Spin and orbital degeneracy problems in the DFT method. Relation to the Jahn–Teller effect

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Abstract

The problems in the density functional theory arising when it is applied to the spin- and orbitally-degenerate states are discussed. It is rigorously proved that the electron density of an arbitrary N-electron system cannot, in principle, depend upon the total spin S and for all values of S has the same form as it has for a single-determinantal wave function. It is also proved that the diagonal element of the density matrix is invariant with respect to the symmetry of the state and in the frame of density matrix description there is no difference between degenerate and nondegenerate states. Thus, the problems in DFT connected with the total spin and degenerate states cannot be rigorously solved within the framework of the density matrix formalism.
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1. Introduction

In the last two decades, the density functional theory (DFT) [1–3] has been widely used for solution of different problems in atomic, molecular, and solid-state physics. The numerous results of the DFT calculations performed in this period [4–8] demonstrated that its gradient corrected versions yield quite reliable results in the prediction of the global minima on the potential energy surfaces and give reasonable binding energies for different classes of atomic and molecular complexes in the ground states comparable with the *ab initio* calculations by the Møller–Plesset perturbation theory in the second order (MP2). The great advantage of the DFT methods is in its applicability to calculation of large systems for which *ab initio* methods are very expensive or limited by currently available computing power.

In spite of great success in the application of the DFT method to the ground-state properties, it was long ago rec-ognized [9,4] that DFT cannot be directly applied to calculation of the spin and space multiplet structure. The special procedures developed for overcoming these difficulties [4,9–14], strictly speaking, are all beyond the DFT scope [14], see also the discussion in Ref. [15]. For instance, the so-called multiplet-sum method (MSM) [9,12,13], in which the linear combinations of single-determinantal DFT energies are constructed in correspondence with the appropriate linear combinations of the Slater determinants for the state with the definite value of the total spin, does not follow from the pure DFT formalism; the same concerns to the restricted open-shell Kohn–Sham method (ROKS) [11]. It is important to mention that both methods do not treat correctly the correlation functionals, see discussion in Section 2.

The Kohn–Sham (KS) equations [16], on which the DFT methods are based, depend upon the ground-state electron density $\rho(r)$ that is the diagonal element of the spinless one-electron reduced density matrix [17]

$$\rho(\mathbf{r}_1) = N \sum_{\sigma_1,\ldots,\sigma_N} \int |\Psi(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N)|^2 dV^{(1)}, \qquad (1)$$

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where sum is taken over the whole spin space and integration is performed over the configuration space of all electrons except the first. The Kohn–Sham equations (as the Hartree–Fock equations) correspond to the independent particle approximation. The Hohenberg–Kohn theorem [18] and based on it the KS equations were formulated for nondegenerate ground-state described by a single-determinantal wave function. This limitation, as was accepted by most of the DFT users, was removed by the Levi–Lieb constraint search procedure [19,20]. In this procedure one searches a set of antisymmetric wave functions that leads to the same electronic density and then constructs a combination of these functions that minimizes the expectation value of the energy. As was demonstrated by Bersuker [21] and follows from our results (Section 3), in reality the constraint search cannot solve the problems arising in DFT in the case of degenerate states.

The spin-dependent DFT was developed first by von Barth and Hedin [22] who formulated the KS equations in so-called local spin density approximation (LSDA). The latter operates with different electron densities for different spin projections (ρ_α and ρ_β). The LSDA method, as the unrestricted Hartree–Fock method [23], corresponds to a state with a definite value of the spin projection S_z, but does not correspond to the state with a definite value of the total spin S. Its solution includes all possible values of $S \geqslant S_z$ that may exist in the studied N-electron system, in other words, it is spin-contaminated. The proper S is extracted from unrestricted KS calculations by some projection procedure that does not always lead to correct result; the new approaches for analysis of the spin contamination see in Refs. [24,25]. Note, the generalization of DFT by the pair density formulation [26,27] did not reveal new possibilities of treating states with definite S.

As was mentioned by McWeeny [28]: "electron spin is in a certain sense extraneous to the DFT". On the example of the two-electron system in the singlet and triplet spin states, McWeeny [28] showed that knowing only the electron density, one cannot identify the spin sate.

