Density-functional theory beyond the Hohenberg-Kohn theorem

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A density-functional theory that treats all states of an electronic system on the same footing is introduced. The corresponding Kohn-Sham formalism can be applied to ground and excited states alike, does not suffer from a v-representability problem, and represents a rigorous formal basis for the common, but so far unjustified practice to treat excited states by Kohn-Sham methods. The presented density-functional theory emerges from a generalization of the constrained-search procedure. The new Kohn-Sham formalism is based on generalized adiabatic connections introduced here. The possible topologies of those generalized adiabatic connections are discussed. A density-based stationarity principle and a density theorem that represents a more general counterpart of the Hohenberg-Kohn theorem are presented. A method to take into account exactly exchange interactions in the presented Kohn-Sham formalism is introduced, implemented, and applied to atoms. [S1050-2947(99)01105-1]

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I. INTRODUCTION AND SUMMARY

Density-functional theory (DFT) [1–7] is the most widely used theory for the investigation of electronic systems. It is almost exclusively applied within the framework of the Kohn-Sham (KS) formalism [2,3,8]. Despite its dominant position in molecular and solid state physics, traditional DFT, i.e., present DFT in contrast to the DFT developed in this work, exhibits a number of serious shortcomings and limitations.

First, ground and excited states play very different roles. The ground state is a central quantity in traditional DFT. Many of its properties can be calculated accurately and efficiently with present DFT methods. Excited states and their properties, on the other hand, are not directly accessible in traditional DFT, except those excited states that are the energetically lowest of their symmetry [9]. Nevertheless, a treatment of excited states is, in principle, possible on the basis of traditional DFT. Indeed, ensemble formalisms for excited states were suggested by Theophilou [10] and by Gross *et al.* [11–13]. Görling presented a formalism to treat excited states on the basis of the ground-state KS orbitals [14]. However, so far both types of formalisms could be applied only to a few atomic systems [15,16]. The reason is that reliable generally applicable approximations for the required specific density functionals are lacking. The implementation of ensemble formalisms is furthermore impeded by technical difficulties. Thus a direct investigation of excited states is *de facto* not possible within traditional DFT. In practice, excitation energies of atoms and molecules can be determined indirectly through time-dependent DFT [17–26]. This, however, leads to the unsatisfying necessity to resort to a time-dependent theory in order to describe a property of a stationary state.

A second weakness of traditional DFT is that its applicability within the KS formalism depends on a quantity, the KS model system, whose existence is not guaranteed but has to be assumed. While this assumption, the v-representability assumption [2,3], seems to be justified in most cases, there are some systems, e.g., certain lanthanide and actinide atoms, for which it may not hold true [27].

In this work a more general density-functional theory and the corresponding generalization of the KS formalism is introduced. The DFT of this work emerges from a generalization of the constrained-search [28–30] procedure. The new KS formalism is based on generalized adiabatic connections (GAC's) introduced here, and is therefore called the GAC-KS formalism [31–34]. A density-based stationarity principle and a density theorem that represents a more general counterpart of the Hohenberg-Kohn (HK) theorem are presented. The formalism of this work treats all states of an electronic system on the same footing, makes a direct KS treatment of excited states possible, and does not suffer from a v-representability problem.

A KS formalism for excited states suggested by Fritsche [35,36] also is based on a generalization of adiabatic connections. The formalism of Fritsche relies on a relation between changes of the electron density and changes of the correlated pair density [36]. The validity of this relation has been the subject of controversial discussions. Here, in Appendix A, it is shown that the relation, in general, does not hold true. The formalism of this work is founded on an entirely different basis, a generalization of the constrained-search procedure, namely, and at no point refers to the pair density or related quantities and thus is not plagued by the problems of Fritsche's formalism.

The introduced new KS formalism can be applied as easily as the traditional one. Indeed, a frequently used, however so far formally unjustified, approach to treat excited states can be identified as a crude approximate application of the new KS formalism. It is common practice to straightforwardly treat excited states within the standard KS scheme by simply leaving energetically low KS orbitals unoccupied [4]. Unless the considered excited state is the lowest of its symmetry [9], this procedure is completely unjustified within the traditional KS formalism. Nevertheless, it often yields good results. The formalism of this work represents a sound formal basis for this procedure and therefore explains its success.

In order to fully exploit the potential of the DFT presented here and of the corresponding KS formalism, it is necessary to develop reliable approximations for the density functionals occurring in the new theory. The crude approach of simply approximating the density functionals of the new theory by those from traditional DFT can be considered only as a first preliminary step towards this goal. As a possible next step, a method for the exact treatment of the exchange functionals is suggested in this work. For atoms, such an exact-exchange GAC-KS method is shown to be feasible. As an illustration, excitation energies of alkaline atoms are calculated. An exact-exchange GAC-KS method for molecules is currently developed [37].

The paper is organized as follows. In Sec. II, traditional DFT is reexamined. In particular, it is shown that, in contrast to a widely adopted point of view, the Hohenberg-Kohn (HK) theorem is not a sufficient foundation for traditional DFT. The constrained-search procedure, on the other hand, is shown to suffice as a basis for traditional DFT. In Sec. III A, the constrained-search procedure is generalized. In Sec. III B, the more general DFT of this work is established. To that end, two lemmas are proven and then used to derive a density-based stationarity principle and a density theorem that may be considered as a more general counterpart of the HK theorem of traditional DFT. Section III C introduces generalized adiabatic connections between noninteracting and interacting electronic systems. In Sec. III D the GAC-KS formalism, the analog of the traditional KS formalism, is presented. The GAC-KS formalism is derived under a certain assumption on the topology of GAC's. Section IV discusses the accessibility of the density functionals arising in the new formalism and introduces an exact-exchange GAC-KS method. As an illustration, excitation energies of alkaline atoms are calculated within the new formalism in Sec. V. Section VI contains concluding remarks. In Appendix A, the validity of the relation of Refs. [35, 36] between changes of the correlated pair density and the density is scrutinized. GAC's that do not exhibit the required topology are considered in Appendix B.

II. TRADITIONAL DENSITY-FUNCTIONAL THEORY AND THE STANDARD KOHN-SHAM FORMALISM

In this section the structure of traditional DFT and of the standard KS formalism is reexamined and the starting points for the generalization and modifications suggested in this work are discussed. The development of DFT began with the discovery of the HK theorem [1] and according to a widely adopted point of view the HK theorem plays *the* central role within DFT. Indeed, the HK theorem is often considered as a sufficient basis for traditional DFT including the standard KS formalism. This, however, is not true. Therefore, in this work traditional DFT is considered from a somewhat different angle with the constrained-search procedure [28–30] instead of the HK theorem placed at the center of the theory.

The HK theorem states that two electronic systems with external potentials that differ by more than a constant cannot have ground states with the same electron density. The theorem holds true only for local external potentials, i.e., for electronic systems with a Hamiltonian operator of the form $\hat{T} + \alpha\hat{V}_{ee} + \hat{v}$ with $\hat{v}$ being the operator generated by a local

potential $v(\mathbf{r})$. Here, $\hat{T}$ and $\hat{V}_{ee}$ are the operators of the kinetic energy and of the electron-electron interaction, respectively. The constant α with values between zero and one, $0 \leqslant \alpha \leqslant 1$, is the coupling constant of the electrons. For real physical systems the coupling constant equals 1. The HK theorem, however, is valid for arbitrary positive values of α which can be even larger than 1 and thus can lie outside the range of α relevant in this work. From the HK theorem it follows that the ground-state electron density of an electronic system uniquely determines the corresponding external potential up to an additive constant [1–3]. Additionally the density determines the particle number. Thus the ground-state electron density determines the Hamiltonian operator and subsequently all properties of the electronic system.

The HK theorem allows one to define the Hohenberg-Kohn functional $\widetilde{F}[\tilde{\rho}, \alpha]$, a functional of ground-state densities $\tilde{\rho}$ and coupling constants α given by the expectation value

$$\widetilde{F}[\tilde{\rho}, \alpha] = \langle \widetilde{\Psi}[\tilde{\rho}, \alpha] | \hat{T} + \alpha\hat{V}_{ee} | \widetilde{\Psi}[\tilde{\rho}, \alpha] \rangle \qquad (1)$$

of the ground state $\widetilde{\Psi}[\tilde{\rho}, \alpha]$ belonging to $\tilde{\rho}$ and α. The tilde on $\tilde{\rho}$ indicates that $\tilde{\rho}$ is a ground-state density, i.e., that it is the density of the ground state of a Hamilton operator of the form $\hat{T} + \alpha\hat{V}_{ee} + \hat{v}$. Such densities are called v-representable [2,3] for the corresponding value of α. The tilde on $\widetilde{F}$ and $\widetilde{\Psi}$ indicates that the HK functional $\widetilde{F}[\tilde{\rho}, \alpha]$ and the wave function $\widetilde{\Psi}[\tilde{\rho}, \alpha]$ are defined only for v-representable densities. The ground-state density $\tilde{\rho}$ yields $\widetilde{F}[\tilde{\rho}, \alpha]$ in an indirect way for a given α: $\tilde{\rho}$ determines the external potential and the electron number N and thus the Hamiltonian operator; the Hamiltonian operator then leads to the ground state $\widetilde{\Psi}[\tilde{\rho}, \alpha]$ which finally gives $\widetilde{F}[\tilde{\rho}, \alpha]$ by Eq. (1). These dependencies may be symbolized by

$$\tilde{\rho}(\mathbf{r}) \rightarrow v(\mathbf{r}), N \rightarrow \hat{T} + \alpha\hat{V}_{ee} + \hat{v} \rightarrow \widetilde{\Psi}[\tilde{\rho}, \alpha] \rightarrow \widetilde{F}[\tilde{\rho}, \alpha]. \quad (2)$$

For a specific particle number N, coupling constant α, and external potential $v(\mathbf{r})$, the inequality

$$\widetilde{F}[\tilde{\rho}, \alpha] + \int d\mathbf{r}\, v(\mathbf{r})\tilde{\rho}(\mathbf{r}) \geqslant \widetilde{F}[\rho_0, \alpha] + \int d\mathbf{r}\, v(\mathbf{r})\rho_0(\mathbf{r})$$
$$(3)$$

holds true. In inequality (3), $\tilde{\rho}$ is an arbitrary v-representable density, in other words $\tilde{\rho}$ is the density of the ground state of a Hamiltonian operator $\hat{T} + \alpha\hat{V}_{ee} + \hat{v}'$ with some external potential $v'(\mathbf{r})$ which, in general, is different from the given potential $v(\mathbf{r})$. On the other hand, ρ_0 shall be the electron density of the ground state of the Hamilton operator $\hat{T} + \alpha\hat{V}_{ee} + \hat{v}$ with the given external potential $v(\mathbf{r})$. With definition (1), inequality (3) follows directly from the fact that the ground state $\widetilde{\Psi}[\rho_0, \alpha]$ yields a lower energy expectation value with $\hat{T} + \alpha\hat{V}_{ee} + \hat{v}$ than any other wave function, thus also a lower energy expectation value than wave functions $\widetilde{\Psi}[\tilde{\rho}, \alpha]$ of ground-state densities $\tilde{\rho}$ that differ from ρ_0. Inequality (3) sometimes is called the second HK theorem, a notation not adopted here.

Inequality (3) suggests to find the ground-state energy $\widetilde{F}[\widetilde{\rho},\alpha]+\int d\mathbf{r}\, v(\mathbf{r})\widetilde{\rho}(\mathbf{r})$ of an electronic system by finding the electron density ρ_0 which minimizes $\widetilde{F}[\widetilde{\rho},\alpha]$ $+\int d\mathbf{r}\, v(\mathbf{r})\widetilde{\rho}(\mathbf{r})$ and by subsequently evaluating $\widetilde{F}[\rho_0,\alpha]$ $+\int d\mathbf{r}\, v(\mathbf{r})\rho_0(\mathbf{r})$. In Thomas-Fermi methods [2,3,38,39] the ground-state density and energy are obtained by a minimization of density functionals for the ground-state energy. At first glance, inequality (3) may be considered as a formal justification of such methods. A closer look, however, reveals that inequality (3) does not suffice for this purpose. The reason is that the HK functional $\widetilde{F}[\widetilde{\rho},\alpha]$ and therefore inequality (3) is defined only for v-representable densities. Criteria that are sufficient to determine whether or not a given density is v-representable are unknown. Therefore, it is not possible to carry out a minimization based on inequality (3). In Thomas-Fermi methods, on the other hand, one minimizes over all densities yielding the correct particle number regardless of whether they are v-representable or not. Thus these methods are not justified by inequality (3) or the HK theorem. This is an example demonstrating that the HK theorem alone is not a sufficient basis for DFT.

