$ | 14.567 | 14.608 | 14.573 | 14.571 | 0.03 | 0.466 | 0.470 |
expected, the order of magnitude of the optimum values of \( a(Z, N) \) were one atomic unit. They ranged between 0.244 a.u. and 0.588 a.u. in ground state calculations of neutral atoms, with a tendency to decrease with \( Z \). The values of \( a(Z, N) \) were always smaller for ionized than for neutral atoms, something also expected since \( a \) is a measure of the mean radius of the electronic cloud, which tends to shrink when \( N \) decreases in relation to \( Z \) because of the stronger attraction by the nucleus. On the contrary, the parameter \( c(Z, N) \) tends to increase with \( Z \). This should also be expected since \( c \) is a measure of the deviation of \( V_{KS}(r) \) from the simple interpolation of the asymptotic forms in \( Z = 1 \) and \( Z \) tending to \( \infty \).

The relative errors of the first ionization potential calculations is one or even two orders of magnitude bigger than the ones in total energy calculations. This is natural, as the ionization potentials are calculated either as differences of two very large numbers (the total ground state energies of the N electron and the N-1 electron system) either by the energy of the highest occupied orbital, according to the approximation which uses Koopaman’s theorem. In any case, the errors are systematically lower than 4%, and almost identical to the ones of the OEP method.

One of the most crucial tests of the proposed method was the comparison of our potential with the KS potential calculated by the OEP method in its most sophisticated version [9], the most accurate up to date method in the framework of DFT. In atomic systems, the two KS potentials were found almost identical, something very important since it means that, at least in the atoms that we tested, it is possible to find a pretty accurate effective potential without iterations.

Of course, the problem of the determination of the kernel \( K \) with higher accuracy remains open and should be one of the main priorities for the future development of the proposed method. Higher order nonlinear corrections of the mapping of the external potential on \( V_{KS} \) might also be necessary. The present method has also been tested for molecules giving quite accurate results as its relative deviation from the exact HF is less than \( 10^{-4} \) [12]. The Moeller Plesset perturbation theory has also been applied for molecules. The results which will be published elsewhere, compare well relative to other methods which do not take into account the symmetry of the basis wave functions.

Finally we remind the main advantage of the method from the point of view of numerical calculations which is the speed of computation which increases dramatically relative to conventional DFT, since one does not have to make a guess of the input KS potential or the corresponding density, but starts from the correct one, although in the form presented in this paper it has two free parameters.

### Appendix 1.

#### Proof of Theorem 1.

**Theorem:** There is no solution of the HF equation which transforms according to an Irrep of the symmetry group of the exact Hamiltonian other than the identity Irrep.

Theorem 1 is also valid for the solutions of the KS equations

**Proof:** Assume that such a solution exists and let it belong to Irrep \( \Gamma \) different from the identity Irrep. Then the many particle HF equation in the second quantization representation is

\[
(T + V) \Phi_{\Gamma} + \int d^3r \int d^3r' \frac{\rho_{\Phi}(r')}{|r' - r|} \hat{\rho}(r) \Phi_{\Gamma} - \sum_s \int d^3r \int d^3r' \rho_{\Phi}^s(r, r') \frac{\hat{\rho}^s(r', r)}{|r' - r|} \Phi_{\Gamma} = E \Phi_{\Gamma}.
\]

(22)

We can write now the density matrix as
\[ \rho_{\Phi}(r, r') = \rho_0(r, r') + \sum_{B \neq 0} \rho_B(r, r'). \]  

(23)

Then the Hartree and the Exchange operator will have terms other than those belonging to the identity Irrep. Let us call them \( V'_H \) and \( V'_{xc} \). Then

\[ (V'_H + V'_{xc}) | \Phi_{\Gamma} \rangle = \sum_{A \neq \Gamma} | \Phi_A \rangle = 0. \]  

(24)

But the operator \( (V'_H + V'_{xc}) \) is positive definite and has no zero eigenstates. Hence it is not possible for \( | \Phi_{\Gamma} \rangle \) to be an eigenstate of the HF operator.

The proof for the case of DFT is much easier as we have only the local potential and the local potentials have no eigenstates in the space of square integrable functions.

For a better understanding of the above theorem we consider the HF equation for the spin orbitals \( | \varphi_i \rangle \) of the HF Sladets \( | \Phi \rangle = | \varphi_1, ..., \varphi_i, ..., \varphi_N \rangle \). This equation has the form

\[ \left[-\frac{1}{2} \nabla^2 + V(r)\right] \varphi^s_i(r) + \int d^3r' \frac{\rho_{\Phi}(r', r')}{|r'-r|} \varphi^s_i(r) - \int d^3r' \frac{\rho^s_{\Phi}(r, r')}{|r'-r|} \varphi^s_i(r') = \epsilon_i \varphi^s_i(r) \]  

(25)

where \( s \) is the spin up and spin down index. It is easy to verify the above theorem by using the spin-orbital HF equation. In order to construct a Sladet belonging to a certain Irrep of the symmetry group \( G \) of the Hamiltonian, one chooses \( | \varphi_i \rangle \) to belong to a certain Irrep of \( G \). Assume now that one of the \( \varphi_i(r) \) transforms according to the identity Irrep of \( G \) and let us call it. Then in separating \( \rho_{\Phi}(r, r') \) into \( \rho_0(r, r') + \sum \rho_A(r, r') \) we find that \( \varphi^s_i(r) \) satisfies the equations

\[ \int d^3r' \frac{\rho^A(r', r')}{|r'-r|} \varphi^s_i(r) - \int d^3r' \frac{\rho^A(r, r')}{|r'-r|} \varphi^s_i(r') = 0. \]

The above equation is an eigenstate equation with eigenvalue 0. But this is not possible since this is an eigenstate of a positive definite operator.

One can verify easily the above theorem by considering a Sladet of 2\( M+1 \) electrons, where \( M \) orbitals are doubly filled and is single filled with spin up. By taking into account that the corresponding state has \( s = \frac{1}{2} \) and \( s_2 = \frac{1}{2} \) we find that the spin up density matrix differs from the one with spin down. Then the spacial parts of the spin up orbitals are different from those of spin down. But this is contrary to our symmetry preserving Sladet, where \( M \) orbitals are doubly filled.

The proof for the KS equation is similar but simpler since we have only local potentials. By using the same procedure we reach an eigenvalue equation as above, but with only a local part, namely \( V^A(r) \varphi^s_i(r) = 0 \). But this is not possible as the \( \varphi^s_i(r) \) must be square integrable.

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