A novel density functional theory for atoms, molecules, and solids

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A theorem is proved stating that in atoms, molecules, and solids, only the set of the spherical parts of the density around each nucleus determines uniquely the external potential. Therefore, the induced Kohn and Sham (KS) potential has spherical symmetry around each nucleus, and furthermore, it has the symmetry of the external potential. In this way, the inconsistencies of standard density functional theory (DFT) concerning the asymmetry of the KS potential are remedied. As a result of the above, the ground state is uniquely determined by this set of spherical densities. In the case of a symmetry group G of a Hamiltonian **H**, the minimizing subspace of the Hamiltonian for each irreducible representation of G is uniquely determined by this set of spherical densities. Thus, the present theory opens the way for new density functionals and more accurate molecular calculations as it exploits local symmetries. Moreover, the theory of "Atoms in Molecules" formulated by Bader, by using the open quantum mechanics theory, can be explained in terms of DFT [R. F. W. Bader, Atoms in Molecules. A Quantum Theory (Oxford University Press, Oxford, 1990)]. *Published by AIP Publishing.* https://doi.org/10.1063/1.5038262

I. INTRODUCTION

The difficulty in determining the eigenstates of a many electron Hamiltonian is due to the interaction term $H_{int} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$ as a result of which the many variable wave function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ cannot be expressed as a single Slater determinant (SlD). Therefore, Thomas[1] and Fermi[2] in 1927, the time of the early quantum mechanics, developed a theory where the energy of a ground state was expressed as a functional of the density. This theory, however, was based on intuition until Hohenberg and Kohn[3] proved that there is one to one correspondence between the ground state and its corresponding density. In this formulation, however, one had to find an explicit expression of the kinetic energy in terms of the density and this was not an easy task, as one can see from the rich literature covering this topic.[4]

Since the initial rigorous foundation of Density Functional Theory (DFT), there were many developments, a milestone of which was the Kohn and Sham, KS, theory,[5] where a non-interacting Slater determinant $|\Phi\rangle$ having the same density $\rho_\Phi(\mathbf{r}) = \langle\Phi|\hat{\rho}(\mathbf{r})|\Phi\rangle$ as the exact ground state $|\Psi\rangle$ could in principle give the properties of the actual physical system. In this way, part of the exact ground state kinetic energy could be calculated from $\langle\Phi|T|\Phi\rangle$ instead from a functional of the density. The advantage of this formulation is that one could construct the noninteracting $|\Phi\rangle = |\phi_1, \ldots, \phi_N\rangle$ by solving a system of one particle Schrodinger type equations for the spin orbitals $\phi_i(\mathbf{r})$,

$$-\frac{1}{2}\nabla^2\phi_i(\mathbf{r}) + V_{KS}(\mathbf{r})\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}), \quad (1)$$

where the KS potential $V_{KS}(\mathbf{r}) = V(\mathbf{r}) + V_h(\mathbf{r}) + V_{xc}(\mathbf{r})$ is the sum of the exact external potential $V(\mathbf{r})$, the Hartree potential $V_h(\mathbf{r})$, and the exchange and correlation potential $V_{xc}(\mathbf{r})$ which is derived by the functional derivative $\frac{\delta}{\delta\rho(\mathbf{r})}E_{xc}(\rho)$ of the exchange and correlation energy,

$$E_{xc}(\rho) = \langle\Psi(\rho)|T + H_{int}|\Psi(\rho)\rangle - E_H(\rho) - \langle\Phi(\rho)|T|\Phi(\rho)\rangle, \quad (2)$$

where $|\Psi\rangle$ is the state which minimizes $\langle\Psi|T + H_{int}|\Psi\rangle$ under the constraint $\langle\Psi|\hat{\rho}(\mathbf{r})|\Psi\rangle = \rho(\mathbf{r})$, and similarly $|\Phi(\rho)\rangle$ is the state minimizing the kinetic energy $\langle\Phi|T|\Phi\rangle$ under the constraint $\langle\Phi|\hat{\rho}(\mathbf{r})|\Phi\rangle = \rho_\Psi(\mathbf{r})$, where $\rho_\Psi(\mathbf{r})$ is the exact ground state density of the system under consideration.[6] In this way, at least part of the kinetic energy is determined with some accuracy, whereas earlier attempts for determining the kinetic energy directly from the density failed. (Note here that the exact $\langle\Psi|T + H_{int}|\Psi\rangle$ is larger than the KS kinetic energy since the KS one is the minimum under the density constraint.)