The v-representability problem can be solved [28–30] by defining a more general HK functional $F[\rho,\alpha]$ by a constrained search as

$$F[\rho,\alpha]=\min_{\psi\to\rho}\langle\Psi|\hat{T}+\alpha\hat{V}_{ee}|\Psi\rangle. \qquad (4)$$

The minimization in Eq. (4) runs over all wave functions yielding the electron density ρ. The minimum, by definition the absolute minimum, can be shown to exist [40] for all well-behaved densities independent of whether or not the densities are v-representable. Thus $F[\rho,\alpha]$ is defined for all densities, not only for v-representable ones. The minimizing wave function is denoted $\Psi[\rho,\alpha]$. By

$$\min_{\psi\to\rho}\langle\Psi|\hat{T}+\alpha\hat{V}_{ee}|\Psi\rangle\to\Psi[\rho,\alpha] \qquad (5)$$

it is expressed that minimization (4) determines $\Psi[\rho,\alpha]$. The dependency of the HK functional $F[\rho,\alpha]$ and the corresponding minimizing wave function on the density can now be symbolized by

$$\rho(\mathbf{r})\to\Psi[\rho,\alpha],F[\rho,\alpha], \qquad (6)$$

a relation that is much simpler than the one of scheme (2) for $\widetilde{F}[\widetilde{\rho},\alpha]$. For v-representable densities $\widetilde{\rho}$ the functionals $\widetilde{F}[\widetilde{\rho},\alpha]$ and $F[\widetilde{\rho},\alpha]$ as well as $\widetilde{\Psi}[\widetilde{\rho},\alpha]$ and $\Psi[\widetilde{\rho},\alpha]$ can be shown to be identical [2,3].

Inequality (3) can now be rewritten for the HK functional $F[\rho,\alpha]$,

$$F[\rho,\alpha]+\int d\mathbf{r}\, v(\mathbf{r})\rho(\mathbf{r})\geqslant F[\rho_0,\alpha]+\int d\mathbf{r}\, v(\mathbf{r})\rho_0(\mathbf{r}). \qquad (7)$$

Now arbitrary densities ρ, not only ground-state densities $\widetilde{\rho}$, can be substituted in the left-hand side of inequality (7). Thus inequality (7) represents a sound formal basis for Thomas-Fermi-like methods. Note that the HK theorem is no longer invoked in this justification of Thomas-Fermi-like methods. Moreover, the constrained-search definition (4) of the HK functional immediately yields the HK theorem: If for a given α two electronic systems with different external potentials had the same ground-state density ρ_0, then they would have the same ground state $\Psi[\rho_0,\alpha]$ because $\Psi[\rho_0,\alpha]$, by definition, yields the lowest value for the sum of the kinetic and the electron-electron interaction energy while the interaction energy with the external potential is identical for all wave functions yielding the ground-state density ρ_0. However, two electronic system with external potentials differing by more than a constant cannot have the same ground state if potentials are restricted to be local. The crucial point shown here is that the constrained-search procedure given in Eq. (4) is a more fundamental basis for DFT than the HK theorem because the constrained-search procedure not only leads to the HK theorem but furthermore yields, independently of the HK theorem, inequality (7), solves the v-representability problem, and thus justifies Thomas-Fermi methods.

In the DFT introduced in this work, a constrained search is carried out not only for the absolute minimum as in Eq. (4) but for stationary points in general. The resulting generalization of Eq. (4) yields functionals that are more general than the HK functional $F[\rho,\alpha]$ and the corresponding generalization of Eq. (5) leads to more wave functions than just the minimizing wave functions $\Psi[\rho,\alpha]$.

While Thomas-Fermi methods, in principle, are very appealing, they are unsuitable for practical purposes because sufficiently accurate approximations for the unknown functional $F[\rho,\alpha]$ are not available. In practice, DFT is almost exclusively employed via the KS formalism. Within the KS formalism one calculates a model wave function, the KS wave function, which is associated with the real physical ground-state wave function. From the KS wave function one then deduces properties of the physical system, in particular the ground-state energy. The KS wave function is defined by three condition: (i) It is an eigenstate of a model system of hypothetical noninteracting electrons, i.e., it is an eigenstate of a Hamiltonian operator of the form $\hat{T}+\hat{v}_s$ with $\hat{v}_s$ being generated by a local effective potential $v_s(\mathbf{r})$, the KS potential, (ii) it yields the same electron density as the real physical ground state, (iii) it is a specific eigenstate of the noninteracting Hamiltonian operator $\hat{T}+\hat{v}_s$, namely the ground state. Because of the HK theorem these conditions guarantee that for a given physical electron system not more than one KS wave function can exist and that the KS wave function therefore is well defined.

Condition (iii) is necessary for the application of the HK theorem. This condition, however, also reintroduces a v-representability problem into the traditional KS formalism even though the constrained-search definition (4) of the HK functional is not plagued by v-representability problems. While the KS wave function is unique if it exists, there is no guarantee that it exists. This has to be assumed. In other words, the KS formalism is based on the v-representability condition that every ground-state electron density of a physical interacting system is also the ground-state density of a noninteracting KS system. From practical experience one may conclude that this assumption holds true in most cases.

On the other hand, there is evidence for violations of this assumption, e.g., in lanthanide and actinide atoms with open f shells [27].

For the determination of the KS wave function, the functional derivatives with respect to the density of the HK functionals at $\alpha = 0$ and $\alpha = 1$ are required [2,3]:

$$v_s(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \left. \frac{\delta F[\rho, \alpha = 1]}{\delta \rho(\mathbf{r})} \right|_{\rho(\mathbf{r}) = \rho_0([v_{\text{ext}}]; \mathbf{r})}$$
$$- \left. \frac{\delta F[\rho, \alpha = 0]}{\delta \rho(\mathbf{r})} \right|_{\rho(\mathbf{r}) = \rho_0([v_{\text{ext}}]; \mathbf{r})}. \tag{8}$$

In Eq. (8), $v_{\text{ext}}(\mathbf{r})$ is the known external potential of a considered physical electron system, usually the potential of the nuclei and $\rho_0([v_{\text{ext}}]; \mathbf{r}$ is the ground-state density of this system. Throughout this work $v_{\text{ext}}(\mathbf{r})$ designates exclusively external potentials of fully interacting electron systems while $v(\mathbf{r})$ stands for external potentials of systems with arbitrary coupling constant. At this point it is again important to define the HK functionals via the constrained-search procedure because in order to take in Eq. (8) the functional derivatives of density functionals at the ground-state density $\rho_0([v_{\text{ext}}]; \mathbf{r})$ it is necessary that the functional is defined in a vicinity of this density. For the HK functionals $\widetilde{F}[\widetilde{\rho}, \alpha]$ this would require that a vicinity of v-representable densities exists around each v-representable density. Whether this is the case or not is unclear. Here the importance of the constrained-search procedure shows up again.

In the GAC-KS formalism introduced in the next section, model wave functions are introduced in a different way. The model wave functions again are required to yield the same density as the considered state of the real physical electron system and again have to be eigenfunctions of a noninteracting Hamiltonian operator with local effective potential. But it is *no longer required that the model wave functions are ground states* of such a noninteracting Hamiltonian operator. In other words, from the conditions defining the standard KS system, conditions (i) and (ii) are retained in the definition of the model wave functions of the GAC-KS formalism, whereas condition (iii) is no longer involved. Therefore, no v-representability problem plagues the GAC-KS formalism. Instead of condition (iii), a generalized adiabatic connection between interacting and noninteracting states is used to completely define the model wave functions. Because condition (iii) is no longer involved, the resulting GAC-KS formalism treats ground and excited states alike.

An important difference from the traditional KS formalism is that the HK theorem is not required in the derivation of the GAC-KS formalism. The density theorem emerging as a generalization of the HK theorem in the DFT of this work also is not required. The density theorem is obtained as an interesting but not crucial spin-off.

III. DFT BEYOND THE HK THEOREM, GAC-KS FORMALISM

In density-functional theory it is common to assume that functionals are differentiable with respect to the density or

the coupling constant of the electrons [2,3]. This assumption will also be made throughout this work.

Only electron systems with properly normalizable wave functions, i.e., finite systems, are considered. Systems with an exponentially decaying asymptotic electron density, like atoms or molecules, are therefore placed in a large but finite box in order to enforce normalizable unbound states. Periodic systems are treated before the thermodynamic limit is taken by considering a large but finite number of unit cells embedded in periodic boundary conditions.

For simplicity, electronic systems will be treated in this work as if they had no symmetries and only nondegenerate eigenstates. Real systems always exhibit symmetries. Even if no symmetries in real space are present, there still exists full rotational symmetry in spin space if, as in this work, relativistic effects are neglected. Symmetries can be taken into account in the present formalism along the lines of Ref. [41], which suggests a treatment of symmetries in traditional DFT.

A. Functionals $Q[\rho, \nu, \alpha]$

Functionals $Q[\rho, \nu, \alpha]$ are defined as expectation values

$$Q[\rho, \nu, \alpha] = \langle \Psi[\rho, \nu, \alpha] | \hat{T} + \alpha \hat{V}_{ee} + \hat{v} | \Psi[\rho, \nu, \alpha] \rangle \tag{9}$$

of wave functions $\Psi[\rho, \nu, \alpha]$. The $\Psi[\rho, \nu, \alpha]$ are those wave functions that yield the electron density ρ and for that, additionally, the expectation value $\langle \Psi[\rho, \nu, \alpha] | \hat{T} + \alpha \hat{V}_{ee} | \Psi[\rho, \nu, \alpha] \rangle$ is stationary with respect to variations $\delta_{\Psi \to \rho}$ of $\Psi[\rho, \nu, \alpha]$ which leave the electron density unchanged, i.e., variations that turn $\Psi[\rho, \nu, \alpha]$ into a wave function with the same electron density. That means that the $\Psi[\rho, \nu, \alpha]$ are those wave functions with density ρ for which the condition

$$\delta_{\Psi \to \rho} \langle \Psi | \hat{T} + \alpha \hat{V}_{ee} | \Psi \rangle = 0 \tag{10}$$

holds true. The parameter ν labels all existing wave functions $\Psi[\rho, \nu, \alpha]$ of a given density ρ in some arbitrary order. The $\Psi[\rho, \nu, \alpha]$ shall be called *ρ-stationary wave functions* (of the density ρ and the coupling constant α). If the ρ-stationary wave functions $\Psi[\rho, \nu, \alpha]$ of a given ρ and α are all isolated, then the labels ν are integers, otherwise also labels ν being real numbers may occur. A ρ-stationary wave function $\Psi[\rho, \nu, \alpha]$ is isolated if around $\Psi[\rho, \nu, \alpha]$ there exists a neighborhood in the Hilbert space in which no other ρ-stationary wave function of the same density ρ and of the same coupling constant α is present. Wave functions that are distinguished just by a constant phase factor, as usual, are considered as identical.

In order to compare the functional $Q[\rho, \nu, \alpha]$ with the HK functional $F[\rho, \alpha]$, it is expressed in the form

$$Q[\rho, \nu, \alpha] = \underset{\nu, \Psi \to \rho}{\text{stat}} \langle \Psi | \hat{T} + \alpha \hat{V}_{ee} | \Psi \rangle. \tag{11}$$

The expression $\text{stat}_{\nu, \Psi \to \rho} \langle \Psi | \hat{O} | \Psi \rangle$ stands for the νth stationary value of the expectation value $\langle \Psi | \hat{O} | \Psi \rangle$ of an operator $\hat{O}$ under the constraint that the wave functions Ψ yield the electron density ρ. Because the labeling of the stationary values is arbitrary, they are determined in two steps. Within

the set of wave functions that yield the density ρ, one first determines all wave functions for which the expectation value $\langle\Psi|\hat{O}|\Psi\rangle$ is stationary with respect to all variations $\delta_{\Psi\to\rho}$ that do not change the density. Subsequently, one then labels all the stationary points. The Hohenberg-Kohn functional $F[\rho,\alpha]$ is contained in the set of functionals $Q[\rho,\nu,\alpha]$ because the absolute minimum $\min_{\Psi\to\rho}\langle\Psi|\hat{T}+\alpha\hat{V}_{ee}|\Psi\rangle$ of Eq. (4) is a stationary point.

