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Potential-Driven Adiabatic Connection in Density Functional Theory

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Abstract: As density functional theory conventionally assumes that the density of a chosen model system (e.g., the Kohn—Sham system) is the same as the exact one, one might expect that approximations to the exact density introduce supplementary errors by falsifying the density. In fact, this is not true: by modeling the exchange-correlation holes for all densities, density functional approximations avoid this problem. The technique used to show it is a potential-driven adiabatic connection which hopefully will also permit constructing new approximations in the spirit of DFT.

Introduction

DFT. In density functional theory (DFT), the Schrödinger equation is solved for model systems where the interaction between particles is fictitious, that is, not the physical, Coulomb one. In the Kohn—Sham model,[1] for example, the interaction is reduced to its simplest form: it is set to zero. The energy of the model is, of course, different from that of the physical system. Insight into the nature of this difference, which is needed for obtaining the energy, can be obtained by considering an "adiabatic connection", a process in which the interaction is progressively modified from that of the model to that of the physical system.[2-5] The evolution between the model and the physical system can be characterized by a parameter, λ, which varies between λ_0, characterizing the model, and λ_1, characterizing the physical system.

In its most widespread formulation, the expression of the correction to the model energy, needed to obtain the exact energy, contains the evolution of the pair density, $P_2(r_1,r_2)$ along the adiabatic connection. Modeling $P_2(r_1,r_2)$ was not only successfully used for constructing many of the density functional approximations (see, e.g., refs 6−12) but is also explicitly used in methods like the random phase approximation (see, e.g., refs 13 and 14). In its most widespread variant, although P_2 is a function of λ, the one-particle density $n(r)$ does not vary along the adiabatic connection.[3,4]

Model Densities May Not Be Exact. With a density functional approximation (DFA), the model does not yield the exact density; in general, $n^{\lambda_0} \neq n^{\lambda_1}$. In the following, a simple example will be given. It can be considered exaggerated, but it has the advantage that accurate numbers are known for it.[15] The system of two noninteracting particles in the potential $-\zeta/r$ will be assumed to be an approximation of the exact Kohn—Sham system which yields the density of the He atom. The choice of $\zeta = 1.344$ yields the exact asymptotic decay of the density of the He atom. This model system thus reproduces exactly only a given property of the physical density, not the physical density itself. One can numerically construct a system in which the interaction between electrons is of the Coulomb type but has the density of this model, $n^{\lambda_0} = 2(\zeta^3/\pi) \exp(-\zeta r)$,[15] and calculate the ground-state energy of the fully interacting system having this density, in the external potential of the He atom. Keeping the density constant produces a very large error in the total energy ($\approx$0.13 hartree). Not surprisingly, the largest error comes from the electrostatic part of the electron—electron interaction, $\approx$0.37 hartree, and the difference in the one-particle part of the energy is on the same order of magnitude, $\approx$0.3 hartree. If one concentrates, however, on the parts which are modeled in DFT, the situation is better: the correlation energy obtained for the physically interacting system with n^{λ_0} is −0.043 hartree, reasonably close to that of the He atom (see, e.g., ref 16), −0.042 hartree. However, the exchange energy differs considerably; it is −0.840 hartree[15] for the system with n^{λ_0}, versus −1.025 for the He atom (see, e.g., ref 16).

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This example seems to support the idea that one should take into account the change of the density between the model and the physical system.

Objective. The objective of this paper is to show that, with a slightly modified adiabatic connection, the problem of variable density is in fact avoided by DFAs. The key idea is that one has to take into account that DFAs provide models for all densities. Furthermore, it will be argued that the modified adiabatic connection allows going beyond DFAs in a systematic way. Of course, like in all methods of quantum chemistry, this last step has to be payed with more computational effort.