In this paper, we shall show that much less information is necessary in order to determine the exact ground state of atoms, molecules, and solids—namely, instead of the density $\rho(\mathbf{r})$, the ground state is determined by the spherical parts of the set of densities $\rho_i^0(\mathbf{r}) = \int d\Omega \rho(\mathbf{r}+\mathbf{R}_i)$; i.e., $\rho_i^0(\mathbf{r})$ is the density $\rho(\mathbf{r})$ with the 0 of the coordinate axes positioned at the nucleus at $\mathbf{R}_i$. Thus, e.g., for an atom, $\rho^0(\mathbf{r})$ is the spherical part of the density. The advantage of using the set of $\rho_i^0(\mathbf{r})$ is that the KS potential in a molecule or solid is a sum of potentials $V_i(\mathbf{r})$, $V_{h,i}(\mathbf{r})$, and $V_{xc,i}(\mathbf{r})$ which are spherically symmetric with centers in the atomic nuclei at $\mathbf{R}_i$, and thus, numerical calculations are easier relative to those which ignore local symmetry. This property is also useful in the search of the mapping of the external potential $V(\mathbf{r})$ to $V_{KS,i}(\mathbf{r})$, using the Gidopoulos-Davidson variational principle,[7,8] and its further

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developments[9] since, instead of the universal density mapping, one can search for the maps of the $V_i(\mathbf{r}) = -Z_i \frac{e^2}{|\mathbf{r}-\mathbf{R}_i|}$ to $V_{KS,i}(\mathbf{r})$ which is also spherically symmetric with center $\mathbf{R}_i$. Obviously, this mapping is affected by the total potential $V(\mathbf{r})$.

DFT can also give excited states when the external potential is invariant under a geometric symmetry described by a group G, like in the case of crystals, because as one can easily show, there is one to one correspondence between the external potential and the subspace density $\rho^\Gamma(\mathbf{r}) = \sum_\gamma \langle \Psi_\gamma^\Gamma | \hat{\rho}(\mathbf{r}) | \Psi_\gamma^\Gamma \rangle$ of the subspace S^Γ which minimizes the energy $E^\Gamma = \sum_\gamma \langle \Psi_\gamma^\Gamma | H | \Psi_\gamma^\Gamma \rangle$. (Here by Γ we denote an irreducible representation, Irrep, of the group G.) In developing a KS theory for this case, one has to search for a KS potential $V_{KS}^\Gamma(\mathbf{r})$ invariant under the same group G as that of the external potential. This property is satisfied because the subspace density is invariant under G and thus the same holds for the Hartree potential which satisfies Poisson's equation $\nabla^2 V_H^\Gamma(\mathbf{r}) = -4\pi \rho^\Gamma(\mathbf{r})$ because ∇^2 is an operator invariant under translations and rotations. The same holds for $V_{xc}^\Gamma(\mathbf{r})$. Contrarily, a single state density $\rho_\gamma^\Gamma(\mathbf{r})$ is not invariant under G and so is the Hartree potential. Thus, the exact density $\rho_\gamma^\Gamma(\mathbf{r})$, for Irreps of dimension larger than one cannot be reproduced by the KS equation. However, the spherical part $\rho_{0,\gamma}^\Gamma(\mathbf{r})$ of $\rho_\gamma^\Gamma(\mathbf{r})$ determines unique S^Γ, and from this, one can determine the single states $|\Psi_\gamma^\Gamma\rangle$ from their transformation properties, i.e., from the equation $g|\Psi_\gamma^\Gamma\rangle = \sum_\beta D_{\beta\gamma}^\Gamma(g)|\Psi_\beta^\Gamma\rangle$, where $D_{\beta\gamma}^\Gamma(g)$ are the matrix elements of the Irrep Γ of the group G. In order to show the advantage of using $\rho^0(\mathbf{r})$ instead of the whole density, let us consider the case of an atom where its ground state $|\Psi_m^l\rangle$ is an eigenstate of the angular momenta L^2 and L^z due to the spherical symmetry of the external potential. In this case, the density $\rho(\mathbf{r}) = \langle \Psi_m^l | \hat{\rho}(\mathbf{r}) | \Psi_m^l \rangle$ is not spherically symmetric unless $l = 0$. Then, the resulting Hartree potential is not spherically symmetric either because, by Poisson's equation $\nabla^2 V_h(\mathbf{r}) = -4\pi \rho(\mathbf{r})$, any asymmetry of the density will be transferred to the Hartree potential. The same holds for the exchange and correlation potential since the total KS potential must be spherically symmetric. Thus, the Kohn and Sham potential, calculated by the whole density and not by its spherical part, has no spherical symmetry, and therefore, the orbitals $\phi_i(\mathbf{r})$ of the KS equation are not eigenfunctions of L^2 and L^z. Therefore, the exact density $\rho(\mathbf{r})$ cannot be reproduced by the sum of $|\phi_i(\mathbf{r})|^2$.[10] Then, one must be satisfied with only an approximation of the KS density to that of the actual physical system. An example is given by Fertig and Kohn who tried to determine the KS potential for a given density,[11] comprising nonspherical parts, where the asymmetry of the density forced them to impose a spherical symmetry constraint. However, in using only the spherical part of the density, no such constraint is necessary.[12] Furthermore, in the case of degeneracy, one can show that the space of degeneracy is determined uniquely by $\rho_0(r)$ and all states with different m have the same $\rho_0(r)$, as shown in Appendix A. Then the subspace density $\rho(\mathbf{r}, S) = \sum \langle \Psi_m^l | \hat{\rho}(\mathbf{r}) | \Psi_m^l \rangle$ is connected with $\rho_0(r)$ by the relation $\rho(\mathbf{r}, S) = (2l + 1)\rho_0(r)$.