By

$$\operatorname*{stat}_{\nu,\Psi\to\rho}\langle\Psi|\hat{T}+\alpha\hat{V}_{ee}|\Psi\rangle\to\Psi[\rho,\nu,\alpha]\tag{12}$$

it is expressed that the νth stationary point determines the wave function $\Psi[\rho,\nu,\alpha]$ in a similar but more general way as the minimum (5) determines the wave function $\Psi[\rho,\alpha]$. The latter is a ρ-stationary wave function, i.e., $\Psi[\rho,\alpha]$ is contained in the set of wave functions $\Psi[\rho,\nu,\alpha]$.

The dependencies between densities ρ, functionals $\Psi[\rho,\nu,\alpha]$, and wave functions $\Psi[\rho,\nu,\alpha]$ may be symbolized by the scheme

$$\rho(\mathbf{r})\to\Psi[\rho,\nu,\alpha],Q[\rho,\nu,\alpha]\tag{13}$$

that resembles scheme (6) of traditional DFT. However, one density now determines a whole set of wave functions and functionals. Both the minimizations (4) and (5) and the finding of stationary points in Eqs. (11) and (12) are carried out by a constrained search, a search over the subset of wave functions that yield a given electron density. The difference between Eqs. (4) and (5) on the one hand and Eqs. (11) and (12) on the other is that in the latter all stationary points, not only the absolute minimum, are searched for.

The functional derivative of $Q[\rho,\nu,\alpha]$ with respect to the electron density for fixed ν and α shall be denoted by

$$q([\rho,\nu,\alpha];\mathbf{r})=\delta Q[\rho,\nu,\alpha]/\delta\rho(\mathbf{r}).\tag{14}$$

In the formalism considered here, the electron number is fixed. As a result, functional derivatives with respect to the electron density are defined only up to an additive constant because changes $\delta\rho(\mathbf{r})$ of the electron density have to obey the condition $\int d\mathbf{r}\,\delta\rho(\mathbf{r})=0$ which guarantees particle number conservation. That means the functional derivative of $Q[\rho,\nu,\alpha]$ with respect to the density is represented by a set of functions with the functions differing by an additive constant. The function $q([\rho,\nu,\alpha];\mathbf{r})$ shall be one arbitrary member of this set.

B. Relation of $\Psi[\rho,\nu,\alpha]$ and $Q[\rho,\nu,\alpha]$ to eigenstates and potentials, generalization of Thomas-Fermi methods

The relation of ρ-stationary wave functions $\Psi[\rho,\nu,\alpha]$ and of functionals $Q[\rho,\nu,\alpha]$ to eigenvalues and potentials of electronic systems is described with the help of two lemmas. The first lemma, lemma I, states that *each eigenstate Ψ_i of an electronic system with coupling strength α is ρ-stationary for the coupling constant α.* In other words, each eigenstate Ψ_i of an electronic system with coupling constant α is a member of the set of wave functions $\Psi[\rho_i,\nu,\alpha]$ corresponding via the constrained-search (12) to the electron density ρ_i of Ψ_i, $\Psi_i=\Psi[\rho_i,\nu,\alpha]$. Lemma I follows from the basic

stationarity principle of quantum mechanics. This principle states that the eigenstates of a Hamiltonian operator $\hat{T}+\alpha\hat{V}_{ee}+\hat{v}$, with the operator $\hat{v}$ being generated by a local external potential $v(\mathbf{r})$, are those wave functions for which the expectation value $\langle\Psi_i|\hat{T}+\alpha\hat{V}_{ee}+\hat{v}|\Psi_i\rangle$ is stationary with respect to any variation $\delta_{\Psi\to N}$ turning Ψ_i into another normalized N-electron wave function. The expectation value $\langle\Psi_i|\hat{T}+\alpha\hat{V}_{ee}+\hat{v}|\Psi_i\rangle$ is therefore also stationary for the subset $\delta_{\Psi\to\rho}$ of variations. This leads to

$$0=\delta_{\Psi\to\rho}\langle\Psi_i|\hat{T}+\alpha\hat{V}_{ee}+\hat{v}|\Psi_i\rangle=\delta_{\Psi\to\rho}\langle\Psi_i|\hat{T}+\alpha\hat{V}_{ee}|\Psi_i\rangle.\tag{15}$$

The second equality in Eq. (15) follows because $\delta_{\Psi\to\rho}\langle\Psi_i|\hat{v}|\Psi_i\rangle=0$ due to the fact that the variation $\delta_{\Psi\to\rho}$ does not change the density. Equation (15) identifies Ψ_i as a member of the set of ρ-stationary wave functions $\Psi[\rho_i,\nu,\alpha]$; see Eq. (10).

Lemma II states that *each ρ-stationary wave function $\Psi[\rho,\nu,\alpha]$ is an eigenstate of an electronic system with coupling strength α and with the external potential $v(\mathbf{r})$ given by*

$$v(\mathbf{r})=-q([\rho,\nu,\alpha];\mathbf{r})+\mu.\tag{16}$$

In Eq. (16), μ is an arbitrary additive constant. In order to prove lemma II, an arbitrary variation $\delta\Psi$ (of type $\delta_{\Psi\to N}$) of a wave function $\Psi[\rho,\nu,\alpha]$ accompanied by a corresponding variation $\delta\rho$ of the density is decomposed according to

$$\delta\Psi=\delta\Psi_1+\delta\Psi_2\tag{17}$$

with

$$\delta\Psi_1=\Psi[\rho+\delta\rho,\nu,\alpha]-\Psi[\rho,\nu,\alpha]\tag{18}$$

and

$$\delta\Psi_2=\delta\Psi-\delta\Psi_1.\tag{19}$$

The first variation $\delta\Psi_1$ converts $\Psi[\rho,\nu,\alpha]$ into a wave function $\Psi[\rho+\delta\rho,\nu,\alpha]$ that also is ρ-stationary for the coupling constant α, however, for the density $\rho+\delta\rho$. The parameter ν shall remain unaffected by the variation. The second variation $\delta\Psi_2$ then, by construction, does not change the density in first order, i.e., $\delta\Psi_2$ is of type $\delta_{\Psi\to\rho}$. The equation

$$\langle\delta\Psi|\hat{T}+\alpha\hat{V}_{ee}+\hat{v}|\Psi[\rho,\nu,\alpha]\rangle+\text{c.c.}$$

$$=\langle\delta\Psi_1|\hat{T}+\alpha\hat{V}_{ee}+\hat{v}|\Psi[\rho,\nu,\alpha]\rangle+\text{c.c.}$$

$$=\langle\delta\Psi_1|\hat{T}+\alpha\hat{V}_{ee}|\Psi[\rho,\nu,\alpha]\rangle+\text{c.c.}$$

$$+\langle\delta\Psi_1|\hat{v}|\Psi[\rho,\nu,\alpha]\rangle+\text{c.c.}$$

$$=\delta Q[\rho,\nu,\alpha]+\int d\mathbf{r}\,v(\mathbf{r})\,\delta\rho(\mathbf{r})$$

$$=\int d\mathbf{r}[q([\rho,\nu,\alpha];\mathbf{r})+v(\mathbf{r})]\delta\rho(\mathbf{r})=0\tag{20}$$

now proves lemma II. The first equality in Eq. (20) follows from

$$\langle \delta\Psi_2|\hat{T}+\alpha\hat{V}_{ee}+\hat{v}|\Psi[\rho,\nu,\alpha]\rangle + \text{c.c.} = 0. \quad (21)$$

Equation (21) holds true because of two arguments. First, because $\langle \delta\Psi_2|\hat{T}+\alpha\hat{V}_{ee}|\Psi[\rho,\nu,\alpha]\rangle + \text{c.c.} = 0$ due to the fact that $\delta\Psi_2$ is of type $\delta_{\Psi\to\rho}$ and $\Psi[\rho,\nu,\alpha]$ is ρ-stationary. Second, because $\langle \delta\Psi_2|\hat{v}|\Psi[\rho,\nu,\alpha]\rangle + \text{c.c.} = 0$ due to the fact that $\delta\Psi_2$ as variations of type $\delta_{\Psi\to\rho}$ does not change the density in first order. In Eq. (20), $\delta Q[\rho,\nu,\alpha]$ is the change of the functional Q resulting from changing $\Psi[\rho,\nu,\alpha]$ to $\Psi[\rho+\delta\rho,\nu,\alpha]$. For the last equality in Eq. (20) it is used that particle number conservation requires $\int d\mathbf{r}\,\mu\,\delta\rho(\mathbf{r}) = \mu\int d\mathbf{r}\,\delta\rho(\mathbf{r}) = 0$.

A corollary to lemmas I and II is that *the external potential $v(\mathbf{r})$ of any electronic system with coupling constant α is a functional $-q([\rho_i,\nu,\alpha];\mathbf{r}) + \mu$ of the electron density ρ_i of any of its eigenstates Ψ_i.* This corollary can be deduced as follows. Lemma I proves that every eigenstate Ψ_i belongs to the set of ρ-stationary wave functions $\Psi[\rho_i,\nu,\alpha]$. Lemma II shows that every ρ-stationary wave function $\Psi[\rho_i,\nu,\alpha]$ is an eigenstate of an electronic Hamiltonian operator with coupling constant α and external potential $-q([\rho_i,\nu,\alpha];\mathbf{r}) + \mu$. The potential $-q([\rho_i,\nu,\alpha];\mathbf{r}) + \mu$ must equal the external potential $v(\mathbf{r})$ because a wave function, here $\Psi_i = \Psi[\rho_i,\nu,\alpha]$, cannot be an eigenstate of two electronic Hamiltonian operators with the same coupling strength α but with external potentials that differ by more than a constant. The latter statement holds true only for electronic systems with external potentials that are local. However, only such electronic systems are considered in this work.

The corollary, respectively lemmas I and II, proves the following density theorem, which represents a generalization of the HK theorem: *An electron density determines the external potentials of all electronic systems that have at least one eigenstate with this electron density.* A corollary of this theorem is that *an electron density determines all properties of all electronic systems that have at least one eigenstate with this electron density.*

Lemmas I and II together establish a density-based stationarity principle. For a given coupling strength α this density-based stationarity principle reads as follows: *All ρ-stationary wave functions of a given density ρ are eigenstates of an electronic system and an eigenstate of any electronic system that yields the density ρ is a ρ-stationary wave function of ρ.* The density-based stationarity principle is a counterpart to the common stationarity principle of quantum mechanics. The quantum-mechanical stationarity principle determines all eigenstates belonging to a given external potential, i.e., all eigenstates of an electronic Hamiltonian operator with this external potential. The corresponding electron densities can be obtained from the eigenstates. The density-based stationarity principle determines all eigenstates belonging to a given electron density, i.e., all wave functions that yield this density and are eigenstates of an electronic Hamiltonian operator. The corresponding external potentials are given by Eq. (16). Note that, to some extent, electron densities and external potentials change roles if one goes from one stationarity principle to the other.