The Modified Adiabatic Connection

Family of Hamiltonians. Let us consider a family of model Hamiltonians, $\lambda_0 \le \lambda \le \lambda_1$:

$$H^\lambda \equiv H(v^\lambda, w^\lambda) = T + V^\lambda + W^\lambda \quad (1)$$

where

$$V^\lambda = \sum_{i=1,N} v^\lambda(r_i) \quad (2)$$

is a local one-particle potential,

$$V_{ne} = \sum_{i=1,N} v_{ne}(r_i) \quad (3)$$

is the physical, local one-particle potential ($v^{\lambda_1} \equiv v_{ne}$), and

$$W^\lambda = \sum_{i<j} w(r_i, r_j) \quad (4)$$

is an operator which describes a fictitious two-particle interaction, which becomes, for $\lambda = \lambda_1$, the physical two-particle interaction

$$V_{ee} = \sum_{i<j} v_{ee}(r_i, r_j) \quad (5)$$

where $v_{ee}(r,r') = 1/|r - r'|$, in hartree atomic units.

In order to compare with DFT, v^λ is further decomposed:

$$v^\lambda(r) = v_{ne}(r) + v_h(r; n, v_{ee} - w^\lambda) + v_{xc}^\lambda(r) \quad (6)$$

where

$$v_h(r; n, w) \equiv \int d^3 r' \, n(r') \, w(r, r') \quad (7)$$

and v_{xc}^λ is defined by eq 6. Below, for analyzing approximations, we will proceed in a different way: we will choose some $v_{xc}^\lambda(r)$ and use eq 6 to define v^λ; v_{xc}^λ will be chosen to vanish as $\lambda \rightarrow \lambda_1$, to ensure that $v^{\lambda_1} \rightarrow v_{ne}$.

Energy Expression. To obtain the total energy, we will write, also in analogy to DFT,

$$E = \langle \Psi^\lambda | T + V_{ne} + W^\lambda | \Psi^\lambda \rangle + U[n^\lambda; v_{ee} - w^\lambda] + E_{xc}[v^\lambda, w^\lambda] \quad (8)$$

where Ψ is an antisymmetric wave function; Ψ^λ will be used as a notation for a minimizing Ψ. Ψ^λ yields the one-particle density $n^\lambda(r)$. Furthermore,

$$U[n; w] \equiv \frac{1}{2} \iint n(r) \, n(r') \, w(r, r') \quad (9)$$

is a Hartree (i.e., electrostatic) term, and E_{xc} is defined by eq 8.

Please notice that the last two terms on the right-hand side of eq 8 vanish when $\lambda = \lambda_1$.

Variation with λ. In order to study the change with respect to λ, after taking the derivative of eq 8 with respect to λ, we get

$$0 = \langle \Psi^\lambda | \partial_\lambda W^\lambda | \Psi^\lambda \rangle - U[n^\lambda; \partial_\lambda w^\lambda] - \int v_{xc}^\lambda \partial_\lambda n^\lambda + \partial_\lambda E_{xc}[v^\lambda, w^\lambda] \quad (10)$$

To obtain eq 10, we have used the variational character of Ψ^λ for H^λ,

$$\partial_\lambda \langle \Psi^\lambda | T + V_{ne} + W^\lambda | \Psi^\lambda \rangle = \partial_\lambda \langle \Psi^\lambda | T + V^\lambda + W^\lambda | \Psi^\lambda \rangle + \partial_\lambda \int d^3 r \, (v_{ne} - v^\lambda) \, n^\lambda = \langle \Psi^\lambda | \partial_\lambda V^\lambda + \partial_\lambda W^\lambda | \Psi^\lambda \rangle - \int d^3 r \, n^\lambda \, \partial_\lambda v^\lambda + \int d^3 r \, (v_{ne} - v^\lambda) \, \partial_\lambda n^\lambda = \langle \Psi^\lambda | \partial_\lambda W^\lambda | \Psi^\lambda \rangle + \int d^3 r \, (v_{ne} - v^\lambda) \, \partial_\lambda n^\lambda \quad (11)$$

and

$$\partial_\lambda U[n^\lambda; v_{ee} - w^\lambda] = \int d^3 r \, v_h(r; n^\lambda, v_{ee} - w) \partial_\lambda n^\lambda - \frac{1}{2} \iint d^3 r \, d^3 r' \, n(r) \, n(r') \, \partial_\lambda w^\lambda \quad (12)$$

as well as eq 6.

