Connections between variation principles at the interface of wave-function and density-functional theories

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A recently proposed variation principle [N. I. Gidopoulos, Phys. Rev. A **83**, 040502(R) (2011)] for the determination of Kohn–Sham effective potentials is examined and extended to arbitrary electron-interaction strengths and to mixed states. Comparisons are drawn with Lieb's convex-conjugate functional, which allows for the determination of a potential associated with a given electron density by maximization, yielding the Kohn–Sham potential for a non-interacting system. The mathematical structure of the two functionals is shown to be intrinsically related; the variation principle put forward by Gidopoulos may be expressed in terms of the Lieb functional. The equivalence between the information obtained from the two approaches is illustrated numerically by their implementation in a common framework. *Published by AIP Publishing.* https://doi.org/10.1063/1.4985883

I. INTRODUCTION

Variation principles lie at the heart of many quantum-chemical theories, giving practical prescriptions for how to obtain the best electronic energy, wave function, or electron density via optimization. They may also offer insight into the connections between traditional *ab initio* wave-function based approaches and density-functional theory (DFT). In this work, we examine a new variation principle, proposed by Gidopoulos in Ref. 1 for the determination of the non-interacting system of relevance to Kohn–Sham theory.

The variation principle proposed by Gidopoulos consists of minimizing the left-hand side of the inequality

$$\langle \Psi | \hat{H}_0(v) | \Psi \rangle - E_0(v) \geq 0, \tag{1}$$

with respect to the variations of the potential v, for a fixed electronic wave function Ψ corresponding to a system of interest—typically, the physical ground-state wave function for the system. The energy $E_0(v)$ in Eq. (1) is the ground-state energy of a non-interacting system, associated with the non-interacting Hamiltonian $\hat{H}_0(v) = \hat{T} + \sum_i v(\mathbf{r}_i)$, where $\hat{T}$ is the kinetic energy operator. As discussed in Ref. 1, the minimization of the left-hand side of Eq. (1) yields the Kohn–Sham non-interacting potential v_s associated with a non-interacting system that has the same density as that of the chosen input wave function Ψ. The same variation principle was also described earlier by Davidson[2] and used as a tool to understand the analytic properties of the first-order reduced density matrix

associated with Ψ. This complements its use in Ref. 1, where it provides a tool for the optimization of the potential v. Here we refer to Eq. (1) as the *Gidopoulos–Davidson variation principle*.

At first glance, the Gidopoulos–Davidson variation principle appears to be markedly different from alternative approaches for determining the Kohn–Sham system corresponding to a reference wave function or density. For example, in Levy's constrained-search approach to DFT,[3,4] a constraint on the electron density is explicitly applied to determine the Kohn–Sham system. More closely related is the Lieb variation principle, which for a non-interacting system corresponds to maximizing the left-hand side of the inequality[5]

$$E_0(v) - (v|\rho) \leq T_s(\rho) \tag{2}$$

with respect to the variations of the potential v for a given input electron density ρ. Here we introduce the notation $(v|\rho) = \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$. Both the Gidopoulos–Davidson and Lieb variation principles involve an unconstrained optimization over v, yielding the Kohn–Sham potential v_s as their optimizer. Furthermore, their functional derivatives are identical up to a sign.[1,5]

These observations motivate us to explore the connection between the Lieb and Gidopoulos–Davidson variation principles in Eqs. (1) and (2), respectively. We begin by reviewing standard variation principles in Sec. II. In Sec. III, we highlight the connections between the Gidopoulos–Davidson and Lieb variation principles, including extensions to general interaction strengths and to mixed states. A brief review of the adiabatic connection (AC) is then given in Sec. IV,

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providing a link between the generalized functionals and the exchange–correlation energy DFT.

Having established the close connection between these alternative variation principles, we present some results from numerical implementation in a common framework in Sec. V, highlighting the equivalent information they yield both in the non-interacting limit and for arbitrary interaction strengths. In Sec. VI, we make some concluding remarks and discuss possible directions for future work.

II. VARIATION PRINCIPLES

In this section, we review the Rayleigh–Ritz variation principles for pure and mixed electronic states and the Hohenberg–Kohn and Lieb variation principles of DFT.

A. Rayleigh–Ritz variation principle

Consider an electronic system described by a Hamiltonian of the form

$$\hat{H}_\lambda(v) = -\frac{1}{2}\sum_i \nabla_i^2 + \sum_i v(\mathbf{r}_i) + \sum_{i>j} w_\lambda(|\mathbf{r}_i - \mathbf{r}_j|)$$
$$= \hat{T} + \hat{V} + \hat{W}_\lambda, \qquad (3)$$

where $\hat{T}$ is the kinetic-energy operator, $\hat{V}$ is the external potential operator, and $\hat{W}_\lambda$ is the electron–electron repulsion operator for a given electron–electron interaction strength $\lambda \in [0, 1]$ such that $w_0 = 0$ (for non-interacting systems) and $w_1 = 1/|\mathbf{r}_i - \mathbf{r}_j|$ (for physical systems). At a given interaction strength λ, the ground-state energy of an N-electron eigenfunction Ψ of the Hamiltonian $H_\lambda(v)$ can be defined in the context of wave-function theory by varying the wave function Ψ according to the *Rayleigh–Ritz variation principle*,

