Excited-state density functional theory

(Results of the OTKA project K123988)

Preliminaries, aims of the project

Density functional theory provides a huge simplification of the many–electron problem as only the electron density needs to be employed instead of the wave function. Originally it was a ground-state theory [1]. The first rigorous generalization of density functional theory for excited states was developed by Theophilou [2]. The subspace theory of Theophilou was enlarged into the theory of unequally weighted ensembles of excited states by Gross, Oliveira and Kohn [3]. However, the subspace and ensemble theories are complicated by the requirement that a whole ensemble of states has to be considered. Therefore, we proposed a theory for individual excited-states [4, 5]. The Levy-Nagy constrained-search functional [4, 5] is still complicated as not only the density of the given state but also the external potential (or the ground-state density) is needed. Therefore, the principal investigator proposed a theory for Coulomb systems [6, 7]. This approach was generalized by Ayers, Levy and Nagy [8] during the previous OTKA project K 100590.

We showed that the Coulomb density is special because it determines not only its Hamiltonian but the degree of excitation as well. Unlike existing formulations, additional functionals and indices are not required and the equations of excited-state density functional theory strongly resemble those of the ground-state theory. For practical computation the Kohn-Sham version of the theory was also derived [9].

The aims of the project were to extend the theory to degenerate states, to explore the most important properties of the exchange-correlation functional, to derive exact relations, theorems utilizing information-theoretical concepts.

The aims of the project have been achieved. 32 publications appeared. Several conference lectures were presented.

Results

Ayers-Levy-Nagy theory

The first aim of the project was the extension of our recently introduced excited-state theory to degenerate systems. To this end we identifined time-independent universal functionals of ensemble densities for individual degenerate excited levels of Coulomb systems. We proved that the ensemble Coulomb densities determine not only the Hamiltonian but the degree of excitation as well. We derived the Euler equation depending on only the ensemble density of the given degenerate excited level. We introduced the corresponding noninteracting system and derived the appropriate system of Kohn-Sham equations [10].

Then, the Ayers-Levy-Nagy theory was reconsidered using the nodal variational principle. It is much easier to solve the Kohn-Sham equations, because only the correct number of nodes of the orbitals should be insured instead of the orthogonality [11].

It is interesting to find out how these functionals behave under coordinate scaling. Relations for the scaled exchange, correlation, exchange-correlation and kinetic functionals have been presented. The exact form of the exchange-correlation functional is not known even for the ground state. Therefore, one needs approximation to perform calculations. It turned out that exact relations are useful in constructing approximate functionals for the ground state. It is supposed that this statement is true for excited states as well. Via coordinate scaling one can constract exact constraints that the excited-state functionals should satisfy. These relations are expected to be advantageous for designing approximate forms of excited-state functionals [12]. Later, other exact relations were also derived [13, 14].

The localized Hartree-Fock (LHF) and the Krieger, Li and Iafrate (KLI) methods were generalized for excited states and combined with a local Wigner-type correlation. Illustrative examples were presented for some highly excited states of Li and Na atoms [15].

We have applied density functional theory to investigate random Cu-Au alloys and order-disorder transformation in Fe-Ni [16, 17].

Spherical density functional theory

In a recent paper Theophilou [18] proved that in molecules and solids, a set of spherically symmetric densities determines uniquely the external potential. The principal investigator presented an alternative derivation of Theophilou's new theorem and proved a more general version via constrained search. Euler equations and Kohn-Sham equations have been derived for spherically symmetric densities [19].

Then, it was demonstrated that any of the spherically symmetric densities obeys a Schrödinger-like differential equation which is equivalent to the Euler equation of this density. The exact effective potential was derived and its form was explicitly given in terms of wave-function expectation values. The spherically symmetric densities reflect several properties of atoms and show some resemblance to the "Atoms in Molecules", though the two concepts are quite different [20].

Later, the theory was extended to degenerate states. Euler equations and Kohn-Sham equations were derived and a novel form of the virial theorem was presented. It was emphasized that degenerate states of atoms can be rigorously treated as spherically symmetric when a subspace density is used with equal weighting factors [21].

In this spherical theory, a 'set-representability problem' arises: does a density exist for a given set of spherically symmetric densities? This representability problem was solved using the potential instead of the density as basic variable. The spherical subspace potential functional theory was established [22, 23, 24, 25].