In this paper, we consider the general case on N-electron system in a state with an arbitrary total spin S and prove the independence of the electron density in respect to S. As we discuss below, the problems in DFT with description of spin- and space-degenerate states are connected with an inherent property of the electron density. Namely, the electron density of a quantum state does not depend upon the permutation and space symmetry of the state. We begin with consideration of states with a definite value of the total spin.

2. Total spin and DFT

As is well-known, the value of the total spin S of an arbitrary N-electron system is uniquely connected with the permutation symmetry of the spin wave function characterized by the Young diagram $[\tilde{\lambda}]$ with N boxes [29,30]. The total wave function, corresponding to the spin S and

satisfying the Pauli principle, can be constructed as a bilinear combination of the coordinate, $\Phi_{rt}^{[\lambda]}$, and spin, $\Omega_{\tilde{r}}^{[\tilde{\lambda}]}$, wave functions symmetrized according to the conjugate representations $\Gamma^{[\lambda]}$ and $\Gamma^{[\tilde{\lambda}]}$ of the permutation group with the dual Young diagrams [30,31],

$$\Psi_t^{[\lambda]} = \frac{1}{\sqrt{f_\lambda}} \sum_r \Phi_{rt}^{[\lambda]} \Omega_{\tilde{r}}^{[\tilde{\lambda}]}, \tag{2}$$

where index t enumerates the different bases that can be constructed for $\Gamma^{[\lambda]}$ and f_λ is the dimension of irreducible representations $\Gamma^{[\lambda]}$ and $\Gamma^{[\tilde{\lambda}]}$.

In nonrelativistic quantum mechanics, all properties of the studied system are completely determined by the coordinate wave function $\Phi_{rt}^{[\lambda]}$. The latter can be built on some nonsymmetric product of orthonormal orbitals (for simplicity we consider the single-occupied orbital configuration)

$$\Phi_0 = \varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)\ldots\varphi_N(\mathbf{r}_N), \tag{3}$$

$$\int \varphi_n^*(r)\varphi_m(r)d^3r = \delta_{nm}, \tag{4}$$

in the form [30,31]

$$\Phi_{rt}^{[\lambda]} = \sqrt{\frac{f_\lambda}{N!}} \sum_P \Gamma_{rt}^{[\lambda]}(P)P\Phi_0, \tag{5}$$

where $\Gamma_{rt}^{[\lambda]}(P)$ are the matrix elements of representation $\Gamma^{[\lambda]}$ and P runs over all $N!$ permutations of the permutation group π_N. The Young diagram $[\lambda]$ is uniquely connected with the value of spin S. Thus, each value of S corresponds to a definite expectation value of energy due to the permutation symmetry of the corresponding coordinate wave function.

As we prove in Theorem 1, it is not true for the energy functional expressed via the electron density because of some specific properties of the latter. Note that for the two-electron system, it was long ago known that the electron density is the same for the singlet and triplet states. Below we present the proof for the general case.

Theorem 1. *The electron density of an arbitrary N-electron system, characterized by the N-electron wave function corresponding to the total spin S and constructed on some orthonormal orbital set, does not depend upon the total spin S of the state and always preserves the same form as it is for a single-determinantal wave function.*

Proof. Let us substitute the total wave function in the form Eq. (2) and the coordinate wave function, expressed by Eq. (5), in the definition of electron density Eq. (1). Since the spin wave functions $\Omega_{\tilde{r}}^{[\tilde{\lambda}]}$ are orthonormal, Eq. (1) reduces to

$$\rho_t^{[\lambda]}(\mathbf{r}) = \frac{N}{f_\lambda} \sum_r \int |\Phi_{rt}^{[\lambda]}|^2 dV^{(1)}$$

$$= \frac{1}{(N-1)!} \sum_r \sum_{P,Q} \Gamma_{rt}^{[\lambda]}(P)^* \Gamma_{rt}^{[\lambda]}(Q) \int P\Phi_0^* Q\Phi_0 dV^{(1)}. \tag{6}$$

Due to the orthonormality condition Eq. (4), the integral in Eq. (6) is equal to

$$\delta_{PQ} \int |P\Phi_0|^2 dV^{(1)}$$

and Eq. (6) becomes

$$\rho_t^{[\lambda]}(\mathbf{r}) = \frac{1}{(N-1)!} \sum_P \sum_r \Gamma_{rt}^{[\lambda]}(P)^* \Gamma_{rt}^{[\lambda]}(P)$$
$$\times \int |P\Phi_0|^2 dV^{(1)}. \tag{7}$$