$$E_\lambda(v) = \inf_{\Psi \in \mathcal{W}_N} \left\langle \Psi \left| \hat{H}_\lambda(v) \right| \Psi \right\rangle, \qquad (4)$$

where $\mathcal{W}_N$ is the set of all L^2-normalized, antisymmetric N-electron wave functions with a finite kinetic energy,

$$\mathcal{W}_N = \left\{ \Psi \mid \langle\Psi|\Psi\rangle = 1 \ , \ \sum_{i=1}^N \langle\nabla_i\Psi|\nabla_i\Psi\rangle < \infty \right\}. \qquad (5)$$

The Rayleigh–Ritz variation principle is well defined for all potentials v belonging to the vector space $\chi^* = L^{3/2} + L^\infty$, which includes all Coulomb potentials.[5]

It is often more useful to work with mixed rather than pure states, giving the *canonical-ensemble Rayleigh–Ritz variation principle*

$$E_\lambda(v) = \inf_{\hat{\gamma} \in \mathcal{K}_N} \operatorname{tr} \hat{\gamma}\hat{H}_\lambda(v), \qquad (6)$$

where $\mathcal{K}_N$ is the set of all admissible ensemble density matrices,

$$\mathcal{K}_N = \left\{ \sum_i \lambda_i |\Psi_i\rangle\langle\Psi_i| \mid \lambda_i \geq 0, \sum_i \lambda_i = 1, \Psi_i \in \mathcal{W}_N \right\}. \qquad (7)$$

Although the ground-state energy can always be defined as the greatest lower bound in either Eq. (4) or (6), the formulation in terms of ensembles is more flexible, allowing for mixed-state solutions. This extra flexibility is important to establish correspondence between the optimizers in the Rayleigh–Ritz variation principle commonly used in *ab initio* theory and the Hohenberg-Kohn variation principle used in DFT.[6]

B. Hohenberg–Kohn and Lieb variation principles

Being concave and continuous, the ground-state energy defined in Eq. (4) may be expressed in terms of the *Hohenberg–Kohn variation principle*

$$E_\lambda(v) = \inf_{\rho \in \chi} (F_\lambda(\rho) + (v|\rho)), \qquad (8)$$

where Lieb's universal density functional F_λ is obtained from the ground-state energy by the *Lieb variation principle,*[5]

$$F_\lambda(\rho) = \sup_{v \in \chi^*} (E_\lambda(v) - (v|\rho)). \qquad (9)$$

The functionals E_λ and F_λ are a conjugate pair, related by mutual Legendre–Fenchel transforms. The vector spaces of admissible densities and potentials are the Banach spaces $\chi = L^3 \cap L^1$ and $\chi^* = L^{3/2} + L^\infty$, respectively, encompassing all N-representable densities $\rho \in \chi$ and all Coulomb potentials $v \in \chi^*$, with which the density has a finite interaction energy.

The Lieb functional defined above is equivalent to the Levy–Lieb constrained-search functional when defined in terms of ensembles,

$$F_\lambda(\rho) = \inf_{\hat{\gamma}\to\rho} \operatorname{tr} \hat{\gamma}\hat{H}_\lambda(0), \qquad (10)$$

where $\hat{H}_\lambda(0) = \hat{T} + \hat{W}_\lambda$. The relationship between the functionals may be better understood by rewriting the Lieb variation principle of Eq. (9) in the form

$$F_\lambda(\rho) = \sup_{v \in \chi^*} \left(\inf_{\hat{\gamma} \in \mathcal{K}_N} \operatorname{tr} \hat{\gamma}\hat{H}_\lambda(v) - (v|\rho) \right) \qquad (11)$$

$$= \sup_{v \in \chi^*} \inf_{\hat{\gamma} \in \mathcal{K}_N} \left(\operatorname{tr} \hat{\gamma}\hat{H}_\lambda(0) - (v|\rho - \rho_{\hat{\gamma}}) \right), \qquad (12)$$

which may be viewed as the minimization of $\operatorname{tr} \hat{\gamma}\hat{H}_\lambda(0)$ with respect to $\hat{\gamma}$ subject to the constraint that $\rho_{\hat{\gamma}} - \rho = 0$ with Lagrange multiplier v, corresponding precisely to the Levy–Lieb constrained-search functional in Eq. (10).

We note that the Levy constrained-search functional for pure states

$$\overline{F}_\lambda(\rho) = \inf_{\Psi\to\rho} \langle\Psi|\hat{H}_\lambda(0)|\Psi\rangle \qquad (13)$$

is an upper bound to the Lieb functional $\overline{F}_\lambda(\rho) \geq F_\lambda(\rho)$, with equality whenever ρ is pure-state representable. Importantly, $\overline{F}_\lambda$ gives the same ground-state energy $E_\lambda(v)$ as F_λ in the Hohenberg–Kohn variation principle for all potentials v, the only difference being that the minimizing densities with $\overline{F}_\lambda$ are always pure states.