For a given density and coupling constant α there exists one Eq. (16) for each eigenstate of an electronic system with that density. Equation (16) for different values of ν deter-
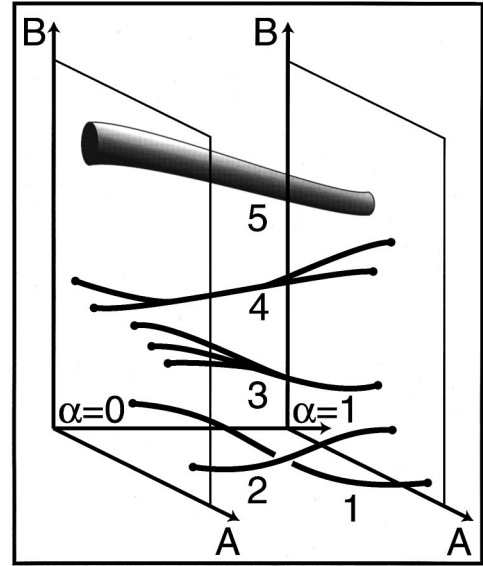

FIG. 1. Symbolic representation of different types of generalized adiabatic connections (GAC's): Structures 1 and 2 are isolated GAC's, structures 3 and 4 are bunches of GAC's, and structure 5 is a tube of GAC's. The Hilbert space of antisymmetric N-particle wave functions is represented by planes perpendicular to the coupling constant axis. For $\alpha=0$ and $\alpha=1$ these planes are displayed by symbolic axes A and B.

mines all external potentials $v(\mathbf{r})$ that lead to at least one eigenstate with that density.

On the basis of the lemmas and theorems derived so far, the Thomas-Fermi scheme can be generalized to be, in principle, applicable to any eigenstate of an electronic system, not only to the ground state. The treatment of an electronic system characterized by a given external potential $v(\mathbf{r})$ and electron number N with the generalized Thomas-Fermi scheme comprises two steps. First, one searches for all densities ρ_i which have, at least for one value of ν, a functional derivative $-q([\rho_i,\nu,\alpha];\mathbf{r}) + \mu$ that equals the external potential. Then, second, one determines the total energies of the eigenstates determined by the found ρ_i by evaluating $Q([\rho_i,\nu,\alpha];\mathbf{r}) + \int d\mathbf{r}\,v(\mathbf{r})\rho_i(\mathbf{r})$ for those ν for which $-q([\rho_i,\nu,\alpha];\mathbf{r}) + \mu = v(\mathbf{r})$. While this generalized Thomas-Fermi approach is of academic interest, a practical application seems to be even less feasible than that of the standard Thomas-Fermi approach.

C. Generalized adiabatic connection

Generalized adiabatic connections (GAC's) shall be the paths of the ρ-stationary wave functions $\Psi[\rho,\nu,\alpha]$ if the coupling constant goes from zero to one while the density ρ and the values of the parameter ν are fixed. The set of all GAC's for a given density ρ establishes a relation between the sets of ρ-stationary wave functions at $\alpha=0$ and at $\alpha=1$, i.e., between the set given by all $\Psi[\rho,\nu,\alpha=0]$ and the set given by all $\Psi[\rho,\nu,\alpha=1]$. Figure 1 represents a symbolic picture of the GAC's and the relations between ρ-stationary wave functions at $\alpha=0$ and $\alpha=1$ for some density. For illustrational purposes it is assumed that the three basic types of GAC's are present for the considered density. How far these basic types of GAC's occur for electron densities of real

systems is discussed later on. The GAC's are structures in a high-dimensional space that is obtained by extending the Hilbert space of antisymmetric N-particle wave functions by an additional dimension for the coupling constant. In Fig. 1 each plane perpendicular to the coupling constant axis represents the Hilbert space of antisymmetric N-particle wave functions. For $\alpha=0$ and $\alpha=1$ these planes are indicated by the symbolic axes A and B. The Hilbert space of antisymmetric N-particle wave functions, of course, is not a two-dimensional but a high-dimensional space. At each value of the coupling constant α the ρ-stationary wave functions $\Psi[\rho,\nu,\alpha]$ for a given ρ are represented by a point in the corresponding plane symbolizing the Hilbert space of antisymmetric N-particle wave functions. The points representing $\Psi[\rho,\nu,\alpha]$ for different values of α but fixed values of ρ and ν then form a GAC.

Various types of GAC's may occur. A GAC may be *isolated*, like the GAC's 1 and 2 in the figure. An adiabatic connection shall be isolated if at each value of α the corresponding ρ-stationary wave function $\Psi[\rho,\nu,\alpha]$ is isolated. (Isolated ρ-stationary wave functions were defined in Sec. III A.) Isolated GAC's can be labeled by the parameter ν of the ρ-stationary wave functions $\Psi[\rho,\nu,\alpha]$ building it. Note that the wave functions $\Psi[\rho,\nu,\alpha]$ of different isolated GAC's may yield identical expectation values of the operator $\hat{T}+\alpha\hat{V}_{ee}$ at one, several, or even all values of α. In other words, the functionals $Q[\rho,\nu,\alpha]$ and $Q[\rho,\nu',\alpha]$ with $\nu'\neq\nu$ which refer to different isolated GAC's of the same density may have the same value. Thus, if the expectation value $\langle\Psi[\rho,\nu,\alpha]|\hat{T}+\alpha\hat{V}_{ee}|\Psi[\rho,\nu,\alpha]\rangle=Q[\rho,\nu,\alpha]$ of two GAC's of the same density is equal at a certain value of the coupling constant α, that does not mean that the two GAC's have a common point. Figure 1 shows such a situation for GAC's 1 and 2 if the symbolic axis B is defined dependently on α in such a way that it gives the value of $\langle\Psi|\hat{T}+\alpha\hat{V}_{ee}|\Psi\rangle$. That means the simple picture of crossing energy levels does not apply here. (Remember that the real Hilbert space of antisymmetric N-particle wave functions is not two but even much higher dimensional.)

A more complicated structure of adiabatic connections arises if for a given density ρ several isolated ρ-stationary wave functions at $\alpha=0$ are related to isolated ρ-stationary wave functions at $\alpha=1$ by GAC's that have common points. The resulting structures shall be called *bunches of GAC's*. Examples for bunches of GAC's are the structures 3 and 4 in Fig. 1. In this case the end points of the GAC's at $\alpha=0$ no longer are labeled by a single label ν but by two labels ν and η. The label ν now designates the bunch while different end points of the bunch at $\alpha=0$ are labeled by η. The corresponding wave functions at $\alpha=0$ are then given by $\Psi[\rho,\nu,\eta,0]$. In a similar way the end points of the adiabatic connections at $\alpha=1$ are designated by the label ν of the bunch and a label κ indicating the different end points of the bunch at $\alpha=1$. The corresponding wave functions at these end points are given by $\Psi[\rho,\nu,\kappa,1]$. The described labeling scheme applies only to the end points of the adiabatic connection at $\alpha=0$ or $\alpha=1$ but this is all that is needed in this work.

A set of GAC's given at each value of α by a connected set of ρ-stationary wave functions $\Psi[\rho,\nu,\alpha]$ is shown in Fig.

1 as structure 5. A set of ρ-stationary wave functions $\Psi[\rho,\nu,\alpha]$ of the same ρ and α is connected if it cannot be decomposed into isolated sets. A set of ρ-stationary wave functions $\Psi[\rho,\nu,\alpha]$ of the same ρ and α is isolated if, around each member of the set, one can find a neighborhood in the Hilbert space which contains no ρ-stationary wave function except those that are members of the set. A structure of the type of structure 5 shall be called a *tube of GAC's*. Connected sets of ρ-stationary wave functions and therefore also tubes of GAC's seem not to occur in real systems. The discussion of such structures is included for completeness.

If for any two values α and α' a tube of GAC's establishes one-to-one mappings between the $\Psi[\rho,\nu,\alpha]$ and $\Psi[\rho,\nu,\alpha']$ yielding the tube of GAC's at α and α', respectively, then the adiabatic connections and the corresponding $\Psi[\rho,\nu,\alpha]$ for any value of α can be labeled by parameters ν which are real (or at least rational) numbers. Otherwise the tube of GAC's contains bunchlike structures and the bunches building the set can be labeled by the real parameter ν. A labeling of the corresponding wave functions at the end point $\alpha=0$ and $\alpha=1$ requires additional parameters as discussed in the preceding paragraph. However, in this work, such a labeling will turn out to be not necessary for tubes of GAC's containing bunchlike structures.

Note that, for any value of α, there are other wave functions which are not ρ-stationary lying ''between'' the $\Psi[\rho,\nu,\alpha]$ of a connected set. More precisely, any subset of the Hilbert space that, for some value of α, completely contains a connected set of wave functions $\Psi[\rho,\nu,\alpha]$ also contains other wave functions that are not members of the set. An obvious reason for this is that any neighborhood of a wave function $\Psi[\rho,\nu,\alpha]$ contains wave functions that have a different electron density.

The functionals $Q[\rho,\nu,\alpha]$ associated with a connected set of ρ-stationary wave functions $\Psi[\rho,\nu,\alpha]$ of a given ρ and α all have the same value. The reason is that any two $\Psi[\rho,\nu,\alpha]$ can be connected by a path which always can be divided into infinitesimal steps going from one ρ-stationary wave function $\Psi[\rho,\nu,\alpha]$ of the connected set to another ρ-stationary wave function $\Psi[\rho,\nu,\alpha]$ of the set. These infinitesimal steps are changes $\delta_{\Psi\to\rho}$ of the wave functions $\Psi[\rho,\nu,\alpha]$ which do not change the density and therefore, due to the definition of the $\Psi[\rho,\nu,\alpha]$, Eqs. (10) and (12) do not change the value of the corresponding $Q[\rho,\nu,\alpha]$. If the functional derivatives $q[\rho,\nu,\alpha]+\mu$ corresponding to a connected set of wave functions $\Psi[\rho,\nu,\alpha]$ differ from each other then, because of lemmas I and II, the $\Psi[\rho,\nu,\alpha]$ would be eigenstates of different Hamiltonian operators. This can be assumed to not be the case [37]. Therefore the functional derivatives $q[\rho,\nu,\alpha]+\mu$ of a connected set of $\Psi[\rho,\nu,\alpha]$ can be assumed to be equal and then the members of a connected set of ρ-stationary wave functions $\Psi[\rho,\nu,\alpha]$ all belong to one set of degenerate eigenstates of a Hamiltonian operator $\hat{T}+\alpha\hat{V}_{ee}+\hat{v}$ with an external potential $v(\mathbf{r})$ that is given by the corresponding functional derivatives $-q[\rho,\nu,\alpha]+\mu$.

Real systems may have degenerate states with the same electron density, however these states correspond to isolated ρ-stationary wave functions. In an atom, for example, two of three degenerate P eigenstates, namely those with magnetic quantum number 1 or -1, have the same electron density. An infinitesimal admixture of the state with magnetic quan-

tum number 0 or -1 to the state with magnetic quantum momentum number 1, however, changes the electron density. Thus the eigenstates in the neighborhood of the one with magnetic quantum number 1 have different electron densities and the eigenstate is an isolated ρ-stationary wave function.

Other cases of GAC's than those displayed in Fig. 1 may occur, e.g., bunches of tubes of GAC's an isolated GAC that branches at some $\alpha > 0$ and at a larger $\alpha < 1$ reunites again into one isolated GAC, or tubes of GAC's that, from a certain value of α on, collapse into one isolated GAC. These cases are combinations or generalizations of the three types of adiabatic connections discussed above and can be treated in an analogous fashion.