Integrated Formulas. Equation 10 can be integrated over λ, between λ_0 and λ_1, to yield

$$E_{xc}[v^{\lambda_0}, w^{\lambda_0}] = \int_{\lambda_0}^{\lambda_1} d\lambda (\langle \Psi^\lambda | \partial_\lambda W^\lambda | \Psi^\lambda \rangle - U[n^\lambda; \partial_\lambda w^\lambda] - \int v_{xc}(r; n^\lambda, v_{ee} - v^\lambda) \, \partial_\lambda n^\lambda) \quad (13)$$

One can also use the exchange-correlation part of the pair density produced by Ψ^λ, $P_2(r_1, r_2; \Psi^\lambda)$,

$$P_{xc}(r_1, r_2; \Psi^\lambda) = P_2(r_1, r_1; \Psi^\lambda) - n^\lambda(r_1) \, n^\lambda(r_2) \quad (14)$$

to rewrite eq 13 as

$$E_{xc}[v^{\lambda_0}, w^{\lambda_0}] =$$
$$\int_{\lambda_0}^{\lambda_1} d\lambda \frac{1}{2} \iint d^3 r \, d^3 r' \, P_{xc}(r_1, r_2; \Psi^\lambda) \, \partial_\lambda w^\lambda(r, r') - \int_{\lambda_0}^{\lambda_1} d\lambda \int v_{xc}^\lambda(r) \, \partial_\lambda n^\lambda(r) \quad (15)$$

Hamiltonian-Driven Adiabatic Connections. In the derivation of the formulas above, the adiabatic connection was driven by the change in the Hamiltonian, in particular, by the change of the one- and two-body potential: it was potential-driven. One can also produce model Hamiltonians by changing the kinetic energy operator. For example, one can keep the two-body operator equal to v_{ee} for all λ's (cf., e.g., ref 17). With such a one-body-operator-driven adiabatic connection, one can produce expressions for the correlation

energy which depend on the one-body density matrix along the adiabatic connection, $\gamma(r,r'; \Psi^\lambda)$.

This type of adiabatic connection will not be discussed here, as it is only seldom used to produce approximations to the universal correlation energy functional.

Relationship to DFT

Relationship to Exact DFT. The adiabatic connection formula of DFT is well-known.[3] The resulting equation has the same form as eq 15 without the last term on the right-hand side, as n does not vary with λ. One should keep in mind that in DFT E_{xc} is not determined by v^{λ_0} and w^{λ_0}, but by n and w^{λ_0},

$$E_{xc}[n, w^{\lambda_0}] = \int_{\lambda_0}^{\lambda_1} d\lambda \frac{1}{2} \iint d^3r\, d^3r'\, P_{xc}(r, r'; \Psi^\lambda)\, \partial_\lambda w^\lambda(r, r')$$
(16)

and that v^λ is constructed by using in eq 6:

$$v_{xc}^\lambda(r) = \delta E_{xc}[n, w^{\lambda_0}]/\delta n(r)$$
(17)

Density Functional Approximations. In practice, DFAs are made to define the model systems: E_{xc} is in general replaced by some approximation, $\tilde{E}_{xc}$:

$$\tilde{E}_{xc}[\tilde{n}^{\lambda_0}, \lambda_0] = \int_{\lambda_0}^{\lambda_1} d\lambda \frac{1}{2} \iint d^3r\, d^3r'\, \tilde{P}_{xc}(r, r'; \tilde{n}^{\lambda_0}(r))\, \partial_\lambda w^\lambda(r, r')$$
(18)