As shown in Ref. 6, there is a one-to-one correspondence between the ground-state densities obtained from the Hohenberg–Kohn variation principle with the Lieb functional as in Eq. (8) and from the Rayleigh–Ritz variation principle with ensembles as in Eq. (6) but not with pure states as in Eq. (4).

III. GIDOPOULOS–DAVIDSON VARIATION PRINCIPLE

The variation principle of Gidopoulos in Ref. 1 allows for the determination of the non-interacting system of relevance to Kohn–Sham theory and may be written in the form

$$D_0(\Psi) = \inf_{v \in \chi^*} \left(\langle \Psi | \hat{H}_0(v) | \Psi \rangle - E_0(v) \right), \qquad (14)$$

where $\Psi \in \mathcal{W}_N$ is an electronic wave function corresponding to the physical system of interest; typically the physical ground-state wave function of $\hat{H}_1(v)$ for some $v \in \chi^*$. The energy $E_0(v)$ is the ground-state energy of the non-interacting system, defined according to Eq. (4). Note that $D_0(\Psi)$ is well defined since $\langle \Psi | \hat{H}_0(v) | \Psi \rangle - E_0(v) \geq 0$ for each $\Psi \in \mathcal{W}_N$ by the Rayleigh–Ritz variation principle.

A. Relationship to Lieb variation principle

The Gidopoulos–Davidson variation principle is related in a simple manner to the non-interacting Lieb variation principle

$$F_0(\rho) = \sup_{v \in \chi^*} (E_0(v) - (v|\rho)). \qquad (15)$$

To see the relation, we decompose the non-interacting expectation value $\langle \Psi | \hat{H}_0(v) | \Psi \rangle$ in the manner

$$\langle \Psi | \hat{H}_0(v) | \Psi \rangle = T(\Psi) + (v | \rho_\Psi), \qquad (16)$$

where $T(\Psi) = \langle \Psi | \hat{T} | \Psi \rangle$ and ρ_Ψ are the kinetic energy and density yielded by Ψ, respectively. A comparison of the functionals in Eqs. (14) and (15) then gives

$$D_0(\Psi) = T(\Psi) - F_0(\rho_\Psi) = T(\Psi) - \overline{F}_0(\rho_\Psi), \qquad (17)$$

where we in the last step have replaced the Lieb functional by the Levy constrained-search functional, noting that ρ_Ψ is pure-state representable. We conclude that that *the Gidopoulos–Davidson functional* of a given system is simply the total kinetic energy of this system minus the non-interacting Levy constrained-search functional.

Since the non-interacting Levy functional is the non-interacting Kohn–Sham kinetic energy,

$$F_0(\rho) = T_s(\rho), \qquad (18)$$

we find that the Gidopoulos–Davidson functional is the Kohn–Sham kinetic-energy correlation energy,

$$D_0(\Psi) = T(\Psi) - T_s(\rho_\Psi), \qquad (19)$$

or alternatively,

$$D_0(\Psi) = \langle \Psi | \hat{T} | \Psi \rangle - \inf_{\Phi \mapsto \rho_\Psi} \langle \Phi | \hat{T} | \Phi \rangle, \qquad (20)$$

where Φ is a single Slater determinant describing the non-interacting Kohn–Sham system.

The relationship of the Gidopoulos–Davidson functional to the correlation kinetic energy is well known.[1] Here we see that, for pure states, the non-interacting Gidopoulos–Davidson and Lieb variation principles yield the same Kohn–Sham system from different directions. The Lieb variation principle minimizes the value of the non-interacting kinetic energy T_s, subject to a density constraint, whilst the Gidopoulos-Davidson variation principle maximizes the correlation kinetic energy $T_c = T - T_s$ subject to a similar density constraint. Following the discussion in Sec. II B, we observe that the potential in the Gidopoulos–Davidson variation principle in Eq. (14) may be viewed as the Lagrange multiplier for the density constraint in Eq. (20).

B. Objective functions

The Gidopoulos–Davidson and Lieb functional are also related in a simple way. Expressing the functionals in terms of their objective functions, we find

$$D_0(\Psi) = \inf_{v \in \chi^*} G_0(v, \Psi), \qquad (21)$$

$$F_0(\rho) = \sup_{v \in \chi^*} L_0(v, \rho), \qquad (22)$$

where

$$G_0(v, \Psi) = \langle \Psi | \hat{H}_0(v) | \Psi \rangle - E_0(v), \qquad (23)$$

$$L_0(v, \rho) = E_0(v) - (v | \rho). \qquad (24)$$

Hence, we obtain in agreement with Eq. (17),

$$G_0(v, \Psi) = T(\Psi) - L_0(v, \rho_\Psi). \qquad (25)$$

The functional $L_0(v, \rho)$ is concave in v and affine in ρ, whereas $G_0(v, \Psi)$ is convex in v. After a generalization to mixed states, G_0 becomes convex also in the second variable; see Sec. III D.