Before closing this section, it is worth recalling that spherical potentials were intuitively introduced within the muffin tin approximation for the purpose of making easier band structure calculations for crystals by Korringa in 1947[13] and by Kohn and Rostoker in 1953.[14] Thus, they considered that the potential was spherically symmetric within a sphere of radius R from each atomic nucleus and constant outside. The same approximation was also used in several applications after the advent of DFT. In particular, the Exact Muffin Tin Orbitals (EMTO) method was introduced, where the single electron equations were solved exactly for the optimized overlapping muffin tin potential. This theory was applied successfully by Szunyogh et al. for deriving the density and other properties of surfaces and interfaces.[15] In a paper by Asato,[16] full self-consistency calculations were carried out for metals and semiconductors and compared with the EMT0 approximation. The EMTO results, although much easier to calculate, compared well with the full DFT calculations.[16] It is interesting therefore to find how good these approximations are compared to the results of the present theory. A detailed presentation of the EMTO method and its further developments can be found in the book by Vitos "Computational Quantum Mechanics for Material Engineers."[17]

The new formulation of DFT is presented in Sec. II. In Sec. III, the theoretical and numerical advantages are discussed, and in Sec. IV, we summarize our conclusions.

II. THE NEW DFT THEORY FOR MOLECULES AND SOLIDS

The external potential of a molecule or a solid is a sum of potentials $V_i(\mathbf{r}) = -\frac{Z_i e^2}{|\mathbf{r}-\mathbf{R}_i|}$, each one of which is spherically symmetric about the nucleus of charge Z_i at $\mathbf{R}_i$. Thus,

$$V(\mathbf{r}) = \sum V_i(\mathbf{r}) = -\sum_{i=0}^{k} \frac{Z_i e^2}{|\mathbf{r} - \mathbf{R}_i|}. \quad (3)$$

Let us take $R_0 = 0$. Then since $V_0(\mathbf{r}) = -\frac{Z_0 e^2}{|\mathbf{r}|}$ is spherically symmetric and

$$\rho(\mathbf{r}) = \rho_0(r) + \sum_{l \rangle 0, m} \rho_{lm} Y_m^l(\mathbf{\Omega}), \quad (4)$$

where $Y_m^l(\mathbf{\Omega})$ is the spherical harmonic which is an eigenstate of $\mathbf{L^2}$ with eigenvalue $l(l + 1)$ and $L_z = m$, it follows that

$$\int d^3 r V_0(r)\rho(r) = \int d^3 r V_0(r)\rho_0^0(r) \quad (5)$$

because for l larger than 0,

$$\int Y_m^l(\mathbf{\Omega})d\mathbf{\Omega} = 0. \quad (6)$$

In this notation,

$$\int F(\mathbf{\Omega})d\mathbf{\Omega} = \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi F(\theta, \phi). \quad (7)$$

For the potential $V_j(\mathbf{r})$, we can change variables so that $\mathbf{r}_j' = \mathbf{r} - \mathbf{R}_j$. Then as shown in Appendix B,

$$\int d^3 r V_j(\mathbf{r})\rho(\mathbf{r}) = -\int_0^\infty dr_j r_j^2 \frac{Z_j e^2}{r_j} \rho_j^0(r_j), \quad (8)$$

$\mathbf{r_j} = \mathbf{r} - \mathbf{R}_j$, and

$$\rho_j^0(r_j) = \int d\mathbf{\Omega} \rho(\mathbf{r+R}_j). \quad (9)$$

We shall now prove the basic inequality concerning the present version of DFT.

Theorem 1. The set of densities $\rho_i^0(r)$ determine uniquely the external potential.

The proof is limited to the case that the ground state is not degenerate. The case of degeneracy is given in Appendix C.