$\tilde{P}_{xc}$ is some model for P_{xc}; in LDA, for example, it is that of the uniform electron gas with density $\tilde{n}^{\lambda_0}(r)$. $\tilde{n}^{\lambda_0}$ is the density obtained from $\tilde{\Psi}^{\lambda_0}$, which in turn depends on w^{λ_0} and v^{λ_0}. For the latter, eq 6 is used, and

$$\tilde{v}_{xc}^{\lambda_0}(r; n, w) \equiv \delta \tilde{E}_{xc}[n, \lambda_0]\, \delta n(r)$$
(19)

at $n = n^{\lambda_0}$.

Comparing the equation of DFT, eq 16, with that of DFAs, eq 18, one can notice two differences: (i) the latter uses of a model, and (ii) the model uses n^{λ_0} instead of n^λ. The latter point arises because the DFT assumption was made in the derivation, namely, n was assumed not to change with λ. (When a calculation at λ_0 is done, only n^{λ_0} is known, so that the information about $n^{\lambda(>\lambda_0)}$ is missing.)

Derivative of $\tilde{E}_{xc}$ with Respect to λ. Notice that $\tilde{E}_{xc}$ depends on λ implicitly, via the λ dependence of n^λ, and explicitly, for a given λ, as the functional will change for the same density, as the interaction w^λ changes with λ:

$$\partial_\lambda \tilde{E}_{xc}[n^\lambda, \lambda] = \partial_\lambda \tilde{E}_{xc}[n^\lambda, \tilde{\lambda}]|_{\tilde{\lambda}=\lambda} + \partial_\lambda \tilde{E}_{xc}[n, \lambda]|_{n=n^\lambda} \quad (20)$$

The first term on the right-hand side is the derivative of $\tilde{E}_{xc}$ at fixed λ, which by the chain rule is

$$\partial_\lambda \tilde{E}_{xc}[n^\lambda, \tilde{\lambda}]|_{\tilde{\lambda}=\lambda} = \int \tilde{v}_{xc}(r; n^\lambda, w^\lambda)\, \partial_\lambda n^\lambda(r)$$
(21)

while the last term on the right-hand side of eq 20, the derivative at fixed n, is, by using eq 18,

$$\partial_\lambda \tilde{E}_{xc}[n, \lambda]|_{n=n^\lambda} = -\frac{1}{2} \iint d^3r\, d^3r' \tilde{P}_{xc}(r, r'; n^\lambda(r))\, \partial_\lambda w^\lambda(r, r')$$
(22)

Special Choice for v_{xc}^λ. We now go back to the adiabatic connection in which the density is allowed to vary but specify now a potential which, until now, was arbitrary. We choose

$$v_{xc}^\lambda(r) = \tilde{v}_{xc}(r; n^\lambda, w^\lambda)$$
(23)

By this choice,

$$\Psi^\lambda = \tilde{\Psi}^\lambda$$
$$n^\lambda = \tilde{n}^\lambda$$
(24)

Adiabatic Connection for the Special Choice of v_{xc}^λ. We can use eq 23 in eq 15; next, we use eq 21, followed by eq 20, and finally use eq 22:

$$E_{xc}[v^{\lambda_0}, w^{\lambda_0}] = \int_{\lambda_0}^{\lambda_1} d\lambda \frac{1}{2} \iint d^3r\, d^3r'\, P_{xc}(r_1, r_2; \Psi^\lambda) \times$$
$$\partial_\lambda w^\lambda(r, r') - \int_{\lambda_2}^{\lambda_1} d\lambda \int \tilde{v}_{xc}(r; n^\lambda, w^\lambda)\, \partial_\lambda n^\lambda(r) =$$
$$\int_{\lambda_0}^{\lambda_1} d\lambda \frac{1}{2} \iint d^3r\, d^3r'\, P_{xc}(r_1, r_2; \Psi^\lambda)\, \partial_\lambda w^\lambda(r, r') -$$
$$\int_{\lambda_2}^{\lambda_1} d\lambda (\partial_\lambda \tilde{E}_{xc}[n^\lambda, \tilde{\lambda}]|_{\tilde{\lambda}=\lambda}) =$$
$$\int_{\lambda_0}^{\lambda_1} d\lambda \frac{1}{2} \iint d^3r\, d^3r'\, P_{xc}(r_1, r_2; \Psi^\lambda)\, \partial_\lambda w^\lambda(r, r') -$$
$$\int_{\lambda_2}^{\lambda_1} d\lambda (\partial_\lambda \tilde{E}_{xc}[n^\lambda, \lambda] - \partial_\lambda \tilde{E}_{xc}[n, \lambda]|_{n=n^\lambda}) =$$
$$\int_{\lambda_0}^{\lambda_1} d\lambda \frac{1}{2} \iint d^3r\, d^3r'\, P_{xc}(r_1, r_2; \Psi^\lambda)\, \partial_\lambda w^\lambda(r, r') -$$
$$\int_{\lambda_2}^{\lambda_1} d\lambda (\partial_\lambda \tilde{E}_{xc}[n^\lambda, \lambda]) -$$
$$\int_{\lambda_2}^{\lambda_1} d\lambda \frac{1}{2} \iint d^3r\, d^3r'\, \tilde{P}_{xc}(r, r'; n^\lambda(r))\, \partial_\lambda w^\lambda(r, r')$$

so that, with $\tilde{E}_{xc}[n^{\lambda_0}, \lambda_1] = 0$,

$$E_{xc}[v^{\lambda_0}, w^{\lambda_0}] - \tilde{E}_{xc}[n^{\lambda_0}, \lambda_0] =$$
$$\int_{\lambda_0}^{\lambda_1} d\lambda \frac{1}{2} \iint d^3r\, d^3r'(P_{xc}(r_1, r_2; \Psi^\lambda) - \tilde{P}_{xc}(r, r'; n^\lambda(r)))\, \partial_\lambda w^\lambda(r, r') \quad (26)$$

Interpretation. Equation 26 shows that the error of the model is due to the difference between $P_{xc}(\Psi^\lambda)$ and the model $\tilde{P}_{xc}(n^\lambda)$. As in DFA, the models are defined to work for all densities (as one does not know beforehand what density is of interest); they also work for n^λ. Thus, from the perspective of eq 26 (and that of the modified adiabatic connection), there is no need for any supplementary correction due to density changes.

Relevance for DFAs. When the ground-state energy is computed, eq 26 tells us that we can comfortably ignore the fact that the density of the model is not the exact one—as long as the DFA is based upon a hole model. Most of the existing approximations used (the local density approximation, LDA; most of the generalized gradient approximations, GGAs; etc.) are based on hole models.

Notice also that in "density functional calculations", sometimes potentials are used which are not derivatives of a functional of the density. They show up, for example, when optimized effective potentials are used, or when making approximations for time-depenent DFT, for example, for

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correcting the asymptotic behavior of the approximate Kohn–Sham potential. In such situations, one leaves the standard frame of DFT, but not that of the present approach.

Perspectives

Losses and Gains. A Hamiltonian-driven adiabatic connection is identical to the adiabatic connection in DFT when the density is kept constant. When the density is not kept fixed, it loses the pure beauty of DFT. However, the added flexibility might not only bring theory closer to what is done in practice in DFAs but also might give some hints about how to improve approximations. Finally, many of the successful DFAs were constructed from hole models, and they can continue to be used in the potential-driven adiabatic connection.