C. Functional derivatives of objective functions

To determine the stationary points of the Gidopoulos–Davidson and Lieb variation principles, we note that the ground state energy $E_0(v)$ is differentiable with functional derivative ρ_v if and only if v supports a ground state with a unique density ρ_v. For a given $\Psi \in \mathcal{W}_N$, the expectation value $\langle \Psi | \hat{H}_0(v) | \Psi \rangle$ is always differentiable with respect to v, with functional derivative ρ_Ψ. Hence, assuming differentiability of E_0 at v, we have

$$\frac{\delta G_0(v, \Psi)}{\delta v(\mathbf{r})} = \rho_\Psi(\mathbf{r}) - \rho_v(\mathbf{r}) \qquad (26)$$

and[7]

$$\frac{\delta L_0(v, \rho)}{\delta v(\mathbf{r})} = \rho_v(\mathbf{r}) - \rho(\mathbf{r}). \qquad (27)$$

When $\rho = \rho_\Psi$, the functional derivatives are identical except for the sign difference.

The second derivatives of G_0 and L_0 with respect to the potential v may also be readily evaluated. They are equal to (minus and plus) one half of the non-interacting static density response function of the system,[7]

$$\frac{\delta^2 G_0(v, \Psi)}{\delta v(\mathbf{r}) \delta v(\mathbf{r}')} = -\frac{\delta^2 L_0(v, \rho)}{\delta v(\mathbf{r}) \delta v(\mathbf{r}')} = -\frac{1}{2} \chi_0(\mathbf{r}, \mathbf{r}')$$

$$= -\frac{1}{2} \sum_{ia} \frac{\varphi_i(\mathbf{r}) \varphi_i^*(\mathbf{r}') \varphi_a(\mathbf{r}') \varphi_a^*(\mathbf{r})}{\varepsilon_i - \varepsilon_a} + \text{c.c.}, \qquad (28)$$

where the indices i and a denote occupied and virtual orbitals, respectively, whose orbital energies are ε_i and ε_a. In Ref. 1, focus is placed on the optimization of G_0 with respect to v. In passing, we note that the non-interacting Hamiltonian readily separates into one-electron contributions $\hat{H}_0(v) = \sum_k \hat{h}_k(v)$ with $\hat{h}_k(v) = -\frac{1}{2} \nabla_k^2 + v(\mathbf{r}_k)$ and that the orbitals entering Eq. (28) are the eigenfunctions of this one-electron Hamiltonian. The non-interacting ground-state energy is the sum of the occupied orbital energies, $E_0(v) = \sum_i \varepsilon_i$. We also remark that, although $\pm \frac{1}{2} \chi_0(\mathbf{r}, \mathbf{r}')$ is positive/negative semi-definite, this does not imply that G_0/L_0 are convex/concave in v

since the derivatives in Eq. (28) are not defined for all potentials.

Throughout this discussion we have assumed differentiability of $L_0(v, \rho)$ and $G_0(v, \Psi)$. The functional $L_0(v, \rho)$ is not straightforwardly differentiable as discussed by Lammert;[8] however, this issue can be avoided by using a regularized form as discussed in Ref. 9. Since the derivative of $G_0(v, \Psi)$ amounts to taking the derivative of $-L_0(v, \rho_\Psi)$ [see Eq. (25)], the same regularization techniques can be applied to this functional.

D. Generalization to ensembles

Generalizing the Gidopoulos–Davidson functional for pure states $\Psi \in \mathcal{W}_N$ to canonical ensembles $\hat{\gamma} \in \mathcal{K}_N$, we obtain the functional

$$\mathcal{D}_0(\hat{\gamma}) = \inf_{v \in \chi^*} (\operatorname{tr} \hat{\gamma} \hat{H}_0(v) - E_0(v)).$$
$$= \mathcal{T}(\hat{\gamma}) - \sup_{v \in \chi^*} (E_0(v) - (v|\rho_\Psi)), \quad (29)$$

where $\mathcal{T}(\hat{\gamma}) = \operatorname{tr} \hat{\gamma} \hat{T}$. The ensemble Gidopoulos–Davidson functional is concave. To show concavity, we select $\hat{\gamma}_1, \hat{\gamma}_2 \in \mathcal{K}_N$ and obtain for each $0 < \nu < 1$ the inequality

$$\mathcal{D}_0(\nu \hat{\gamma}_1 + (1 - \nu) \hat{\gamma}_2)$$
$$= \nu \operatorname{tr} \hat{\gamma}_1 \hat{T} + (1 - \nu) \operatorname{tr} \hat{\gamma}_2 \hat{T} - F_0(\nu \rho_1 + (1 - \nu) \rho_2)$$
$$\geq \nu \operatorname{tr} \hat{\gamma}_1 \hat{T} (1 - \nu) \operatorname{tr} \hat{\gamma}_2 \hat{T} - \nu F_0(\rho_1) - (1 - \nu) F_0(\rho_2)$$
$$= \nu \mathcal{D}_0(\hat{\gamma}_1) + (1 - \nu) \mathcal{D}_0(\hat{\gamma}_2), \quad (30)$$

where in the second step, we have used the convexity of the Lieb functional.