Proof. From the lowest energy states $|\Psi\rangle$ and $|\Psi'\rangle$ of the Hamiltonians H and H',

$$H = T + H_{int} + V, \; H' = T + H_{int} + V' \qquad (10)$$

corresponding to the external nonequivalent potentials V and V', the following inequalities hold by the Rayleigh-Ritz variational principle:

$$\langle\Psi|T + H_{int}|\Psi\rangle + \int d^3 r V(\mathbf{r})\rho_\Psi(r)$$
$$< \langle\Psi'|T + H_{int}|\Psi'\rangle + \int d^3 r V(\mathbf{r})\rho_{\Psi'}(\mathbf{r}) \qquad (11)$$

and

$$\langle\Psi'|T + H_{int}|\Psi'\rangle + \int d^3 r V'(\mathbf{r})\rho_{\Psi'}(\mathbf{r})$$
$$< \langle\Psi|T + H_{int}|\Psi\rangle + \int d^3 r V'(\mathbf{r})\rho_\Psi(\mathbf{r}). \qquad (12)$$

Adding by parts and transferring all terms to the left hand site, we get the inequality

$$\int d^3 r [V'(\mathbf{r}) - V(\mathbf{r})][\rho_{\Psi'}(\mathbf{r}) - \rho_\Psi(\mathbf{r})]\langle 0. \qquad (13)$$

Assume now that $V(\mathbf{r}) = \sum V_i(\mathbf{r})$, $V'(\mathbf{r}) = \sum_{i\neq j} V_i(\mathbf{r}) + V_j'(\mathbf{r})$, where $V_i(\mathbf{r})$, $V_j'(\mathbf{r})$ are spherically symmetric potentials with centers $\mathbf{R}_i$, $\mathbf{R}_j$, respectively. Then, the above inequality becomes

$$\int d^3 r [V_j'(\mathbf{r}) - V_j(\mathbf{r})][\rho_{\Psi'}(\mathbf{r}) - \rho_\Psi(\mathbf{r})]\langle 0. \qquad (14)$$

But since

$$\int d^3 r [V'(\mathbf{r}) - V(\mathbf{r})][\rho_{\Psi'}(\mathbf{r}) - \rho_\Psi(\mathbf{r})]$$
$$= \int dr r^2 [V_j'(r) - V_j(r)][\rho_{j\Psi'}^0(r) - \rho_{j\Psi}^0(r)], \qquad (15)$$

our inequality becomes

$$\int dr r^2 [V_j'(r) - V_j(r)][\rho_{j\Psi'}^0(r) - \rho_{j\Psi}^0(r)]\langle 0. \qquad (16)$$

Obviously, when we make a simultaneous change to all $V_j(\mathbf{r})$, by our basic inequality, we get

$$\sum_i \int dr_i' r_i^2 [V_i'(r_i) - V_i(r_i)][\rho_{i\Psi'}^0(r_i) - \rho_{i\Psi}^0(r_i)]\langle 0. \qquad (17)$$

Thus *the set of densities $\rho_{i\Psi}^0(r_i') = \int d\Omega\, \rho_\Psi(\mathbf{r} + \mathbf{R}_i)$ determine uniquely the ground state of a system which is the sum of spherically symmetric potentials with centers $\mathbf{R}_i$* since, if the opposite is true, i.e., $\rho_{i\Psi'}^0(r) - \rho_{i\Psi}^0(r) = 0$ for all i, the above inequality is violated. Q.E.D.

Since the energy is a functional of the set of densities $\rho_i^0(r)$, it follows that the Hartree and the exchange and correlation energies are also functionals of the set of densities $\rho_i^0(r)$. Then, the total energy is a functional of this set of densities and so is the exchange and correlation potential. Thus we can define the Hartree potential at $\mathbf{R}_i$ as

$$V_{ih}'(r) = \frac{Z_i}{N} \int r'^2 dr' \int d\Omega \frac{e^2}{|\mathbf{r}' - \mathbf{r}|} \rho_i^0(r'). \qquad (18)$$

This is a spherically symmetric potential with axes at $\mathbf{R}_i$. Going back to the original axes, this becomes $V_{ih}(\mathbf{r}) = V_{ih}'(\mathbf{r} - \mathbf{R}_i)$.

In the same way, the exchange and correlation energy defined here as

$$E_{xc}(\rho_0, \dots \rho_i \dots)$$
$$= \langle\Psi(\rho_0, \dots \rho_i \dots)|T + H_{int}|\Psi(\rho_0, \dots \rho_i \dots)\rangle$$
$$- \langle\Phi(\rho_0, \dots \rho_i \dots)|T|\Phi(\rho_0, \dots \rho_i \dots)\rangle \qquad (19)$$

is a functional of ρ_i^0. Then the exchange and correlation potential is $V_{xc}^i(r, \rho_i^0) = \frac{d}{d\rho_i^0(r)}E_{xc}(\rho_0, \dots \rho_i \dots)$.

