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Stretched Hydrogen Molecule from a Constrained-Search Density-Functional Perspective

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Constrained-search density functional theory gives valuable insights into the fundamentals of density functional theory. It provides exact results and bounds on the ground- and excited-state density functionals. An important advantage of the theory is that it gives guidance in the construction of functionals. Here we engage constrained search theory to explore issues associated with the functional behavior of "stretched bonds" in molecular hydrogen. A constrained search is performed with familiar valence bond wavefunctions ordinarily used to describe molecular hydrogen. The effective, one-electron hamiltonian is computed and compared to the corresponding uncorrelated, Hartree-Fock effective hamiltonian. Analysis of the functional suggests the need to construct different functionals for the same density and to allow a competition among these functions. As a result the correlation energy functional is composed *explicitly* of energy gaps from the different functionals.

I. INTRODUCTION

Stretched chemical bonds arise in almost any dynamically evolving system that requires making or breaking bonds. Being of such fundamental density functional theory (DFT) methods [1–10] of many kinds have been applied to these situations with decidedly limited success [11, 12]. There are no reasons *in principle* that DFT should fail in most of these situations, and so the limitations are viewed as an artifact of the actual approximations that have been made to date [13–15]. Developing systematic improvements to these functionals has proven particularly difficult.

To overcome these problems, several prominent strategies have emerged. One constrains the energy functional to satisfy a set of limiting cases and conditions [12, 16]. A second takes advantage of the general observation that the Hartree-Fock and local density approximations under and over correlate electrons. The resulting functionals fall into the hybrid DFT category [5, 10, 17]. A third strategy splits the electron-electron repulsion operator into short and long-range components that are modeled differently [17, 18]. Each of these strategies and their combinations benefits from exact or nearly exact limits, bounds, and special cases. In the interest of gaining further strategic insights and finding/constructing/generating an important limiting case, we appeal to the constrained search formulation of DFT [3, 19] to investigate the stretched H_2 molecule in its ground state.

For bound states, one can construct a variational energy E for any trial wavefunction ψ:

$$E[\psi] = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} , \tag{1}$$

where $\hat{H}$ is the hamiltonian operator for some system of interest. Setting the functional derivative of $E[\psi]$ with respect to ψ equal zero recovers the time-independent Schrödinger equation. The solution with lowest energy ψ_0 is the ground state and its energy is $E_0 = E[\psi_0]$. Alternatively, one may guess trial wavefunctions. A search over all trial wavefunctions in the appropriate Hilbert space also yields the ground state energy. Thus, one may write $E_0 = \min_\psi E[\psi]$. In variational form, one often decomposes ψ into a linear combination of basis states. The number of basis states is arbitrary. Increasing the number of basis states and executing the minimization process produces an upper bound to E_0. As is well-known, undertaking the minimization process with wavefunctions is exceedingly difficult for most systems of interest. DFT methods have become prevalent for this reason.

The central quantity in DFT is the particle number-density $n(\mathbf{r})$, produced by averaging over the (spatial) coordinates of all but one particle of the square of ψ. In "Löwdin" normalization, for an N particle system,

$$n(\mathbf{r}) = N \frac{\int d\mathbf{r}_2 \ldots d\mathbf{r}_N |\psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2}{\langle \psi | \psi \rangle} . \tag{2}$$

n is a probability. Density functional theory seeks to express the fundamental problems of electronic structure theory (a restricted class of $\hat{H}$) in terms of n instead of ψ. The key issue in DFT is to define the energy $E[n]$ for an

arbitrary density n that can be derived from physically allowed wavefunctions as defined, for instance, by Lieb [19].

In defining $E[n]$, one most often proceeds by breaking down $\hat{H}$ into independent-particle kinetic energy; three potential energy components, external, classical, and independent-particle (or Hartree-Fock) exchange; and a dependent-particle correlation energy. Hohenberg and Kohn showed that $E[n]$ can be partitioned into a universal part $F[n]$ that is independent of the configuration of the nuclei in the system (for coulombic systems), and the external potential contribution $v_{\rm ext}[n]$ that depends linearly on n [1]. That is,

$$E[n] \equiv F[n] + v_{\rm ext}[n] \,. \tag{3}$$

where

$$v_{\rm ext}[n] \equiv \int d\mathbf{r}\, \hat{v}_{\rm ext}(\mathbf{r}) n(\mathbf{r}) \,. \tag{4}$$

In turn, one identifies independent-particle kinetic energy; two potential energy components, classical, and independent-particle (or Hartree-Fock) exchange; and a dependent-particle correlation energy. However, the dependence of the dependent-particle correlation energy on n is not known. Physical reasoning based on experience with certain model systems, most notably the homogeneous electron gas, is used to estimate the exchange and correlation energies. Recently, different approximations for exchange energies have been mixed in various hybrid schemes [17, 18].