Since Ψ occurs quadratically in $D_0(\Psi)$, a similar proof is precluded for the pure-state Gidopoulos–Davidson functional, which is indeed not concave. Note that, for pure states $\hat{\gamma}_\Psi = |\Psi\rangle\langle\Psi|$, the ensemble Gidopoulos–Davidson functional reduces to the original functional: $\mathcal{D}_0(\hat{\gamma}_\Psi) = D_0(\Psi)$.

E. Generalization to arbitrary interaction strengths

The Gidopoulos–Davidson functional may be extended to interacting systems in the manner

$$D_\lambda(\Psi) = \inf_{v \in \chi^*} \left(\langle\Psi|\hat{H}_\lambda(v)|\Psi\rangle - E_\lambda(v) \right), \quad (31)$$

which is related to the Lieb functional via

$$D_\lambda(\Psi) = \langle\Psi|\hat{T} + \hat{W}_\lambda|\Psi\rangle - F_\lambda(\rho_\Psi) \quad (32)$$

and can re-expressed in the constrained-search form as

$$D_\lambda(\Psi) = \langle\Psi|\hat{T} + \hat{W}_\lambda|\Psi\rangle - \inf_{\Phi \mapsto \rho_\Psi} \langle\Phi|\hat{T} + \hat{W}_\lambda|\Phi\rangle. \quad (33)$$

The first derivative of the objective functional, $G_\lambda(v, \Psi) = \langle\Psi|\hat{H}_\lambda(v)|\Psi\rangle - E_\lambda(v)$, is again a simple density difference,

$$\frac{\delta G_\lambda(v, \Psi)}{\delta v(\mathbf{r})} = \rho_\Psi(\mathbf{r}) - \rho_v(\mathbf{r}), \quad (34)$$

and its second derivative can be expressed in terms of the λ-interacting density response function

$$\frac{\delta^2 G_\lambda(v, \Psi)}{\delta v(\mathbf{r})\delta v(\mathbf{r}')} = -\frac{1}{2} \chi_\lambda(\mathbf{r}, \mathbf{r}'). \quad (35)$$

To perform practical optimizations using Eq. (31), we therefore require knowledge not only of the kinetic energy associated with the input wave function Ψ but also of the λ-interacting two-electron interaction energy, $W_\lambda(\Psi) = \langle\Psi|\hat{W}_\lambda|\Psi\rangle$. In practice, these quantities can be computed from the one- and two-particle reduced density matrices, respectively.

IV. ADIABATIC CONNECTION

The adiabatic connection considers the link between the non-interacting Kohn–Sham auxiliary and physically interacting systems.[10–13] In this approach, the interaction strength λ in Eq. (3) is varied between 0 and 1, whilst imposing the constraint that at each interaction strength, the electron density ρ_λ remains fixed at that of the physical system ρ_1. Most frequently, a linear path between these two limits is considered,[11] where the Coulomb operator is simply scaled linearly by the value of λ. However, generalized ACs[14] have been explored along non-linear paths.[15,16] In the present work, only the linear path is considered but the generalization to non-linear paths is straightforward.

For the Hamiltonian in Eq. (3), the λ-dependent universal density functional can be written in the constrained-search[3–5] form for canonical ensembles,

$$F_\lambda(\rho) = \min_{\hat{\gamma} \to \rho} \operatorname{tr} \hat{H}_\lambda(0)\hat{\gamma}, \quad (36)$$

where the minimization is over all density matrices $\hat{\gamma}$ associated with the input electron density ρ. This functional is convex in ρ, concave in λ, and non-negative for $\lambda \geq 0$. The λ-interacting functional can be related to its non-interacting counterpart via

$$F_\lambda(\rho) = F_0(\rho) + \int_0^\lambda \frac{\partial F_\nu(\rho)}{\partial \nu} \mathrm{d}\nu, \quad (37)$$

where the derivative is well-defined on the real axis as a rightor left-derivative. Evaluation of the derivative and application of the Hellmann–Feynman theorem[17,18] leads to an *ab initio* expression for the exchange–correlation energy

$$E_{\mathrm{xc}}(\rho) = \int_0^1 \mathcal{W}_\lambda(\rho)\mathrm{d}\lambda. \quad (38)$$

Here $\mathcal{W}_\lambda(\rho)$ is the AC integrand

$$\mathcal{W}_\lambda(\rho) = \operatorname{tr} \hat{\gamma}_\lambda^\rho \hat{W} - E_{\mathrm{J}}(\rho), \quad (39)$$

where $\hat{\gamma}_\lambda^\rho$ is the minimizing ensemble state at interaction-strength λ and $E_{\mathrm{J}}(\rho)$ is the Coulomb energy. Furthermore, the exchange and correlation energies may be resolved into separate components, resulting in an expression for the correlation energy alone,

$$E_{\mathrm{c}}(\rho) = \int_0^1 \{\mathcal{W}_\lambda(\rho) - \mathcal{W}_0(\rho)\} \mathrm{d}\lambda. \quad (40)$$

For a review of the adiabatic connection, see Ref. 19.