Since the total KS potential with center at $\mathbf{R}_i$ must be spherically symmetric, it follows that the exchange and correlation potential is also spherically symmetric with axes positioned at $\mathbf{R}_i$. Then using the initial coordinates, we have $V_{xc}^i(r, \rho_i^0) = V_{xc}^i(|\mathbf{r} - \mathbf{R}_i|, \rho_i^0)$. Then $V_{xc}^i(r, \rho_i^0) = \frac{d}{d\rho_i^0(r)}E_{xc}(\rho_i)$, and thus $E_{xc}(\rho_0, \dots, \rho_i \dots) = \sum E_{xc}(\rho_i)$.

Thus we have

Theorem 2. The total KS potential is a sum of potentials, each one of which is spherically symmetric with respect to rotations about the corresponding nuclei, i.e.,

$$V_{KS}(\mathbf{r}) = \sum_i [V_i(|\mathbf{r} - \mathbf{R}_i|) + V_{i,h}(|\mathbf{r} - \mathbf{R}_i|) + V_{i,xc}(|\mathbf{r} - \mathbf{R}_i|)]. \qquad (20)$$

It then follows that in addition to symmetries with respect to translations and rotations, one has local spherical symmetries in the vicinity of each nucleus preserving thus the symmetry of the local KS potential. At the first site, one may conclude that the Hartree and exchange and correlation energies depend only on the local densities. This is not so since the KS equations for the orbitals depend on all $V_{KS,i}(\mathbf{r})$.

As a final remark, the reason that the total Hartree potential is equal to the sum of the spherically local ones is due to the linear relation between the Hartree potential and the density.

III. DISCUSSION

Obviously, one would argue that the present approach is numerically more complicated. Thus, for a crystal, one has to calculate the density with respect to each nucleus and obtain its spherical part and from this the Hartree and exchange and correlation potential. This is not so since the initial translational symmetry is preserved and therefore the KS wave functions are of the form $\phi_\mathbf{k}(\mathbf{r}) = e^{\mathbf{k}\cdot\mathbf{r}} u_\mathbf{k}(\mathbf{r})$, where $u_\mathbf{k}(\mathbf{r} + \mathbf{a}_i) = u_\mathbf{k}(\mathbf{r})$, and $\mathbf{a}_i$ are the lattice constants. Then the density is of the form $\rho(\mathbf{r}) = \sum_\mathbf{k} |u_\mathbf{k}(\mathbf{r})|^2$ and $\rho(\mathbf{r} + \mathbf{a}_i) = \rho(\mathbf{r})$. Then $\rho_i^0(r_i) = \rho^0(|\mathbf{r} - \mathbf{R}_i|)$ and $V_{i,h}(|\mathbf{r}|) = V_{i,h}(|\mathbf{r} - \mathbf{R}_i|)$. Thus

in the case of one nucleus per unit cell, one has to calculate $\rho^0(\mathbf{r})$ and from this all the Hartree and exchange and correlation potentials. In the case of a molecule without any symmetry, one has to define $\rho_i(\mathbf{r}') = \rho(\mathbf{r} + \mathbf{R}_i)$ and calculate the integral $\int \rho_i(\mathbf{r}')d\Omega'$. The calculation of such integrals is not a time consuming numerical procedure. Moreover, the calculation of the Hartree and exchange and correlation potentials is much easier since one has to deal with spherically symmetric densities with only one variable. The calculated $V_{h,i}(r')$ becomes $V_{h,i}(|\mathbf{r} - \mathbf{R}_i|$ when one goes back to the initial coordinates, and this computation does not take much time either. Furthermore the numerical calculations can be easily performed, e.g., with Gaussians at $\mathbf{R}_i$. Then, if we take the simplest case that $\rho(\mathbf{r}) = \sum c_i e^{-\lambda_i(\mathbf{r}-\mathbf{R}_i)^2}$, only the Gaussian centered at $\mathbf{R}_0 = 0$ is significant for $\rho_0(\mathbf{r})$ since $\int e^{-\lambda_i(r^2+R_i^2-2rR_i\cos\omega)}d\Omega = 2\pi\frac{1}{2\lambda_i rR_i}[e^{-\lambda_i(r-R_i^2)} - e^{-\lambda_i(r+R_i^2)}]$. Thus, maximum is approximately when $r = R_i$, .i.e., for $R_i \neq 0$, it is significant in a spherical shell surrounding the nucleus at 0. Thus, the main contribution to $\rho_0(\mathbf{r})$ comes from the local density at 0. In the same way, the main contribution to $\rho_j^0(\mathbf{r}')$ comes from $c_j e^{-\lambda_j(\mathbf{r}-\mathbf{R}_j)^2}$. Then, the exchange and correlation potentials are practically local potentials at each atomic nucleus $\mathbf{R}_j$. Thus, in the numerical applications, one has to deal mainly with potentials which are spherically symmetric in the vicinity of the atomic nuclei.