D. Generalized adiabatic connection Kohn-Sham formalism

The GAC-KS formalism will be derived first for the special case of isolated GAC's and will then be generalized. For a given density ρ the wave functions $\Psi[\rho, \nu, \alpha = 1]$ at the end points of the GAC's at $\alpha = 1$, according to lemma 2, are eigenstates Ψ_k of fully interacting electron systems with external potentials $v_{ext}(\mathbf{r})$ that equal $-q[\rho, \nu, \alpha = 1] + \mu$, i.e., the $\Psi[\rho, \nu, \alpha = 1]$ are eigenstates of Hamiltonian operators $\hat{T} + \alpha \hat{V}_{ee} + \hat{v}_{ext}$ with $v_{ext}(\mathbf{r}) = -q([\rho, \nu, \alpha = 1]; \mathbf{r}) + \mu$. From now on Ψ_k or Ψ_i shall designate exclusively eigenstates of fully interacting systems. The eigenstates Ψ_k as ρ-stationary wave functions of ρ and $\alpha = 1$ are adiabatically connected to ρ-stationary wave functions $\Psi[\rho, \nu, \alpha = 0]$ of the same density ρ but $\alpha = 0$. In the case of isolated GAC's a one-to-one mapping between the $\Psi[\rho, \nu, \alpha = 1]$ and the $\Psi[\rho, \nu, \alpha = 0]$ results. Now lemma 2 is invoked again. It guarantees that the $\Psi[\rho, \nu, \alpha = 0]$ are eigenstates Φ_ℓ of noninteracting model systems with Hamiltonian operators $\hat{T} + v_s$. Eigenstates of a noninteracting model system shall be designated by Φ_ℓ or Φ_j to distinguish them from the eigenstates Ψ_k or Ψ_i of an interacting electronic system. The corresponding potentials are denoted by $v_s(\mathbf{r})$. The potentials $v_s(\mathbf{r})$ equal $-q([\rho, \nu, \alpha = 0], \mathbf{r}) + \mu$. Because the model systems are noninteracting, their eigenstates are Slater determinants built of orbitals that are eigenstates of single-particle Schrödinger equations with Hamiltonian operators $\hat{T} + \hat{v}_s$ if no degeneracies are present. In case of degeneracies Φ_ℓ can be a symmetry-determined linear combination of Slater determinants which differ only by degenerate orbitals. (Whether $\hat{T} + \hat{v}_s$ stands for a noninteracting N-particle or for the corresponding single-particle Hamiltonian operator depends on the context.) In contrast to traditional DFT, the Slater determinant Φ_ℓ is not necessarily built by the energetically lowest orbitals because Φ_ℓ does not have to be the ground state of $\hat{T} + \hat{v}_s$.

The wave functions $\Psi[\rho, \nu, \alpha = 1]$ at the $\alpha = 1$ end points of the generalized adiabatic connections of *one* density but different ν, in general, are eigenfunctions Ψ_k of *different* interacting systems with *different* external potentials $v_{ext}(\mathbf{r}) = -q([\rho, \nu, \alpha = 1], \mathbf{r}) + \mu$. Similarly, the noninteracting model systems and their potentials $v_s(\mathbf{r}) = -q([\rho, \nu, \alpha = 0], \mathbf{r}) + \mu$ for *one* density but varying values of ν are, in general, *different*. On the other hand, one is usually interested in a number of different eigenstates of *one* given inter-

acting system. Those eigenstates Ψ_i belong to the same interacting Hamiltonian operator with *one* external potential $v_{ext}(\mathbf{r})$ but the eigenstates Ψ_i, of course, in general have *different* densities. Each eigenstate Ψ_i is a ρ-stationary wave function $\Psi[\rho_i, \nu, \alpha = 1]$ with ρ_i being the density of the eigenstate. The value of the parameter ν depends on how the generalized adiabatic connections for the density ρ_i are labeled. For each of the densities ρ_i the functional derivative $-q([\rho_i, \nu, \alpha = 1], \mathbf{r}) + \mu$ equals $v_{ext}(\mathbf{r})$ for that value of the parameter ν for which $\Psi[\rho_i, \nu, \alpha = 1] = \Psi_i$. If one considers all eigenstates of a noninteracting Hamiltonian operator with effective potential $v_s(\mathbf{r})$, a similar picture arises. The eigenstates Φ_j yield different densities ρ_j and for each ρ_j the potential $v_s(\mathbf{r})$ equals the functional derivative $-q([\rho_j, \nu, \alpha = 0], \mathbf{r}) + \mu$ if the parameter ν corresponds to the ρ-stationary wave function Φ_j, i.e., if $\Psi[\rho_j, \nu, \alpha = 0] = \Phi_j$.

Each eigenstate Ψ_i of a real physical system is associated with a unique eigenfunction Φ_j of a unique noninteracting model system via a GAC if the GAC's are assumed to be isolated. As in the standard KS formalism, Φ_j shall be called the KS wave function and the model system shall be called the KS system. By construction, the density ρ_j of the KS wave function Φ_j equals that of the corresponding wave function Ψ_i, i.e., Φ_j like Ψ_i yields the density ρ_i and $\rho_j = \rho_i$. Note that many KS systems are associated with one physical system, in general one KS system for each eigenstate Ψ_i.

In order to determine the KS system and wave function associated with a specific eigenstate Ψ_i of a given real electron system and in order to determine the energy of the physical eigenstate with the help of the associated KS wave function, various energy functionals have to be defined. These energy functionals are components of the functionals $Q[\rho_i, \nu, \alpha]$ at $\alpha = 0$ and $\alpha = 1$ and therefore depend on the density ρ_i and the parameter ν labeling the associated GAC. However, the labeling of the GAC's for the density ρ_i is arbitrary. The parameter ν therefore is not uniquely defined. This problem is solved by replacing the variables ρ_i and ν in the functionals $\Psi[\rho_i, \nu, \alpha]$ and $Q[\rho_i, \nu, \alpha]$. In this way the necessity to find a universal labeling scheme that uniquely defines ν is avoided and the evaluation of the functionals $Q[\rho_i, \nu, \alpha]$ and their components is facilitated. In the case of isolated GAC's, the variables ρ_i and ν uniquely determine $\Psi[\rho_i, \nu, \alpha = 0] = \Phi_j$ and conversely $\Phi_j = \Psi[\rho_i, \nu, \alpha = 0]$ belongs to a unique $\rho_i = \rho_j$ and a unique ν. Therefore, in functionals the variables ρ_i and ν can be replaced by the KS wave function Φ_j. The KS wave function Φ_j is the wave function that is actually calculated in the GAC-KS scheme and thus is an available quantity.

By generalizing the corresponding definitions of the standard KS formalism, the functionals $T_s[\Phi_j]$, $U[\Phi_j]$, $E_x[\Phi_j]$, and $E_c[\Phi_j]$ of the noninteracting kinetic energy, the Coulomb energy, the exchange energy, and the correlation energy, respectively, are defined as

$$T_s[\Phi_j] = T_s[\rho_i, \nu] = \langle \Phi_j | \hat{T} | \Phi_j \rangle, \qquad (22)$$

$$U[\Phi_j] = U[\rho_i] = \frac{1}{2} \int d\mathbf{r} \, d\mathbf{r}' \frac{\rho_i(\mathbf{r}) \rho_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \qquad (23)$$

$$E_x[\Phi_j] = E_x[\rho_i, \nu] = \langle \Phi_j | \hat{V}_{ee} | \Phi_j \rangle - U[\Phi_j], \quad (24)$$

and

$$E_c[\Phi_j] = E_c[\rho_i, \nu] = Q[\rho_i, \nu, \alpha = 1] - Q[\rho_i, \nu, \alpha = 0]$$
$$- U[\rho_i] - E_x[\rho_i, \nu]$$
$$= \langle \Psi_i | \hat{T} + \hat{V}_{ee} | \Psi_i \rangle - \langle \Phi_j | \hat{T} + \hat{V}_{ee} | \Phi_j \rangle. \quad (25)$$

The corresponding Coulomb, exchange, and correlation potentials are given by functional derivatives

$$u([\Phi_j]; \mathbf{r}) = u([\rho_i]; \mathbf{r}) = \delta U[\rho]/\delta\rho(\mathbf{r})|_{\rho(\mathbf{r}) = \rho_i(\mathbf{r})}$$
$$= \int d\mathbf{r}' \rho_i(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|, \quad (26)$$

$$v_x([\Phi_j]; \mathbf{r}) = v_x([\rho_i, \nu]; \mathbf{r}) = \delta E_x[\rho, \nu]/\delta\rho(\mathbf{r})|_{\rho(\mathbf{r}) = \rho_i(\mathbf{r})}, \quad (27)$$

and

$$v_c([\Phi_j]; \mathbf{r}) = v_c([\rho_i, \nu]; \mathbf{r}) = \delta E_c[\rho, \nu]/\delta\rho(\mathbf{r})|_{\rho(\mathbf{r}) = \rho_i(\mathbf{r})}, \quad (28)$$

respectively. The functional derivatives are taken at $\rho_i(\mathbf{r})$ for a fixed parameter ν. That means the definition of the potentials v_x and v_c refers to the variables ρ_i and ν. However, after having defined v_x and v_c in the variables ρ_i and ν one can then change to the variable Φ_j.

In the traditional KS formalism, exchange and correlation functionals also can be expressed as functionals of the KS wave function or equivalently the KS orbitals, as in the GAC-KS formalism. However, implicitly the functionals would remain functionals of the density whereas in the GAC-KS formalism they are implicit functionals of the density and the parameter ν. Orbital-dependent functionals are preferable to traditional density functionals because they are much more flexible and because the KS orbitals contain much more information than the density.

By combining the definitions (14) and (22)–(28) with Eq. (16) for $\alpha = 0$ and $\alpha = 1$ and for $v(\mathbf{r})$ being $v_s(\mathbf{r})$ and $v_{\text{ext}}(\mathbf{r})$, an equation for the potential $v_s(\mathbf{r})$, the KS potential, is obtained:

$$v_s(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + u([\Phi_j]; \mathbf{r}) + v_x([\Phi_j]; \mathbf{r}) + v_c([\Phi_j]; \mathbf{r}). \quad (29)$$

Because the wave function Φ_j is an eigenfunction of $\hat{T} + \hat{v}_s$, it obeys the noninteracting Schrödinger equation

$$[\hat{T} + \hat{v}_{\text{ext}} + \hat{u} + \hat{v}_x + \hat{v}_c]\Phi_j = E_{s,j}\Phi_j \quad (30)$$

with eigenvalue $E_{s,j}$. The eigenvalue $E_{s,j}$ is an auxiliary quantity that will not be used any further in this work. Equation (30), the analog of the KS equation of traditional DFT, shall be called the GAC-KS equation. The GAC-KS equation, like the traditional KS equation, decouples in corresponding single-particle equations for the KS orbitals. Equation (30) or the corresponding single-particle equations have to be solved in a self-consistency scheme because parts of the Hamiltonian operator, namely u, $\hat{v}_x$, and $\hat{v}_c$, depend on

the eigenstate Φ_j and thus on the orbitals building Φ_j. In the GAC-KS scheme, in contrast to the traditional KS scheme, not the energetically lowest but some other set of orbitals is occupied. The energy E_i of the real interacting eigenstate Ψ_i corresponding to Φ_j is given by

$$E_i = T_s[\Phi_j] + U[\Phi_j] + E_x[\Phi_j] + E_c[\Phi_j]$$
$$+ \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\rho([\Phi_j]; \mathbf{r}). \quad (31)$$

In the GAC-KS scheme each eigenstate Ψ_i of a given real interacting system is adiabatically connected to a certain state Φ_j of a certain noninteracting model system. However, remember that two different eigenstates of *one* real interacting system, in general, are adiabatically connected to two different eigenstates of *two different* noninteracting systems with two different effective potentials $v_s(\mathbf{r})$. That means for each eigenstate Ψ_i the GAC-KS scheme has to be carried out separately, i.e., for each Ψ_i the corresponding $v_s(\mathbf{r})$ and Φ_j are determined separately.

A crucial point is that, in general, Ψ_i corresponds to a Φ_j with $j \neq i$. The ground state Ψ_0 of a real physical system, for example, does not have to be related to the ground state Φ_0 of a noninteracting model system. Thus the v-representability assumption is not required. For the special case that $j = i = 0$ the GAC-KS scheme reduces to the traditional KS scheme, see Fig. 2(a).