To make practical use of these expressions, approaches for the calculation of the λ-interacting wave functions yielding a chosen electron density are required; see, for example, Refs. 20–22. The constraint that the density is fixed for all λ may be easily enforced by supplying fixed arguments ρ and Ψ

to Eqs. (9) and (31) for all λ. We now discuss our implementation of the (generalized) Gidopoulos–Davidson variation principle, exploring the close connections to the generalized Lieb functional numerically.

V. RESULTS

From the discussion in Sec. III, it is evident that the Gidopoulos–Davidson and Lieb optimizations are sufficiently closely related that they may be implemented in a common computational framework. We first discuss some details of our implementation; we then demonstrate the equivalence of the two approaches by performing numerical optimizations for a set of small atomic and molecular systems.

A. Computational details

The variation principle given in Eq. (31) allows a value to be obtained for the generalized Gidopoulos–Davidson functional by evaluating its infimum with respect to v. If the density yielded by the reference wave function ρ_Ψ is v-representable, the infimum becomes a minimum. To vary v such that an optimization over the potential may be carried out in a practical computational scheme, the potential is modeled using the basis-set expansion of Wu and Yang[7,23]

$$v_\lambda(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + (1-\lambda)v_{\text{ref}}(\mathbf{r}) + \sum_t b_t g_t(\mathbf{r}). \quad (41)$$

Here $v_{\text{ext}}(\mathbf{r})$ is the external potential due to the interaction of the electrons with the atomic nuclei, $v_{\text{ref}}(\mathbf{r})$ is a fixed reference potential chosen to ensure that $v_\lambda(\mathbf{r})$ has the correct asymptotic behaviour, and $\{g_t\}$ are a set of Gaussian basis functions with coefficients $\{b_t\}$. The reference potential employed in the present work is the Fermi–Amaldi potential.[24] With this choice of potential expansion, the derivatives corresponding to Eqs. (34) and (35) may be readily implemented as described in Refs. 7, 21, and 22, allowing the objective functional to be effectively optimized with respect to the set of coefficients $\{b_t\}$.

An un-contracted form of the Gaussian basis set aug-cc-pVTZ[25,26] in the spherical-harmonic basis is used for both the orbital expansion and for the potential expansion in Eq. (41), for all systems. An approximate Newton method is employed to accelerate convergence of the optimization,[27]

in which the Hessian is regularized using a truncated singular value decomposition with a threshold of 10^{-6} a.u. In all calculations, the convergence threshold was set to 10^{-6} a.u. on the L^2 norm of the objective functional gradient. To obtain a reasonably accurate approximation to the Kohn–Sham system, the input quantities for each functional $F_\lambda(\rho_\Psi)$ and $D_\lambda(\Psi)$ were determined at the coupled-cluster singles-and-doubles (CCSD) level of theory. All calculations were carried out with the QUEST rapid development platform,[28] an electronic-structure code developed in Python and exploiting just-in-time compilation using the Numba package.[29,30]

B. Kohn–Sham non-interacting system

In Table I, the optimized values of the non-interacting Lieb functional $F_0(\rho_\Psi)$ and Gidopoulos–Davidson functional $D_0(\Psi)$ are presented for a series of closed-shell atoms and for the hydrogen molecule at several bond lengths. Additionally, Kohn–Sham energy components are presented, including the internuclear repulsion energy E_{nn}, the non-interacting kinetic energy T_{s}, the electron–nuclear attraction E_{ne}, the Coulomb energy E_{J}, the exchange energy E_{x}, and the correlation energy E_{c}. These components have the same definition when computed from $F_0(\rho_\Psi)$ and $D_0(\Psi)$. For comparison, the total kinetic energy T and total electron–electron interaction energy W are included, along with the total interacting ground-state energy E_1.

The consistency of the optimizations was verified by comparing the optimized values of $F_0(\rho_\Psi)$ and $D_0(\Psi)$ presented in Table I with the energetic components T_{s} and T_{c}, respectively. The value of T_{s} was determined from the Kohn–Sham orbitals obtained at $\lambda = 0$ and the value of T_{c} was obtained by the subtraction of T_{s} from T, where the latter was determined directly from the $\lambda = 1$ calculation.

The H_2 molecule provides a simple prototypical system with which the variation between dynamic and static correlation may be explored. At equilibrium geometry, the electron densities of the two hydrogen atoms overlap substantially, thus binding the molecule and leading to both kinetic and potential contributions to the correlation energy. As the interatomic bond is extended, the system approaches that of two isolated hydrogen atoms, with no kinetic correlation energy; see Table I, where the value of the Gidopoulos–Davidson

TABLE I. Optimized functional values and energy components calculated in the aug-cc-pVTZ basis using the variation principles of Eqs. (14) and (15). All quantities are in atomic units.