Applications for atoms have been carried out by Nagy and Bene[18] and also by the present author and Papaconstantinou[19] in the framework of the subspace theory, which for this case coincides with the present theory since the subspace density normalized to N particles is the same as the spherical part of the density of a single state. Applications for atoms and molecules were carried out using the direct mapping theory,[20] where the optimized effective potential $V_{oe}(\mathbf{r})$ was expressed as a direct mapping of the external potential, namely,

$$V_{oe}(\mathbf{r}, C_0, \lambda_0, \ldots C_i, \lambda_i \ldots) = -\sum[\frac{Z_i}{|\mathbf{r} - \mathbf{R}_i|} + C_i\frac{1 - e^{\lambda_j|\mathbf{r}-\mathbf{R}_j|}}{|\mathbf{r} - \mathbf{R}_i|}].$$

(21)

The parameters C_i and λ_i of $V_{oe}(\mathbf{r})$ are determined by minimizing the Hartree-Fock energy

$$\langle\phi_1, \ldots \phi_N|H|\phi_1, \ldots \phi_N\rangle$$

(22)

with orbitals $\phi_i(\mathbf{r})$ determined by the one particle Schrodinger equation with potential $V_{oe}(\mathbf{r})$. As shown by Gidopoulos,[8] the optimized effective potential is an approximation to the KS potential when it includes only the exchange potential with the correlation potential ignored. Although the above expression for $V_{oe}(\mathbf{r})$ is mostly intuitive, it gave quite good numerical results for atoms and molecules in calculations carried out by Glushkov[20] and co-workers[21,22]

IV. CONCLUSIONS

The density functionals for atoms, molecules, and solids are functionals of a set of densities centered at the atomic nuclei and the same holds with the KS potentials. The use of the present formulation may facilitate numerical calculations because of the local spherical symmetry of the KS potential.

Moreover, the present theory does not involve symmetry inconsistencies as it happens with standard DFT. We hope that, using this approach, DFT calculations may improve a lot, as unnecessary data like the nonspherical parts of the local densities are ignored. It may also initiate improvements of the explicit forms of the exchange and correlation functionals. Furthermore, it may lead to an advancement of the direct mapping theories where the external potential is mapped to the KS one[8,9,23] as one has to find as a first approximation only the direct mapping of each potential $V_i(\mathbf{r})$ to $V_{ks,i}(\mathbf{r})$ which is determined mainly by the spherical density about the nucleus at $\mathbf{R}_i$.

The present formulations of DFT give an interpretation of the atoms in molecules theory of Bader[24,25] for which there is a revived interest[26] since all properties of the molecules can be determined by the set of the spherical parts of the densities around each atomic nucleus.[27]

APPENDIX A: PROOF THAT THE LOCAL SPHERICAL DENSITIES DO NOT DEPEND ON THE EIGENVALUE m OF L_z

For spherically symmetric external potentials, $\rho_m^{0,l}(\mathbf{r})$ is independent of the eigenvalue m of L_z.

Proof. The operator $\widehat{\rho}^0(\mathbf{r}) = \int d\Omega\widehat{\rho}\mathbf{r})$ is spherically symmetric since

$$\widehat{\rho}^0(R^\varpi\mathbf{r}) = \int d\Omega\widehat{\rho}(R^\varpi\mathbf{r}),$$

(A1)

and by changing variables to $\mathbf{r}' = R^\varpi\mathbf{r}$ where $\Omega' = R^\varpi\Omega$, we have

$$\int d\Omega\widehat{\rho}(R^\varpi\mathbf{r}) = \int d\Omega'\widehat{\rho}(\mathbf{r}') = \widehat{\rho}^0(\mathbf{r}).$$

(A2)

Thus $\widehat{\rho}^0(\mathbf{r})$ is an irreducible tensor operator with $l = 0$, and therefore, the relations $[L^+, \widehat{\rho}^0(\mathbf{r})] = [L^-, \widehat{\rho}^0(\mathbf{r})] = 0$ hold. Using the relation $L^+|\Psi_m^l\rangle = C_m^l|\Psi_{m+1}^l\rangle$ where $C_m^l = \sqrt{l(l+1) - m(m+1)}$, we find

$$\langle\Psi_{m+1}^l|\widehat{\rho}^0(\mathbf{r})|\Psi_{m+1}^l\rangle = \frac{1}{|C_m^l|^2}\langle L^+\Psi_m^l|\widehat{\rho}^0(\mathbf{r})L^+|\Psi_m^l\rangle$$

$$= \frac{1}{|C_m^l|^2}\langle\Psi_m^l|L^-\widehat{\rho}^0(\mathbf{r})L^+|\Psi_m^l\rangle,$$

and since

$$\langle\Psi_m^l|L^-\widehat{\rho}^0(\mathbf{r})L^+|\Psi_m^l\rangle = \langle\Psi_m^l|\widehat{\rho}^0(\mathbf{r})L^-L^+|\Psi_m^l\rangle,$$

it follows that $L^-L^+|\Psi_m^l> = |C_m^l|^2|\Psi_m^l>$ and therefore

$$\langle\Psi_{m+1}^l|\widehat{\rho}^0(\mathbf{r})|\Psi_{m+1}^l\rangle = \langle\Psi_m^l|\widehat{\rho}^0(\mathbf{r})|\Psi_m^l\rangle.$$