If the ground state $\Psi_0 = \Psi[\rho_0, \nu, \alpha = 1]$ of an interacting system is adiabatically connected to an excited state $\Phi_j = \Psi[\rho_0, \nu, \alpha = 0]$ $(j \neq 0)$ of a noninteracting system, then one of two cases is present in the standard KS formalism. Which one is present depends on the other ρ-stationary wave functions $\Psi[\rho_0, \nu', \alpha = 0] \neq \Phi_j$ of density ρ_0 with $\nu' \neq \nu$ which are not connected to the considered Ψ_0 by a GAC. The first case arises if one of the other ρ-stationary wave functions $\Psi[\rho_0, \nu', \alpha = 0] \neq \Phi_j$ is the ground state of the noninteracting system it is associated with according to lemma 2, i.e., if $\Psi[\rho_0, \nu', \alpha = 0]$ is the ground state of the noninteracting Hamiltonian operator with the effective potential $-q([\rho_0, \nu', \alpha = 0]; \mathbf{r}) + \mu' \neq -q([\rho_0, \nu, \alpha = 0]; \mathbf{r}) + \mu$. Then the wave function $\Psi[\rho_0, \nu', \alpha = 0] \neq \Phi_j$ with $\nu' \neq \nu$ is the KS wave function of the standard KS formalism. That means, in this case, the model systems of the standard and the GAC-KS scheme are different. The standard adiabatic connection, i.e., the adiabatic connection as defined in the standard KS formalism, would be discontinuous in this case, which is symbolically displayed in Fig. 2(b). In Fig. 2 the symbolic axis B shall be chosen dependently on α in such a way that it gives the expectation value $\langle \Psi | \hat{T} + \alpha' \hat{V}_{ee} | \Psi \rangle$. At the coupling constant α' the standard adiabatic connection is discontinuous in Fig. 2(b). Because the GAC-KS formalism does avoid such discontinuous adiabatic connections, it seems to be preferable in such a situation. The second case arises if none of the wave functions $\Psi[\rho_0, \nu', \alpha = 0] \neq \Phi_j$ with $\nu' \neq \nu$ is the ground state of a noninteracting Hamiltonian operator. Then the density ρ_0 is not noninteracting v-representable and the standard KS formalism is not applicable in contrast to the GAC-KS scheme, which is not based on any v-representability assumption. In this case the standard adiabatic connection does not exist for
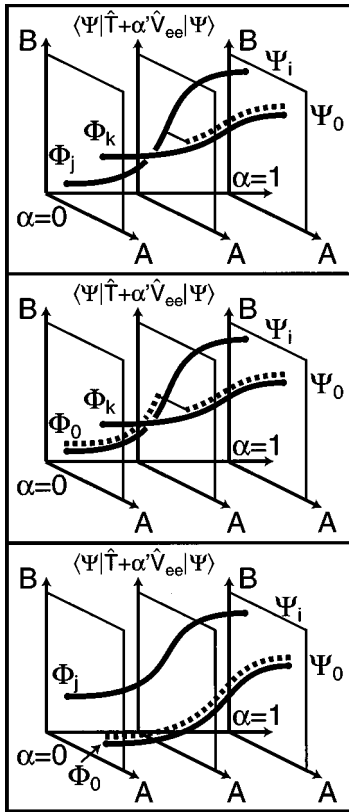
FIG. 2. Generalized versus traditional adiabatic connections (for notation, see Fig. 1). Generalized adiabatic connections are depicted by solid lines, traditional adiabatic connections by dashed lines. Ground states of noninteracting model systems are denoted by Φ_0, excited states by Φ_j or Φ_k. (a) Traditional adiabatic connection is identical to one of the generalized adiabatic connections. (b) Traditional adiabatic connection is discontinuous. (c) Traditional adiabatic connection does not exist for values of the coupling constant which are smaller than α'.

values of the coupling constant which are smaller than α'. See Fig. 2(c) for a symbolic representation of this case.

In practical applications one is usually interested in a number of eigenstates and energy eigenvalues of a given physical electronic system. The ith eigenstate Ψ_i of the real physical electronic system is adiabatically connected to the jth eigenstate of a KS system. However, the relation between i and j is not a priori known and only the energy index j of the KS wave function enters the KS scheme and is known from the start. Thus a GAC-KS treatment of a single selected eigenstate of the real system is not possible unless physical intuition allows one to choose the corresponding value of the index j. The GAC-KS scheme, therefore, is applied in several steps.

(i) An index j is chosen.

(ii) The GAC-KS equations are self-consistently solved for that index j. In each iteration cycle the exchange and correlation potentials are determined from those KS orbitals of the previous cycle that built the jth eigenstate of the KS Hamiltonian operator of the previous cycle.

(iii) After self-consistency has reached the energy of the corresponding physical eigenstate, Ψ_i is determined via Eq. (31).

(iv) After having carried out the GAC-KS scheme for

different indices j, the resulting energies for the corresponding physical eigenstate Ψ_i can be energetically ordered and energy indices i can be attached.

In the set of KS energy indices j emerging in the GAC-KS formalism from the eigenstates of a given physical system, certain numbers may be missing or may appear more than once. If a number j is chosen that is not present in the set of KS energy indices, then the GAC-KS scheme will not lead to a solution, i.e., it will not converge. If a number j is chosen that appears more than once, then it depends on the starting condition of the self-consistency procedure for which eigenstate of the physical system the associated KS wave function is determined.

The complicated relation between the energy indices of the interacting and the noninteracting systems reflects the fact that there exists no simple universal way to relate the energies of real interacting electronic systems to those of noninteracting model systems. Therefore, a formalism should not require assumptions on the energy indices of model states, rather the relation between the energy indices of the physical and the model states should result from the formalism. This is the case in the GAC-KS formalism but not in the standard KS formalism. The latter requires the model system associated with the ground state of a real system to be the ground state of a noninteracting model system.

Next the GAC-KS is generalized in order to cover other cases than that of isolated GAC's. First tubes of GAC's shall be considered. In this case it is sufficient to carry out the GAC-KS scheme with one arbitrary member $\Psi[\rho,\nu,\alpha=0]$ of the set of ρ-stationary wave functions forming the end point of the tube of GAC's at $\alpha=0$. One can even choose a different $\Psi[\rho,\nu,\alpha=0]$ in each iteration of the self-consistency procedure. The reason is that, according to Sec. III B, all wave functions $\Psi[\rho,\nu,\alpha]$ of a continuous set of ρ-stationary wave functions can be assumed to be eigenstates of the same Hamiltonian operator. Therefore, the wave functions $\Psi[\rho,\nu,\alpha=0]$ of a continuous set at $\alpha=0$, the KS wave functions corresponding to a tube of GAC's, are all eigenstates of the same effective potential $v_s(\mathbf{r})$. Furthermore, the functionals $Q[\rho,\nu,\alpha]$ corresponding to such a continuous set of ρ-stationary wave functions $\Psi[\rho,\nu,\alpha]$ all have the same value and the same functional derivative $q([\rho,\nu,\alpha];\mathbf{r})$. Thus all the functionals $T_s[\rho,\nu]$, $E_x[\rho,\nu]$, and $E_c[\rho,\nu]$ as well as the functional derivatives $v_x([\rho,\nu];\mathbf{r})$ and $v_c([\rho,\nu];\mathbf{r})$ belonging to a tube of GAC's are equal. Therefore, the case of a tube of GAC's can be treated simply as if it were the case of an isolated GAC because it is not necessary to distinguish between the members of a continuous set of wave functions $\Psi[\rho,\nu,\alpha]$ at any α. As mentioned in Sec. III C, this case seems not to occur in real systems and therefore seems to be of academic interest only.

In the case of GAC's forming bunches, the assumption is made that each bunch has just one end point at $\alpha=1$ (see structure 3 in Fig. 1). In this case the ρ-stationary wave functions at $\alpha=0$, the corresponding functionals Q at $\alpha=0$, and subsequently the functionals T_s, E_x, and E_c as well as the functional derivatives v_x and v_c depend not only on the density ρ and the bunch index ν but also on the parameter η designating the end point of a given bunch at $\alpha=0$. Because each bunch shall have just one end point at $\alpha=1$, no index κ

to label this end point is required. The variables ρ, ν, and η specify a unique wave function $\Psi[\rho,\nu,\eta,\alpha=0]=\Phi_j$. Conversely, this wave function $\Phi_j=\Psi[\rho,\nu,\eta,\alpha=0]$ determines uniquely the variables ρ, ν, and η. Thus it is possible to replace the variables ρ, ν, and η by Φ_j and the GAC-KS formalism remains essentially unchanged.

Note that, in contrast to the standard KS formalism, it is not required in the GAC-KS formalism that an eigenstate of an interacting physical electron system is related to only one noninteracting KS system. The GAC-KS procedure also works if more than one KS system is associated with one eigenstate of an interacting system.

Whether the assumption that bunches of GAC's do not have more than one end point at $\alpha=1$ is always valid needs further investigation. The behavior of bunches of GAC's not obeying this assumption in the GAC-KS formalism is discussed in Appendix B. Physical intuition suggests that, in real systems, bunches of GAC's do not exist at all, neither those with one nor those with several end points at $\alpha=1$. A physical reason why GAC's should touch seems not to exist and the physical meaning of the points where GAC's touch would be unclear. (See also the remark in Sec. VI that relates the question of whether bunches of GAC's exist to the question of whether many-body perturbation theory converges.) With respect to the validity of the assumption on the end points of bunches of GAC's, also note that if a bunch of GAC's has more than one end point at $\alpha=1$, then the corresponding ρ-stationary wave functions $\Psi[\rho,\nu,\kappa,\alpha]$ are eigenfunctions of different interacting systems with different external potentials (this is shown in Appendix B). Thus in order to violate the assumption, eigenstates of different electron systems with different external potentials, i.e., of two different Hamiltonian operators, would have to somehow evolve, without changing their electron density, into eigenstates of one Hamiltonian operator just by a change in the coupling constant. This shows that the assumption on the end points of bunches of GAC's is likely to hold true and probably is less severe than the v-representability assumption of traditional DFT.

IV. FUNCTIONALS

If the GAC-KS formalism is applied, then the various parts of the total energy E_i, Eq. (31), and the contributions to the effective potential, v_s, Eq. (29), have to be calculated. The contributions $T_s[\Phi_j]$, $U[\Phi_j]$, and $\int d\mathbf{r}\,v_{\text{ext}}(\mathbf{r})\rho([\Phi_j];\mathbf{r})$ of E_i can easily be obtained exactly from the occupied KS orbitals building the KS wave function Φ_j. Among the contributions to v_s, the external potential $v_{\text{ext}}(\mathbf{r})$ is given and the Coulomb potential $u([\Phi_j];\mathbf{r})$ again can be easily evaluated exactly from the occupied KS orbitals via the electron density $\rho[\Phi_j]$. Thus the handling of the energy functionals $E_x[\Phi_j]$ and $E_c[\Phi_j]$ and of the potentials $v_x([\Phi_j];\mathbf{r})$ and $v_c([\Phi_j];\mathbf{r})$ remains to be discussed.

Simple approximations for $E_x[\Phi_j]$, $E_c[\Phi_j]$, $v_x([\Phi_j];\mathbf{r})$, and $v_c([\Phi_j];\mathbf{r})$ result if the electron density $\rho([\Phi_j];\mathbf{r})$ and, if necessary, also gradients of $\rho([\Phi_j];\mathbf{r})$ are substituted into the local-density approximation (LDA) or generalized gradient approximations (GGA's) for the exchange and correlation functionals of the standard KS formalism. Obviously these are quite crude approximations. The LDA and GGA's

depend only on the electron density. Therefore, the dependence of E_x, E_c, v_x, and v_c on the label ν of the involved GAC is completely ignored. As shown in Sec. III D, the KS wave function Φ_j contains all information on both ρ and ν The information on ν, however, is not used in the described LDA and GGA approximations. Moreover, the LDA and GGA's are developed for ground states, not for excited states. If the LDA or a GGA is employed in the described way, then the GAC-KS method turns into a standard KS procedure in which the ground-state electron density is replaced by an excited-state density. This is the common procedure to treat excited states that is mentioned in the Introduction. While this approach has no formal justification within the standard KS formalism, the GAC-KS formalism of this work now gives it a formal justification by identifying it as an approximate GAC-KS procedure. On the other hand, the success of the GAC-KS method in the crude local density or generalized gradient approximations is very promising and suggests the development of improved GAC-KS methods based on specific orbital-dependent approximations for the GAC-KS functionals E_x, E_c, v_x, and v_c.