	F_0	D_0	E_{nn}	T_{s}	E_{ne}	E_{J}	E_{x}	E_{c}	T	W	E_1
He	2.8611	0.0355	0.0000	2.8611	−6.7455	2.0464	−1.0232	−0.0756	2.8967	0.9477	−2.9011
Be	14.5835	0.0661	0.0000	14.5835	−33.6945	7.2122	−2.6725	−0.1534	14.6496	4.3863	−14.6586
Ne	128.5050	0.2720	0.0000	128.5050	−310.9007	65.9350	−12.0691	−0.6071	128.7765	53.2589	−128.8654
H_2 ($R = 0.7$)	1.7263	0.0324	1.4286	1.7263	−4.8614	1.6508	−0.8254	−0.0700	1.7588	0.7554	−0.9187
H_2 ($R = 1.4$)	1.1390	0.0328	0.7143	1.1390	−3.6469	1.3215	−0.6607	−0.0729	1.1718	0.5879	−1.1729
H_2 ($R = 3.0$)	0.8279	0.0418	0.3333	0.8279	−2.6181	0.9539	−0.4769	−0.1184	0.8697	0.3586	−1.0564
H_2 ($R = 5.0$)	0.9520	0.0224	0.2000	0.9520	−2.3809	0.8193	−0.4097	−0.2063	0.9744	0.2033	−1.0033
H_2 ($R = 7.0$)	0.9919	0.0052	0.1429	0.9918	−2.2826	0.7669	−0.3835	−0.2406	0.9971	0.1429	−0.9998
H_2 ($R = 10.0$)	0.9981	0.0005	0.1000	0.9982	−2.1983	0.7245	−0.3623	−0.2623	0.9986	0.1000	−0.9997

functional D_0 decreases as the interatomic bond length R increases, becoming just 0.0005 a.u. at $R = 10.0$ a.u.

C. General interaction strengths

In Fig. 1, results of optimizations pertaining to the generalized Lieb and Gidopoulos–Davidson functionals, according to Eqs. (9) and (31), respectively, are presented for interaction strength λ in the range 0–1. In the upper panel, the Lieb functional $F_\lambda(\rho_\Psi)$ is shown as a function of λ for the H_2 molecule with bond length $R = 0.7$, 1.4, 3.0, 5.0, 7.0, and 10.0 a.u. The variation of $F_\lambda(\rho_\Psi)$ in λ is broadly linear, indicating that $T_{c,\lambda} = T_1 - T_\lambda$ is relatively small and reflecting the dominance of the Coulomb and exchange energies in the two-electron energy W, both of which are linear in λ. The slope of $F_\lambda(\rho_\Psi)$ in λ becomes progressively smaller as the bond length is increased. This behaviour reflects the fact that the H_2 molecule dissociates into two one-electron fragments with $\lambda E_J + \lambda E_x + E_{c,\lambda} \rightarrow 0$ as $R \rightarrow \infty$ (static correlation energy cancelling the Coulomb and exchange energies).

In the lower panel of Fig. 1, the Gidopoulos–Davidson functional $D_\lambda = T_1 - T_\lambda + \lambda(W_1 - W_\lambda)$ is also plotted as a function of interaction strength. This functional adopts the value of T_c at $\lambda = 0$ and decreases with increasing λ to become 0 at $\lambda = 1$. In contrast to the Lieb functional, this small correlation contribution to the energy reveals the higher-order dependence of the correlation energy on λ at increasingly extended bond lengths. As the bond length R increases and
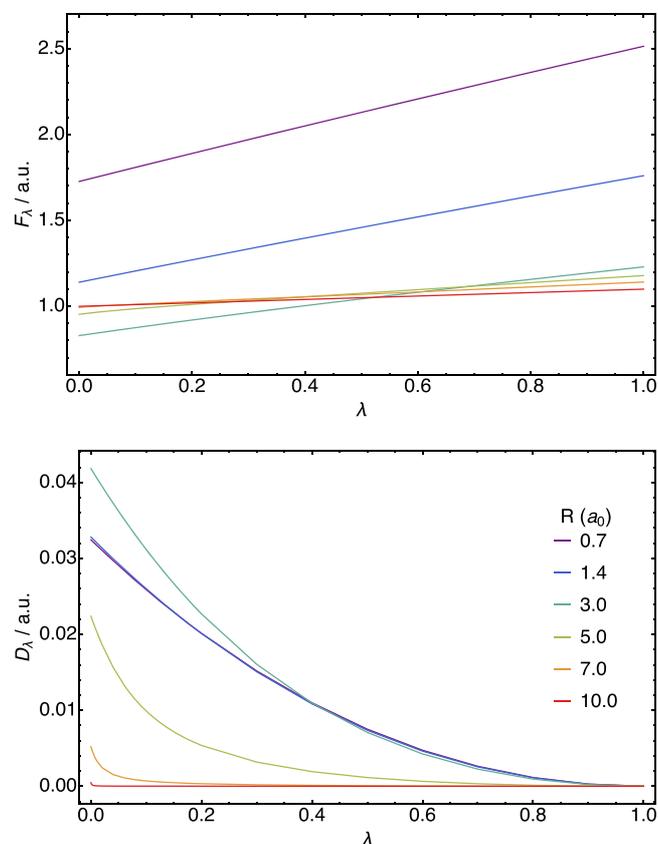
the system approaches one of independent atoms, the value of the Gidopoulos–Davidson functional is smaller at $\lambda = 0$, reflecting a decrease in T_c. However, it also exhibits more pronounced curvature, indicating higher-order dependence on λ as static correlation becomes more significant.