(A3)

Then by induction it follows that for all m',

$$\langle\Psi_{m'}^l|\widehat{\rho}^0(\mathbf{r})|\Psi_{m'}^l\rangle = \langle\Psi_m^l|\widehat{\rho}^0(\mathbf{r})|\Psi_m^l\rangle,$$

(A4)

Q.E.D.

As a corollary, we conclude that the subspace density of the states $|\Psi_m^l\rangle$ is

$$\rho(\mathbf{r}, S) = (2l + 1)\langle\Psi_m^l|\widehat{\rho}^0(\mathbf{r})|\Psi_m^l\rangle. \qquad (A5)$$

APPENDIX B: PROOF THAT ONLY THE SPHERICAL PARTS OF THE LOCAL DENSITIES DETERMINE UNIQUELY THE EXTERNAL POTENTIAL

The relation

$$\int d^3r V(\mathbf{r})\rho(\mathbf{r}) = \sum_{j=1}^{k}\int dr_j r_j^2 \frac{Z_j e^2}{r_j}\rho_j^0(r_j)^M \qquad (B1)$$

holds.

Proof.

$$V(\mathbf{r}) = \sum V_i(\mathbf{r}) = -\sum_{i=0}^{k}\frac{Z_i e^2}{|\mathbf{r} - \mathbf{R}_i|}. \qquad (B2)$$

Since $\int d^3r V(\mathbf{r})\rho(\mathbf{r}) = \sum_{j=1}^{k}\int d^3r V_i(\mathbf{r})\rho(\mathbf{r})$, we can calculate each term separately. Then for the potential $V_j(\mathbf{r}) = -\frac{Z_i e^2}{|\mathbf{r} - \mathbf{R}_j|}$, we can change variables so that $\mathbf{r}'_j = \mathbf{r} - \mathbf{R}_j$. Then since under rotations R_j^{Ω} with center $\mathbf{R}_j$, $R_j^{\Omega}\mathbf{R}_j = \mathbf{R}_j$ and $|R_j^{\Omega}\mathbf{r}'_j| = |\mathbf{r}'_j|$, we have

$$-\frac{Z_i e^2}{|\mathbf{r} - \mathbf{R}_j|} = -\frac{Z_j e^2}{|\mathbf{r}'_j|} = V_j(\mathbf{r}'_j). \qquad (B3)$$

The $V_j(\mathbf{r}'_j)$ is spherically symmetric in the new coordinate system under rotations with center $\mathbf{R}_j$ and thus

$$\int d^3r V_j(\mathbf{r})\rho(\mathbf{r}) = -\int d^3r \frac{Z_j e^2}{|\mathbf{r} - \mathbf{R}_j|}\rho(\mathbf{r})$$

$$= -\int d^3r_j \frac{Z_j e^2}{|\mathbf{r}'_j|}\rho(\mathbf{r}'_j + \mathbf{R}_j). \qquad (B4)$$

Let now $\rho(\mathbf{r}' + \mathbf{R}_j) = \rho_j(\mathbf{r}_j)$; i.e., $\rho_j(\mathbf{r}_j)$ is the same density expressed in the new coordinate system. Then, $\rho_j(\mathbf{r}_j) = \rho_j^0(r_j) + \sum_m^l \rho_m^l(r_j)Y_{j,m}^l(\Omega)$, where $\rho_j^0(r'_j) = \int d\Omega' \rho_j(\mathbf{r})$ and $Y_{j,m}^l(\Omega)$ are the spherical harmonics with center at $\mathbf{R}_j$. Thus $\int_0^{\infty} r'^2 dr' \rho_j^0(r') = \int r'^2 dr' \int d\Omega' \rho(\mathbf{r}') = \int d^3r' \rho(\mathbf{r}') = N$, where N is the number of electrons of our molecule. Then

$$\int d^3r V_j(\mathbf{r})\rho(\mathbf{r}) = -\int d^3r \frac{Z_j e^2}{|\mathbf{r}_j|}\rho_j(\mathbf{r}_j)$$

$$= -\int_0^{\infty} dr_j r_j^2 \frac{Z_j e^2}{|\mathbf{r}_j|}\int d\Omega_j \rho_j(\mathbf{r}_j), \qquad (B5)$$

i.e.,

$$\int d^3r V_j(r)\rho(r) = -\int_0^{\infty} dr_j r_j^2 \frac{Z_j e^2}{r_j}\rho_j^0(r_j), \qquad (B6)$$

where $\mathbf{r}_j = \mathbf{r} - \mathbf{R_j}$.