Taking into account that the sum over r is equal to 1 and each $P \subset \pi_N$ can be presented as $P_{1i}P'$ where $(N$-1)! permutation P' belong to the permutation group π_{N-1} not including the first electron, we arrive at the final result

$$\rho_t^{[\lambda]}(\mathbf{r}) = \sum_{n=1}^{N} |\varphi_n|^2. \tag{8}$$

We obtained the well-known expression of the electron density for the state described by the single-occupied determinantal function. In the same manner it is easy to show that in the case of orbital configuration with arbitrary occupation numbers, the final expression Eq. (8) will also correspond to the electron density for the one-determinantal function but with arbitrary occupation numbers.

Thus, regardless of the permutation symmetry of the coordinate wave function, which is uniquely connected with the value of the total spin S, the electron density for all S, describing by different multi-determinantal wave functions, has the same form as for a single Slater determinant. This result is rather surprising: different linear combinations of determinants correspond to the same expression as it is obtained with one determinant. From this follows that multi-determinantal versions of DFT cannot resolve the problem with the total spin. Due to the independence of the electron density on the total spin S, the density functionals, and, consequently, the conventional KS equations will be the same for all multi-determinantal wave functions corresponding to different S.

The mentioned above MSM and ROKS procedures, elaborated for the study of states with definite S, are based on the wave function formalism, hence they are both beyond the DFT approach. In MSM [9,12,13], the DFT energies are summed in the same way as the Slater determinants describing the state with given S. The functionals arising in this procedure may not be considered as a density functionals corresponding to a given value of the total spin, because, according to Theorem 1, such functionals do not exist. The MSM procedure is, in fact, a some practical recipe *ad hoc* that allows to calculate approximately the multiplet structure, see recent applications to iron coordination compounds [32,33]. It is worth-while to stress an approximate nature of MSM, it includes only the first order elec-

trostatic interactions [13], ignoring the second order (correlation) effects.

In the ROKS procedure [11], the Hamiltonian for the spin-restricted open-shell calculations is constructed similar to the Hamiltonian of the restricted open-shell Hartree–Fock (ROHF) method with an exception of the exchange part which is replaced by the exchange-correlation functional that is multiplied by some factor depending on the total spin S. Evidently, it leads to errors, since the exchange and correlation functionals must have a different dependence on S. Thus, in both procedures MSM and ROKS, the correlation functional does not correspond to the proper S. The same conclusion has to be made with respect to the orbital-dependent functional method by Görling et al. [34–36].

The paradox with an independence of the electron density on the total spin stems from the general invariance of the density matrix with respect to the symmetry of the state. This inherent property of the density matrix will be discussed in the next section.

3. Symmetry properties of the density matrix

Let us consider some degenerate quantum state with symmetry of a point group $\mathbf{G}$. The wave functions pertaining to this state must transform according to one of irreducible representations $\Gamma^{(\alpha)}$ of $\mathbf{G}$. As shown in Refs. [29,30], they can be constructed as

$$\Psi_{ik}^{(\alpha)} = \frac{f_\alpha}{g} \sum_R \Gamma_{ik}^{(\alpha)}(R)^* R\Psi_0, \tag{9}$$

where $\Gamma_{ik}^{(\alpha)}(R)$ are the matrix elements of the representation $\Gamma^{(\alpha)}$, f_α is its dimension, R runs over all g element of the group $\mathbf{G}$, and Ψ_0 is some arbitrary function. The set of f_α functions Eq. (9) with fixed second index k forms a basis for $\Gamma^{(\alpha)}$, index k enumerates different bases.

In a degenerate state, the system can be described with equal probability by any one of the basis vectors of this state. As a result, we can no longer select one of the basis vectors and should use the linear combinations, in which every basis vector enter with the same probability. It can be easily obtained (it was first shown by von Neumann [37]) that the diagonal element of the full density matrix for a degenerate state has the following form

$$D_k^{(\alpha)} = \frac{1}{f_\alpha} \sum_{i=1}^{f_\alpha} |\Psi_{ik}^{(\alpha)}|^2. \tag{10}$$

Theorem 2. *The diagonal element of the full density matrix is invariant with respect to all operations of the group symmetry of the state, that is, it is a group invariant.*