D. Constructing the adiabatic connection

As described in Subsection IV, the AC comprises a link between the non-interacting Kohn–Sham auxiliary system and the physically interacting system through variation in interaction strength, modulated by coupling-constant λ, with the density equal to the physical density of $\lambda = 1$ for all λ. The AC integrand is expressed in Eq. (39), from which an exact definition of the correlation energy may be constructed according to Eq. (40). Given that the exchange energy scales linearly with λ (for the linear-attenuation AC path), the exchange contribution to Eq. (39) is simply a constant and may be subtracted to give the correlation component of the AC integrand,

$$\mathcal{W}_{c,\lambda}(\rho) = \mathcal{W}_\lambda(\rho) - \mathcal{W}_0(\rho). \tag{42}$$

The Gidopoulos–Davidson variation principle of Eq. (31) and the Lieb variation principle of Eq. (9) can both be exploited to calculate this integrand, using the same input ρ_Ψ or Ψ but with a range of different values of λ, to construct the AC using Eq. (42).

The equivalence of the AC curves constructed from the Lieb and Gidopoulos–Davidson functionals is confirmed numerically for the H_2 molecule at the same geometries considered in Table I, with the AC integrands $\mathcal{W}_{c,\lambda}$ plotted as a function of λ in Fig. 2. Here, values of $\mathcal{W}_{c,\lambda}$ computed with the Lieb functional Eq. (9) are represented by solid lines, whilst values obtained from the Gidopoulos–Davidson functional Eq. (31) are denoted by the point markers. It is evident from Fig. 2 that the AC curves of these two methods agree with the convergence of the optimization procedures.

The correlation energy can be computed from these curves using Eq. (40) and the numerical values of E_c are presented in Table I. The ratio $|E_c|/T_c$ has been used to assess the relative importance of static correlation.[31] $|E_c|$ corresponds to the area above each curve in Fig. 2, whilst T_c corresponds to the area between each curve and a horizontal line defined by its

FIG. 1. F_λ of Eq. (9), upper panel, and D_λ of Eq. (31), lower panel (a.u.) as functions of the interaction strength λ for the H_2 molecule at internuclear separations $R = 0.7$, 1.4, 3.0, 5.0, 7.0, and 10.0 a.u.
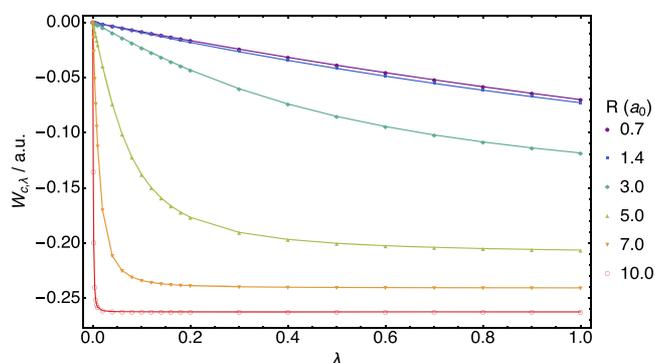

FIG. 2. The correlation adiabatic connection integrand values (a.u.) of Eq. (42), calculated using the optimization of Eq. (9), lines, and Eq. (31), point markers, for the H_2 molecule at internuclear separations $R = 0.7$, 1.4, 3.0, 5.0, 7.0, and 10.0 a.u.

value of $W_1(\Psi)$. As R increases, this ratio grows and the curves approach an L shape characteristic of systems dominated by strong correlation, indicating that the value of T_c is approaching zero, consistent with the effects of hydrogen molecule dissociation discussed in Subsection V C.

VI. CONCLUSIONS

The variation principle proposed in different contexts by Gidopoulos[1] and Davidson[2] has been examined and shown to be closely linked to the Lieb variation principle.[5] For the non-interacting system, the two functionals approach the Kohn–Sham system from different directions. The Lieb functional minimizes the non-interacting kinetic energy T_s subject to the constraint that the density is equal to that of the physical system, whereas the Gidopoulos–Davidson functional maximizes the kinetic correlation energy T_c under the same density constraint. In both cases, an unconstrained optimization can be performed with respect to the potential expansion coefficients in Eq. (41), making the implementation straightforward as described in Refs. 7 and 21. The external potential plays the role of a Lagrange multiplier, which ensures that the density constraint is satisfied at the stationary point for each functional.

An extension of the Gidopoulos–Davidson functional to ensembles was also presented, for which the associated functional can be shown to be concave with respect to $\hat{\gamma}$. This contrasts the pure-state functional which is not concave with respect to Ψ. A further extension to treat general electronic interaction strengths λ was also presented, as has previously been done with the Lieb functional.[5,7,20–22] Utilizing this extension, it was shown that either functional may be used to calculate the adiabatic connection between the Kohn–Sham system of non-interacting electrons and the physically interacting system, highlighting the fact that the two functionals are essentially equivalent, being related simply by a constant $T(\Psi)$ and a change of sign. As such, they are amenable to implementation in a common computational framework.

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