Finally, by using the definitions of the $\rho_j^0(r_j)$, we find

$$\int d^3r V(r)\rho(r) = \sum_{j=1}^{k}\int dr_j r_j^2 \frac{Z_j e^2}{r_j}\rho_j^0(r_j), \qquad (B7)$$

Q.E.D.

APPENDIX C: DFT FOR DEGENERATE STATES

In case that the external potential is invariant under a group of geometric transformations, then the Hamiltonian is also invariant under the same group G and one can search for the minima for each irreducible representation Γ of G. Then, instead of the single state density, one has to take the density $\rho^{\Gamma}(\mathbf{r}) = Tr_{S^{\Gamma}}\widehat{\rho}(\mathbf{r})$ corresponding to the subspace of degeneracy S^{Γ},

$$\rho^{\Gamma}(\mathbf{r}) = \sum_{\gamma}\langle\Psi_{\gamma}^{\Gamma}|\widehat{\rho}(\mathbf{r})|\Psi_{\gamma}^{\Gamma}\rangle. \qquad (C1)$$

This quantity has the symmetry of the Hamiltonian. Thus if Γ is an Irrep of dimension M of the geometric symmetry group G of the external potential, then the whole Hamiltonian is invariant under this group since the kinetic $\widehat{T}$ and interaction operator $\widehat{H}_{int}$ are invariant under all rotations and translations. Then for any g belonging to the group G,

$$\widehat{\rho}(\widehat{g}\mathbf{r}) = g^{-1}\widehat{\rho}(\mathbf{r})g, \qquad (C2)$$

$$\rho^{\Gamma}(g\mathbf{r}) = \sum_{\gamma}\langle\Psi_{\gamma}^{\Gamma}|g^{-1}\widehat{\rho}(\mathbf{r})g|\Psi_{\gamma}^{\Gamma}\rangle = Tr_{S^{\Gamma}}(g^{-1}\widehat{\rho}(\mathbf{r})g), \qquad (C3)$$

where by $Tr_{S^{\Gamma}}(A)$ we denote the trace of the operator A for the subspace S^{Γ}, i.e.,

$$Tr_{S^{\Gamma}}(A) = \sum_{\gamma}\langle\Psi_{\gamma}^{\Gamma}|A|\Psi_{\gamma}^{\Gamma}\rangle. \qquad (C4)$$

Then, since $Tr(AB) = Tr(BA)$, it follows that

$$Tr_{S^{\Gamma}}(g^{-1}\widehat{\rho}(\mathbf{r})g) = Tr_{S^{\Gamma}}(\{\widehat{\rho}(\mathbf{r})gg^{-1}\}). \qquad (C5)$$

Thus $\rho^{\Gamma}(g\mathbf{r}) = \rho^{\Gamma}(\mathbf{r})$, i.e., the subspace density has the symmetry of the external potential. The subspace S^{Γ} minimizing the subspace energy $E(V, S^{\Gamma})$ is defined by the equation

$$E(V, S^{\Gamma}) = \min(T(S''^{\Gamma}) + E_{int}(S''^{\Gamma}) + M\int d^3r \rho_{S''^{\Gamma}}(\mathbf{r})V(\mathbf{r})). \qquad (C6)$$

Thus, if S'^{Γ} is the space minimizing the Hamiltonian $H' = T + H_{int} + \int d^3r\widehat{\rho}(\mathbf{r})V'(\mathbf{r})$ when $V'(\mathbf{r})$ is not equal to $V(\mathbf{r}) + C$, we have the inequalities

$$E(V, S^{\Gamma}) < E(V, S'^{\Gamma}) \text{ and } E(V', S'^{\Gamma}) < E(V', S^{\Gamma}), \qquad (C7)$$

and by adding the inequalities by parts and transferring all terms to the left-hand side, we get an inequality similar to that of the single state case, namely,

$$\int d^3r [\rho_{s'}^{\Gamma}(\mathbf{r}) - \rho_s^{\Gamma}(\mathbf{r})][V'(\mathbf{r}) - V(\mathbf{r})] < 0. \qquad (C8)$$

Thus two different potentials correspond to different subspace densities and different minimizing subspaces. Then one can prove in the same way as in the case of the single ground state that the set of the spherical part of the densities with axes at $\mathbf{R}_i$ determine uniquely the minimizing subspace and the KS potential is again a sum of potentials

$$V_{i,ks}(\mathbf{r}) = -\frac{Z_i e^2}{|\mathbf{r} - \mathbf{R}_i|} + V_{i,h}(|\mathbf{r} - \mathbf{R}_i|) + V_{i,xc}(|\mathbf{r} - \mathbf{R}_i|). \qquad (C9)$$

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