Approximations for the exchange energy and potential can be avoided completely if the exact expressions presented next are employed. The exchange energy $E_x[\Phi_j]$ is simply given by the standard expression for the exchange energy of a Slater determinant

$$E_x = -\frac{1}{2}\sum_a^{\text{occ}}\sum_b^{\text{occ}}\int d\mathbf{r}\,d\mathbf{r}'\frac{\varphi_a^*(\mathbf{r})\varphi_b(\mathbf{r})\varphi_b^*(\mathbf{r}')\varphi_a(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}.$$
(32)

In expression (32), $\varphi_a(\mathbf{r})$ and $\varphi_b(\mathbf{r})$ denote KS orbitals which are two-dimensional spinors in order to represent the spin degree of freedom. A star denotes the Hermitian adjoint, not just the complex conjugate of a KS orbital. If degeneracies due to symmetries are present, then the KS wave function is a symmetry-dependent linear combination of Slater determinants. The corresponding generalization of expression (32) for $E_x[\Phi_j]$ is straightforward. Expression (32) is identical to the expression for the exchange energy in the standard KS formalism [2,3]. However, in contrast to the standard KS formalism, the occupied orbitals entering expression (32) now, in general, are not the energetically lowest ones and solve the GAC-KS instead of the standard KS equations.

The exchange potential $v_x([\Phi_j];\mathbf{r})$ obeys the equation

$$\int d\mathbf{r}'X_s(\mathbf{r},\mathbf{r}')v_x(\mathbf{r}')=\sum_a^{\text{occ}}\sum_s^{\text{unocc}}\varphi_a^*(\mathbf{r})\varphi_s(\mathbf{r})$$

$$\times\frac{\langle\varphi_s|\hat{v}_x^{\text{NI}}|\varphi_a\rangle}{\varepsilon_a-\varepsilon_s}+\text{c.c.}\quad(33)$$

In Eq. (33), $\hat{v}_x'^{\text{NL}}$ is an integral operator with kernel $v_x^{\text{NL}}(\mathbf{r},\mathbf{r}')=\sum_k^{\text{occ}}\varphi_k(\mathbf{r})\varphi_k^*(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$. This means that $\hat{v}_x^{\text{NL}}$ is a nonlocal exchange operator of the same form as the Hartree-Fock exchange operator but built from the occupied KS orbitals. By ε_a and ε_s the eigenvalues of the KS orbitals $\varphi_a(\mathbf{r})$ and $\varphi_s(\mathbf{r})$, respectively, are designated. By

$$X_s(\mathbf{r},\mathbf{r}')=\sum_a^{\text{occ}}\sum_s^{\text{unocc}}\frac{\varphi_a^*(\mathbf{r})\varphi_s(\mathbf{r})\varphi_s^*(\mathbf{r}')\varphi_a(\mathbf{r}')}{\varepsilon_a-\varepsilon_s}+\text{c.c.}\tag{34}$$

the response function corresponding to the KS wave function is denoted. Equation (33) is identical to the corresponding equation in traditional KS theory [42–44]. Again, however, the orbitals entering Eq. (33) now are GAC-KS orbitals that, in general, are not the energetically lowest ones. Equation (33) can be derived similar to the way in which the corresponding equation in the standard KS formalism was derived in Ref. [44]. A closely related approach to derive Eq. (33) is to equate two different forms for the functional derivatives of the exchange energy with respect to the KS potential, namely $\int d\mathbf{r}'[\delta E_x/\delta\rho(\mathbf{r}')][\delta\rho(\mathbf{r}')/\delta v_s(\mathbf{r})]$ and

$$\Sigma_a^{\text{occ}}\int d\mathbf{r}'[\delta E_x/\delta\varphi_a(\mathbf{r}')][\delta\varphi_a(\mathbf{r}')/\delta v_s(\mathbf{r})].$$

Methods to solve Eq. (33) within the standard KS formalism exist for atoms and solids [42,45]. For the exact exchange results presented in the next section, Eq. (33) was solved within the GAC-KS formalism.

A coupling constant expansion for E_c and v_c can be obtained by generalizing the adiabatic connection perturbation theory of Refs. [43,44,46] if no bunchlike structures of GAC are present (see also Sec. VI).

V. APPLICATION OF THE GAC-KS METHOD TO ALKALI-METAL ATOMS

The applicability and the capabilities of the GAC-KS formalism itself are sufficiently demonstrated by the successful LDA and GGA treatments for excited states [4] which now can be considered as GAC-KS calculations. The illustrative example of this section shall introduce GAC-KS methods that go beyond the LDA or GGA, namely GAC-KS schemes that treat the exchange energy and potential exactly by employing Eqs. (32) and (33). The spin-polarized GAC-KS calculation was carried out by generalizing [47] the method of Ref. [42], an exact exchange or optimized potential method based on the standard KS formalism.

The three energetically lowest excitations of Li, Na, and K were calculated by four GAC-KS schemes. In three calculations exchange was treated exactly whereas correlation was either neglected, treated on the LDA level, or taken into account within the GGA [48]. For comparison, also a pure LDA calculation (LDA for exchange and correlation) was carried out. The four calculation are denoted by EXX (Exact Exchange), EXX/LDA, EXX/GGA, and LDA, respectively. Of the considered excited states, only the first one, as the lowest state of its symmetry (^2P), is accessible in the traditional KS formalism [9]. The spin densities of the six ^2P states are not spherically symmetric but exhibit cylindrical symmetry. Therefore, for this state the symmetrized KS formalism of Ref. [41] and its generalization to the GAC-KS case is invoked. That means the calculation of the ^2P state was based on the spherically symmetric contribution of the spin densities of the ^2P states which were obtained by averaging over the spin densities of the ^2P states with the same magnetic spin quantum number.

In Table I the results of the calculations are displayed and

TABLE I. Excitation energies of alkaline atoms in eV.

Transition		LDA	EXX	EXX/LDA	EXX/GGA	CC[a]	Expt.[a]
Li	$2s\rightarrow2p$	1.82	1.84	1.90	1.86	1.85	1.85
	$2s\rightarrow3s$	3.26	3.33	3.53	3.41	3.37	3.37
	$2s\rightarrow3p$	3.70	3.80	4.02	3.88	3.83	3.83
Na	$3s\rightarrow3p$	2.18	1.97	2.10	2.00	2.09	2.10
	$3s\rightarrow4s$	3.17	3.04	3.26	3.14	3.18	3.19
	$3s\rightarrow4p$	3.79	3.57	3.85	3.69	3.74	3.75
K	$4s\rightarrow4p$	1.68	1.41	1.53	1.46	1.60	1.61
	$4s\rightarrow5s$	2.57	2.35	2.57	2.49	2.60	2.61
	$4s\rightarrow5p$	3.06	2.76	3.03	2.93	3.05	3.06

[a]Reference [49].

compared to highly accurate coupled-cluster (CC) results and experimental data [49]. For the light atom Li the EXX yields results that are close to the CC and experimental data. This indicates that correlation plays only a minor role in this case. For Na and K the neglect of correlation has a stronger affect; the EXX results in these cases deviate more significantly from the CC and experimental data. Inclusion of correlation on the LDA or GGA level leads to an improvement for Na and K but the resulting EXX/LDA data are not systematically better than pure LDA values. This finding is not surprising. It is well known that the LDA and the GGA benefit from error cancelation between exchange and correlation. If exchange is treated exactly, these error cancellations, of course, are no longer present. Thus, in order to obtain good results with an exact exchange GAC-KS procedure, correlation has to be treated in an approximation that does not rely on error cancelations with exchange and therefore goes beyond the LDA and the current GGA's.

VI. CONCLUDING REMARKS

There is an interesting connection between the question of whether or not bunchlike structures of GAC's exist and the problem of whether many-body perturbation theory with respect to orders of the coupling constant converges. If bunchlike structures are present, then wave functions $\Psi[\rho,\nu,\alpha]$, functionals $Q[\rho,\nu,\alpha]$, and other quantities cannot be developed in Taylor series with respect to the coupling constant α, and perturbation theory along the adiabatic connection is not possible. Thus information on the applicability of many-body perturbation theory is relevant for answering the question of whether bunchlike GAC exists. Remember, the GAC-KS does not require the absence of bunchlike GAC, the case of exclusively isolated GAC's just represents the simplest scenario. The other way around, an investigation on whether or not bunchlike GAC's exist, may yield new information on the applicability of many-body perturbation theory from an interesting point of view. Note that in many-body perturbation theory one usually considers the dependence of the energy of the eigenstates of *one* Hamiltonian operator on a perturbation parameter. The eigenstates forming different GAC's of a given density, on the other hand, belong to *different* Hamiltonian operators. The standard picture of level crossings, i.e., the crossing of energy curves in the two-dimensional space of energy and perturbation parameter,

therefore, does not apply for GAC's.

For periodic systems, the GAC-KS formalism under certain conditions reduces in the thermodynamic limit to the excited-state formalism of Ref. [14] which is based on the standard KS formalism. In Ref. [14] the excited states of the standard KS Hamiltonian operator which is determined by the ground state are related to the excited states of the interacting physical system under the assumption that the energetical ordering of all states is preserved if the coupling constant runs from zero to one. That means that in the formalism of Ref. [14], ground and excited states always belong to the same Hamiltonian operator. In the GAC-KS formalism, on the other hand, each eigenstate of the physical system, in general, is associated with a different KS Hamiltonian operator. However, the differences between the GAC-KS Hamiltonian operators for states obtained by exciting a small number of electrons become negligible in the limit of an infinite number of unit cells and thus an infinite number of electrons. In this case the two formalisms become equivalent.

In this work the basis for a self-consistent KS treatment of excited states was established. Further work along two lines is highly desirable. First, accurate approximate exchange and, more importantly, correlation functionals for the GAC-KS formalism should be developed. Such approximate functionals have to be orbital dependent. Correlation functionals should not rely on error cancellations between exchange and correlation in order to be applicable in methods that treat the GAC-KS exchange exactly. Second, the topology of generalized adiabatic connections should be further investigated.

APPENDIX A: RELATIONS BETWEEN CHANGES OF THE DENSITY AND THE PAIR DENSITY

In Refs. [35,36] the existence of a unique function $\Gamma_i(\mathbf{r}'',\mathbf{r}',\mathbf{r})$ is asserted that relates by the equation

$$\delta\rho_i^2(\mathbf{r}',\mathbf{r}) = \int d\mathbf{r}'' \Gamma_i(\mathbf{r}'',\mathbf{r}',\mathbf{r})\delta\rho_i(\mathbf{r}'') \qquad \text{(A1)}$$

the changes $\delta\rho_i^2(\mathbf{r}',\mathbf{r})$ and $\delta\rho_i(\mathbf{r}'')$ of the pair density $\rho_i^2(\mathbf{r}',\mathbf{r})$ and of the density $\rho_i(\mathbf{r}'')$, respectively, which are caused by an arbitrary norm-preserving change $\delta\Psi$ of an eigenstate Ψ_i of an electronic Hamiltonian operator. The density of Ψ_i is denoted $\rho_i(\mathbf{r})$. In Eq. (A1) spin summations are assumed to be already carried out in contrast to Refs. [35,36]. Furthermore, the classical part of the pair density is not separated here. Thus the full pair density, not just the correlated pair density as in Refs. [35,36], is considered here.

For the case of Ψ_i being an eigenstate of a noninteracting system, a simple counterexample shows that $\Gamma_i(\mathbf{r}'',\mathbf{r}',\mathbf{r})$ does not exist. A nondegenerate eigenstate of a noninteracting system consists of a single Slater determinant. Now two Slater determinants that are orthogonal to Ψ_i are generated.

The first one is generated by replacing one occupied orbital of Ψ_i by an unoccupied one, the second by replacing two occupied orbitals by unoccupied ones. Next two changes $\delta\Psi_1$ and $\delta\Psi_2$ can be constructed. The change $\delta\Psi_1$ shall be the singly excited Slater determinant times an infinitesimal number, the change $\delta\Psi_2$ is given by the change $\delta\Psi_1$ plus an infinitesimal number times the doubly excited Slater determinant. Both changes yield the same change $\delta\rho_i(\mathbf{r}'')$ of the density because the admixture of a doubly excited Slater determinant does not affect the electron density in first order. The change of the pair density $\delta\rho_i^2(\mathbf{r}',\mathbf{r})$, however, is different for the two changes $\delta\Psi_1$ and $\delta\Psi_2$ of the eigenstate Ψ_i because the admixture of a doubly excited Slater determinant changes the pair density. Equation (A1), however, for both changes would yield the same change $\delta\rho_i^2(\mathbf{r}',\mathbf{r})$ of the pair density because both changes lead to the same change $\delta\rho(\mathbf{r}'')$ of the density. This contradiction shows that a function $\Gamma_i(\mathbf{r}'',\mathbf{r}',\mathbf{r})$ cannot exist.