Choosing v^λ. Analysis of v^λ was used over the years to understand DFAs, which are normally constructed by using an ansatz of the form

$$\tilde{E}_{xc}[n, \lambda_0] = \int d^3r\, n(r)\, \partial_\lambda \tilde{\varepsilon}_{xc}^{\lambda}(n(r), |\nabla n(r)|^2, ...) \quad (27)$$

Unfortunately, the equality does not suffice to define $\tilde{\varepsilon}_{xc}$: the left-hand side is a number, while $\tilde{\varepsilon}_{xc}$ is a function. (In other words, any function which multiplied with n integrates to zero can be added to $\tilde{\varepsilon}_{xc}$ without changing the value of the integral.) However, in DFT, one can compare safely, for a given system, the accurate v_{xc}^{λ}, eq 17, with that obtained from approximations. Thus, one can also use the knowledge gained in the past years for constructing accurate v_{xc}^{λ}'s in DFT and for constructing v^λ for the potential-driven adiabatic connection.

Because of the requirement of using model systems having as the ground-state density the exact one, DFT ensures that the model system is in most cases sufficiently close to the exact one, for example, has the exact electrostatic energy. In practice, however, as the exact density is unknown, DFAs produce only "reasonable" densities. Thus, to have similar performance in the potential-driven adiabatic connection, the v^λ should yield "reasonable" densities, and thus be sufficiently "close" to the v^λ which keeps the density constant. As the terms "reasonable" and "close" are not well-defined, the choice of v^λ is left to further exploration. It is possible to perform calculations in the spirit of DFT without the constraint of using potentials which are derivatives of some density functional. To start the explorations, however, one can imagine using forms of v^λ similar to those existing in DFAs; a few parameters in v^λ could be determined "on the fly", that is, made system-specific, for example, by using perturbation theory, see below.

State Following. In the potential-driven adiabatic connection, the model system does not have to be in its ground state. (Of course, the model for the pair density will have to show some dependence on the state chosen, e.g., by a dependence on the depth of the exchange-correlation hole, cf. refs 18–20.) Because of convenient choices of v^λ, it should not only be possible to follow a given state along the adiabatic connection but also to avoid some of the surprises produced in model systems keeping the ground-state density constant (the change of the nature of the ground

state, artificial degeneracies, missing degeneracies, jumps, etc.). As the potential-driven adiabatic connection has more flexibility, size-consistency problems such as those presented in ref 21 might also be avoided.

Perturbation Series for Improving E_{xc}^{λ}. The idea to use perturbation theory to improve density functionals (see, e.g., ref 22) can also be borrowed for the present context. Considering the system at λ_0, defined by the Hamiltonian H^{λ_0}, one can recover information about the system at H^λ by using perturbation series where the perturbation operator is $H^\lambda - H^{\lambda_0}$. Obtaining the first-order correction to the energy might be not very expensive, as only the wave function (or the reduced density matrices) at λ_0 are needed. The "slope of the correction", being now known, can be used for improving "on the fly" E_{xc}, for example, by readjusting the depth of the exchange-correlation hole.

Such an approach to correct E_{xc} was already used with a different adiabatic connection, where the one-electron part of the Hamiltonian is modified.[17]

By a change of viewpoint, one can see the perturbation series as resulting from taking derivatives with respect to λ. Taking the first derivative with respect to λ in eq 8 is equivalent to considering the first-order perturbation term. Higher derivatives are related to higher orders in perturbation theory. One can consider that, as when deriving eq 10, the total physical energy, E, is independent of λ. This method yields further equations which can be used to constrain E_{xc} using information specific to the system.

The adiabatic connection, eq 13 or eq 15, amounts to replacing the perturbation expansion at one point with first-order perturbation corrections at all points between λ_0 and λ_1. This suggests that one could repeat the calculation at a new λ_0, say λ_0', and use both the information at λ_0 and λ_0' to improve an existing ansatz for an approximation of the exchange-correlation term. This could be useful, for instance, if we either wanted to avoid the effort of higher-order perturbation calculations or we do not trust the perturbation expansion to higher order.

Still another way to exploit the adiabatic connection is to use different potentials and to compute different corrections to it, starting at the same λ_0. Of course, in principle, the physical energy, E, is independent of the path chosen. This constraint may be a path to further improve the approximations for E_{xc}.

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