Proof. We apply an arbitrary operation $R \subset \mathbf{G}$ to the density matrix expression Eq. (10)

$$RD_k^{(\alpha)} = \frac{1}{f_\alpha} \sum_i \sum_l \Gamma_{li}^{(\alpha)}(R)^* \Psi_{lk}^{(\alpha)*} \sum_{l'} \Gamma_{l'i}^{(\alpha)}(R) \Psi_{l'k}^{(\alpha)}$$

$$= \frac{1}{f_\alpha} \sum_{l,l'} \left(\sum_i \Gamma_{li}^{(\alpha)}(R)^* \Gamma_{l'i}^{(\alpha)}(R) \right) \Psi_{lk}^{(\alpha)*} \Psi_{l'k}^{(\alpha)}.$$

Due to the orthogonality relations for the matrix elements of irreducible representations, the sum over i is equal to $\delta_{l'l}$, and we arrive at the final result:

$$RD_k^{(\alpha)} = \frac{1}{f_\alpha} \sum_{l=1}^{f_\alpha} |\Psi_{lk}^{(\alpha)}|^2 = D_k^{(\alpha)}. \qquad (11)$$

This means that for all irreducible representations, characterizing the quantum state, the diagonal element of the density matrix transforms according to the totally symmetric one-dimensional representation A_1 of **G** and in this respect one cannot distinguish between degenerate and nondegenerate states. Thus, the diagonal element of the density matrix is a group invariant.

The invariance of the diagonal elements of the density matrix following from the Theorem 2 could be expected. For the permutation group, this result was already used in Refs. [38,39]. Nevertheless, to the best of our knowledge, it was not discussed in literature. Even in the specialized monograph by Davidson [17], the total symmetry of the reduced density matrix is attributed only to nondegenerate states, but the latter is evident.

The pure electronic degenerate states may not be stationary. In the ordinary stationary case, e.g., for degenerate ground states, the Born–Oppenheimer adiabatic approximation fails and the nonadiabatic approach with the vibronic interaction, mixing electronic states, has to be applied. The broad scope of physical and physico-chemical problems arising in this case includes the Jahn–Teller effect [40,41] inelastic collisions [42], nonadiabatic molecular dynamics [43,44], and etc.

The applicability of the DFT approaches to degenerate states was analyzed in detail by Bersuker [21] who showed that the DFT method cannot, in principle, be applied to degenerate and pseudodegenerate states. On one hand, because in these states the electronic and nuclear motions are nonseparable and cannot be described by appropriate densities. On the other hand, the important in the Jahn–Teller systems Berry phase problem [45,46]: the strong dependence of the resulting energy spectrum and wave functions of the degenerate term of the phase properties of the electronic wave function, is beyond the DFT method. The latter is evident, since in the electron density formalism, operating with the square modulus of the wave function, the phase vanishes.

In Refs. [47,48] the authors claimed that they formulated the non-Born–Oppenheimer DFT. The simple analysis shows that both formulations must be attributed to the Born–Oppenheimer (BO) approximation. As was pointed out in the Ref. [21], the approach developed by Capitani et al. [47] corresponds to the BO approximation in its crude form (the so-called Condon adiabatic approximation), in which the electronic wave function does not depend upon the nuclear coordinates. Although in the approach by Kryachko et al. [48], the electronic density contains the nuclear coordinates, it also corresponds to the BO approximation, since the authors proceed from the multiplicative form of electronic and nuclear densities that is valid only for the nondegenerate states.

Final remark. There is an interesting similarity between the Jahn–Teller effect and the Pauli exclusion principle [39]. Due to the Jahn–Teller effect, the initial electron degeneracy is removed and the ground electronic state of non-linear molecules and solids is described by one-dimensional representations of the point (space) groups. But the same follows from the Pauli exclusion principle, according to which the permitted states of a system of identical particles must belong to symmetric or antisymmetric one-dimensional representations of the permutation group. This similarity in the two different principles connected with the symmetry groups of different nature is worth-while for a special study.

4. Conclusions

From the presented theorems and discussion follows that the problems in DFT with the total spin and, in general, with degenerate states cannot be rigorously solved within the framework of the density matrix formalism, on which DFT is based.

The insertion inside DFT the *ab initio* approaches (e.g., the expressions of the Hartree–Fock method) and exploiting both ρ- and Ψ-formalism can help to solve some of the discussed problems but only for the exchange functional. The construction of the correlation functional depending on the total spin is still unsolved problem.

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