In Refs. [35,36] eigenstates of fully interacting electron systems are considered whereas the counterexample given above refers to eigenstates of noninteracting electron systems. However, for eigenstates of an interacting electron system one also can find two changes $\delta\Psi_1$ and $\delta\Psi_2$ which yield the same change of the density $\rho_i(\mathbf{r}'')$ but different changes of the pair density $\rho_i^2(\mathbf{r}',\mathbf{r})$. This again shows that a function $\Gamma_i(\mathbf{r}'',\mathbf{r}',\mathbf{r})$ cannot exist.

For example, if one infinitesimally changes the external potential of the fully interacting electronic system with the eigenstate Ψ_i, then the eigenstate changes by an infinitesimal change that shall be designated as $\delta\Psi_1$. The corresponding change of the density shall be $\delta\rho(\mathbf{r})$. Another wave function can be generated by performing a constrained search, Eq. (12). Among all wave functions that yield the density $\rho_i(\mathbf{r}) + \delta\rho_i$, the one that minimizes the expectation value of $\hat{T} + \alpha\hat{V}_{ee}$ for α being infinitesimally smaller than 1 is searched. The difference between this wave function and Ψ_i defines a change $\delta\Psi_2$. The change $\delta\Psi_2$ leads to the same change $\delta\rho_i(\mathbf{r})$ of the density as $\delta\Psi_1$, because the density of $\Psi_i + \delta\Psi_2$, by construction, equals that of $\Psi_i + \delta\Psi_1$. Among all wave functions yielding $\rho_i + \delta\rho_i$, $\Psi_i + \delta\Psi_1$, as the ground state of a fully interacting electronic system, is the one that minimizes the expectation value of $\hat{T} + \alpha\hat{V}_{ee}$ for $\alpha = 1$ and not like $\Psi_i + \delta\Psi_2$ for a value of α that is smaller. Therefore, the wave functions $\Psi_i + \delta\Psi_1$ and $\Psi_i + \delta\Psi_2$ have different pair densities and the changes $\delta\Psi_1$ and $\delta\Psi_2$ lead to different changes $\delta\rho_i^2(\mathbf{r}',\mathbf{r})$.

The problem with Eq. (A1) is the claim that it holds true for changes $\delta\rho_i^2(\mathbf{r}',\mathbf{r})$ and $\delta\rho_i(\mathbf{r}'')$ resulting from arbitrary changes $\delta\Psi$ of an eigenstate Ψ_i. If one considers only changes between the ρ-stationary wave functions introduced in Sec. III A, then an equation being equivalent to Eq. (A1) holds true [37]. For a coupling constant $\alpha = 1$ the kernel $\Gamma_i(\mathbf{r}'',\mathbf{r}',\mathbf{r})$ then is the functional derivative of the pair density with respect to the electron density for fixed parameter ν (and in the case for fixed parameter κ). The pair density and its functional derivative then are both functionals not only of the density but also of the parameter ν (and in the case also of κ). According to lemmas I and II (see Sec. III B), each eigenstate of an electronic system is a ρ-stationary wave function and conversely each ρ-stationary wave function is

an eigenstate of an electronic system. Thus an equation like Eq. (A1) holds true for changes turning, for fixed α, an eigenstate of an electronic system into a wave function that again is an eigenstate of an electronic system with the same coupling constant α.

APPENDIX B: BUNCHES OF GENERALIZED ADIABATIC CONNECTIONS WITH MORE THAN ONE END POINT AT $\alpha=1$

In this appendix bunches of GAC's are discussed that have more than one end point at $\alpha=0$ *and* at $\alpha=1$. In this case indices η and κ labeling the end points of a bunch at $\alpha=0$ and $\alpha=1$, respectively, have to be introduced. Then wave functions $\Psi[\rho,\nu,\eta,\alpha=0]$ and $\Psi[\rho,\nu,\kappa,\alpha=1]$, functionals $Q[\rho,\nu,\eta,\alpha=0]$, $Q[\rho,\nu,\kappa,\alpha=1]$, $T_s[\rho,\nu,\eta]$, $E_x[\rho,\nu,\eta]$, and $E_c[\rho,\nu,\eta,\kappa]$, and functional derivatives $v_x([\rho,\nu,\eta];\mathbf{r})$ and $v_c([\rho,\nu,\eta,\kappa];\mathbf{r})$ arise. Note that $\Psi[\rho,\nu,\eta,\alpha=0]$, E_x, and v_x depend only on ν and η but not on κ, whereas $\Psi[\rho,\nu,\kappa,\alpha=1]$ depends on ν and κ but not on η.

The following condition is shown later on to hold for real systems, i.e., atoms, molecules, or solids: The ρ-stationary wave functions $\Psi[\rho,\nu,\kappa,\alpha=1]$ of a bunch of GAC's at $\alpha=1$ are eigenstates of interacting Hamiltonian operators with different external potentials, i.e., $q([\rho,\nu,\kappa',\alpha=1];\mathbf{r})+\mu' \neq q([\rho,\nu,\kappa,\alpha=1];\mathbf{r})+\mu$ if $\kappa' \neq \kappa$. With this assumption the external potentials may be used to label the end points of the bunch of GAC's at $\alpha=1$, i.e., the v_{ext} can be used to replace the labels κ. Thus the variables ρ,ν,η,κ can be replaced by Φ_j and v_{ext} resulting in functionals $T_s[\Phi_j]$, $E_x[\Phi_j]$, $E_c[\Phi_j,v_{\text{ext}}]$, $v_x([\Phi_j];\mathbf{r})$, and $v_c([\Phi_j,v_{\text{ext}}];\mathbf{r})$. Note that the external potentials occur only in the correlation functionals $E_c[\Phi_j,v_{\text{ext}}]$ and $v_c([\Phi_j,v_{\text{ext}}];\mathbf{r})$. Furthermore, note that the potentials v_{ext} are not variables of the functionals in the usual sense, because they cannot be continuously varied. For a given Φ_j only a few external potentials v_{ext} may occur in the functionals; each end point of the corresponding bunch of GAC's at $\alpha=1$ yields one possible v_{ext}.

For a given real interacting electron system the external potential v_{ext} is known; it usually is the potential of the nuclei. Thus all functionals depend only on accessible quantities at those densities that correspond to eigenstates of the real system. At first glance this seems to suggest that the GAC-KS formalism could be applied as before with the only difference being that the correlation functionals E_c and v_c now depend not only on Φ_j but also on v_{ext}. This, however, is not the case. If the GAC-KS procedure is carried out, then the electron density changes during the self-consistency process and reaches the correct density only if the process has converged. With the density also the external potentials given by end points of the corresponding bunch of GAC's at $\alpha=1$ change and, in general, all differ from the *a priori* known v_{ext}. Thus the knowledge of the external potential v_{ext} of the given real electron system is not sufficient to pick the correct end point of the bunch of GAC's during the self-consistency scheme. A second problem is that it is not at all clear how the knowledge in the external potential of the given real system could be used in practice, i.e., one does not know how to approximate functionals depending on Φ_j and v_{ext}.

For Coulomb systems Kato's theorem can be employed. Coulomb systems consist of interacting electrons in the field of point charges. Real systems, i.e., atoms, molecules, and solids, are Coulomb systems if external fields are absent and if the nuclei, as usual, are treated as point charges. Kato's theorem [50] states that the position and the charge of the nuclei of a Coulomb system are uniquely determined by the cusps of the electron density. Kato's theorem holds for ground as well as excited states. In Coulomb systems the nuclei are the only source for the external potential. Thus only one unique Coulomb system can be associated with a given density. Therefore a ρ-stationary wave function of this given density can be either an eigenstate of the one Coulomb system or an eigenstate of an electronic system that is not a Coulomb system. Those ρ-stationary wave functions of the given density that are eigenfunctions of the associated Coulomb system all have to be degenerate and therefore can be distinguished by symmetry. The reason is that for Coulomb systems, because they are real systems, two eigenstates with different main quantum number do not yield the same densities. For real systems in the absence of external fields one can therefore identify the end point of a bunch of GAC's at $\alpha=1$ that corresponds to a Coulomb system as the one that is an eigenstate of the considered real system. One can then further constrain the constrained search for the ρ-stationary wave functions at $\alpha=1$ by an additional condition, namely the condition that the ρ-stationary wave functions additionally are eigenstates of a Coulomb system. In this way one could avoid the use of the external potential for the identification of the relevant end point of the involved bunch of GAC's. Unfortunately this approach is feasible only for densities that are densities of eigenstate of Coulomb systems. However, there seems to be no guarantee that the electron densities emerging during the self-consistency process of a GAC-KS procedure always belong to eigenstates of Coulomb systems.

It remains to show why the external potentials corresponding to different end points of a bunch of GAC's at $\alpha=1$ are different for real electron systems. If two functional derivatives $q([\rho,\nu,\kappa,\alpha=1];\mathbf{r})+\mu$ and $q([\rho,\nu,\kappa',\alpha=1];\mathbf{r})+\mu'$ were equal, then the corresponding two wave functions $\Psi[\rho,\nu,\kappa,\alpha=1]$ and $\Psi[\rho,\nu,\kappa',\alpha=1]$ would be eigenstates of one interacting electronic system with a Hamiltonian operator with the external potential $q([\rho,\nu,\kappa,\alpha=1];\mathbf{r})+\mu=q([\rho,\nu,\kappa',\alpha=1];\mathbf{r})+\mu'$. First, systems shall be considered that exhibit no symmetries and thus no degeneracies due to symmetry. Then different eigenstates have different main quantum numbers. In all real systems two eigenstates with different main quantum number never have the same electron density. Thus the statement on external potentials of bunches of GAC's holds if no symmetries are present. If symmetries are taken into account along the lines suggested in Ref. [41], then a symmetrized GAC-KS formalism results. In such a symmetrized GAC-KS formalism only states with well-defined symmetry quantum numbers occur and only states with the same symmetry quantum number can be adiabatically connected. Thus the GAC's can be characterized by a symmetry quantum number. GAC's with different symmetry quantum number cannot have a common point at any α because states with different symmetry quantum number are different. For example, two

atomic eigenstates with angular momentum quantum number $L=1$ and magnetic quantum number $M=\pm 1$ have the same electron density. The GAC's corresponding to the eigenstates with magnetic quantum number $M=1$ consist exclusively of state with $M=1$, whereas the GAC's belonging to the eigenstate with $M=-1$ consist only of states with $M=-1$. Thus the two GAC's cannot have a common point, i.e., the two eigenstates for $M=\pm 1$ cannot belong to the same bunch of GAC's. In an electronic system with symmetries two eigenstates that have the same density and belong to the same bunch of GAC's therefore must have the same symmetry quantum numbers and thus, as in the absence of symmetries, have different main quantum numbers. Now, again, the fact that in real systems eigenstates with different main quantum numbers never have the same electron density can be invoked.

Whether the statement on external potentials of bunches of GAC's also holds true in model systems needs further investigation. In the homogeneous electron gas, more precisely in a finite system with periodic boundary conditions and a constant external potential, independent of α all eigenstates have the same electron density, a constant density. Furthermore, some eigenstates have the same symmetry quantum number with respect to translational symmetry. In a noninteracting homogeneous electron gas, for example, an eigenstate with the same translational quantum number as the ground state can be obtained by replacing two single-particle states with wave vectors $\mathbf{k}$ and $\mathbf{k}'$ by two single-particle states with wave vectors $\mathbf{q}$ and $\mathbf{q}'$ that obey the condition $\mathbf{q}+\mathbf{q}'=\mathbf{k}+\mathbf{k}'$. Thus eigenstates with the same symmetry labels and the same electron density exist for the homogeneous electron gas. This does not mean that the GAC-KS formalism cannot be applied. Only if two or more of these eigenstates belong to the same bunch of GAC's would the application of the GAC-KS formalism be problematic. Whether eigenstates of the homogeneous electron gas belong to the same bunch of GAC's or not remains an open question. Physical intuition suggests that this is not the case, see Sec. VI. In any case, the homogeneous electron gas is not a real but a model system.

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