Subsequently, this novel spherical theory was extended to individual excited states. The generalization is based on the method developed in the series of papers by Ayers, Levy and Nagy [8, 9, 10]. Generalized Hohenberg-Kohn theorems were proved to the set of spherically symmetric densities using constrained search. A universal variational functional for the sum of the kinetic and electron-electron repulsion energies was constructed. The functional is appropriate for the ground state and all bound excited states. Euler equations and Kohn-Sham equations for the set were derived. The Euler equations can be rewritten as Schrödinger-like equations for the square root of the radial densities and the effective potentials in them can be expressed in terms of wave-function expectation values. The Hartree plus exchange-correlation potentials can be given by the difference of the interacting and the non-interacting effective potentials. (The paper has just been submitted.)

Orbital-free density functional theory

Nowadays, the great majority of DFT calculations are done by solving the Kohn-Sham equations. For a system with many particles there are a lot of Kohn-Sham equations. Therefore, it is reasonable to go back to the original Euler equation [26]. A new orbital-free approach was presented. In this theory, need for the kinetic enegy functional is avoided. Instead, a generating function is defined. It has two extra variables compared to the density and it reduces to the density if these variables are equal to zero. This new orbital-free theory is valid in case of zero and non-zero temperature, as well [27]. This method can be used for spherically symmetric systems. Combining this approach with spherical density functional theory mentioned above a novel orbital-free theory was created [28].

Pair density functional theory

Nowadays, excited-state calculations are mainly done by the time-dependent density functional theory (TDDFT). Generally, accurate results are obtained in a highly efficient way. There are, however, cases, where the adiabatic approximation fails.

A typical example is the double excitation. Therefore the principal investigator generalized the TDDFT to the pair density. The Runge-Gross theorem was proved for the pair density. A 'non-interacting scheme' of electron pairs was constructed via adiabatic connection and equations for the auxilary pair functions were presented [29].

Then, the time-independent pair density functional theory was extended to excited states of Coulomb systems. It was shown that the pair density determines the Hamiltonian of the Coulomb system. A universal kinetic energy functional appropriate for the ground and all bound excited states is defined. The Euler equation can be rewritten as a two-particle auxiliary equation in which the unknown Pauli-like potential should be approximated [30].

Information-theoretical concepts

Information-theoretic concepts have proved to be useful in density functional theory. We extended these concepts to excited states. Euler equations were derived in the orbital-free excited-state density functional theory of Coulomb systems for the specific relative information. Derivation via variational extremization of the relative Fisher information was also presented. We displayed the relationships between the Fisher and Shannon information, the local wave-vector and the relative information [32].

Ensembles of excited states were also studied. It was shown by Ghosh, Berkowitz [33] and Parr that the ground-state density functional theory can be trancripted as a local thermodynamics. Earlier we extended this formalism to ensembles of excited states [34]. These theories, however, are not unique as one of their key quantities, the kinetic energy density, can be defined in several ways. Usually the everywhere positive gradient form is applied, but other forms are also acceptable, provided they integrate to the true kinetic energy. Recently, a kinetic energy density of the ground-state theory maximizing the information entropy has been proposed. Then, an ensemble kinetic energy density leading to extremum information entropy were derived via constrained search. The ensemble temperature is found to be constant [35]. It was also shown that extremization of the Fisher information results a constant temperature. For Coulomb systems there is a simple relation between the total energy and phase-space Fisher information [36].

The phase-spase fidelity between excited states is proportional to the position-space fidelity, with a factor of proportionality depending on total energies. The phase-spase relative entropy is equal to the position-space relative entropy plus a term depending only on the total energies. Relationship between phase-spase fidelity susceptibility and Fisher information was also presented [37].

A review on the relationship of Fisher information and density functional theory was published[38].

Phase-space Rényi entropy and complexity were defined within the thermodynamic picture of density functional theory. The structural entropy defined by Pipek, Varga and Nagy, the LMC statistical complexity introduced by López-Ruiz, Mancini and Calbet and the generalized complexity proposed by López-Ruiz, Nagy, Romera and Sanudo were extended to the phase space. It was shown that in case of constant local temperature the logarithm of the phase-space LMC complexity reduces to the position-space structural entropy defined by Pipek et al. [39]

The phase-space relative Rényi entropy was introduced using the information theoretical and thermodynamic view of density functional theory. In the special case of constant inverse temperature the phase-space relative Rényi entropy is a sum of the position-space relative Rényi entropy and a term arising from the momentum space. This quantity can be considered as a measure of similarity. It includes more information than the position-space measures, since it also incorporates momentum-space knowledge [40].

Information theoretical concepts such as fidelity and phase-space Fisher information have also been studied as markers of topological phase transitions in 2D Dirac materials [41, 42, 43].

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