In constrained-search density functional theory (CS-DFT) [3], to define $E[n]$, one collects together all of the wavefunctions that reduce to a chosen fixed trial $n(\mathbf{r})$. We need to define $F[\psi] = \langle \psi | \hat{F} | \psi \rangle / \langle \psi | \psi \rangle$, where $\hat{F} = \hat{T} + \hat{V}_{ee}$ and $\hat{T}$ and $\hat{V}_{ee}$ are the kinetic energy and electron-electron repulsion operators, respectively. Now the energy $E[n]$ for that $n(\mathbf{r})$ can be assigned to the value that minimizes the energy over that collection of wavefunctions,

$$E[n] = \min_{\psi \to n} E[\psi] = \min_{\psi \to n} F[\psi] + v_{\rm ext}[n] \,, \tag{5}$$

where $\psi \to n$ means that ψ reduces to n [3]. The desired energy functional F has not yet been constructed in a practical way from this expression. Nevertheless, it is possible to examine DFT from the constrained-search for model systems, as well as to to explore other properties of the functional [20–25]. Here we investigate a "stretched" H_2 molecule, one prototype for the problem of stretched bonds [26–30].

II. CONSTRAINED-SEARCH FUNCTIONAL

As an illustration of constrained search theory, we allow only two basis states for the trial wavefunction, $\psi = \psi_1 + \lambda \psi_2$. Recognize that others have constructed functionals based on even more basis states [26, 31]. Then the electron density associated with ψ becomes

$$\tilde{n}(\mathbf{r};\lambda) = \frac{n_{11}(\mathbf{r}) + 2\lambda n_{12}(\mathbf{r}) + \lambda^2 n_{22}(\mathbf{r})}{1+\lambda^2} \,, \tag{6}$$

where state-to-state overlap (S_{12}) has been neglected. The state densities n_{11}, n_{12}, and n_{22} are defined from the relationship $n_{ij}(\mathbf{r}) = \langle \psi_j | \hat{n}(\mathbf{r}) | \psi_i \rangle$, where $\hat{n}(\mathbf{r})$ is the particle number operator at position $\mathbf{r}$.

For this study these basis states have two very special properties. One is that they both reduce to the same density, $n_{11} = n_{22} = n$. The other is that the transition density n_{12} is essentially zero. The first assumption is easy to illustrate from the H_2 molecule with basis states $\psi_1 = (\phi_L(\mathbf{1})\phi_R(\mathbf{2}) + \phi_L(\mathbf{2})\phi_R(\mathbf{1}))/\sqrt{2}$ and $\psi_2 = (\phi_L(\mathbf{1})\phi_L(\mathbf{2}) + \phi_R(\mathbf{1})\phi_R(\mathbf{2}))/\sqrt{2}$, where ϕ_L and ϕ_R are the same orbital ϕ centered on the left (L) and right (R) atoms, respectively. The bold numbers refer to 3D spatial coordinates. Spin variables scale out of this illustration. These are the famous Heitler-London covalent state and its ionic state companion that date back to the beginnings of valence-bond (VB) and molecular-orbital (MO) theories [32–34]. These basis states have been called upon to illustrate Hubbard models and other solid-state concepts related to charge fluctuations and strongly correlated electrons, as well as in the construction of density functionals [26, 27, 29]. ψ_1 dominates for any bond-length of H_2, but ψ_2 does provide about 25 % of the correlation energy, near the equilibrium bond distance, if the basis states are composed of just s-orbitals. We impose no such restriction here on the orbital. These basis states both demonstrably reduce to the same particle density. The second is an approximation that is commonly invoked, but of dubious quality near equilibrium. However it does correspond to the "stretched bond" cases that have figured prominently in the development of contemporary density functionals.

In the stretched bond limit then, $\tilde{n}(\mathbf{r};\lambda) = n(\mathbf{r})$, for *any* λ, to within as small of a tolerance as one chooses. From the continuity of density functionals [19, 35, 36], especially those that satisfying ensemble representability, one has a reasonable expectation that the errors to the functionals introduced by the approximation to the density are small in some sense. Returning to our CS-DFT energy, we now have, for the two-state model,

$$\begin{aligned} F[n] &= \min_{\psi \to n} \frac{F_{11} + 2\lambda F_{12} + \lambda^2 F_{22}}{1+\lambda^2} \\ &\equiv \min_{\lambda} F(\lambda) \,, \end{aligned} \tag{7}$$

where $F_{ij} = \langle \psi_j | \hat{F} | \psi_i \rangle$ are the F-matrix elements. An example of $F(\lambda)$ is shown in Fig. 1. The minimization only involves λ since, by assumption, any linear combination of ψ_1 and ψ_2 gives the same density. Consequently, $F[n]$ might be gotten by finding the zeroes of its derivative

with respect to λ. The well-documented solutions are

$$\lambda_{\pm} = \frac{\Delta F}{2F_{12}} \pm \sqrt{\left[\frac{\Delta F}{2F_{12}}\right]^2 + 1}\,, \tag{8}$$

where $\Delta F = F_{22} - F_{11}$. Because $v_{\rm ext}[n]$ is constant for a chosen fixed n, it can be added and subtracted from the contributions in ΔF, permitting us to realize that $\Delta F = \Delta H = H_{22} - H_{11}$, where $H_{ii} = \langle \psi_i | \hat{H} | \psi_i \rangle$, has the physical meaning of the covalent-ionic energy gap.

Substituting $\lambda_{\pm}$ into $F(\lambda)$, the CS-DFT problem reduces to

$$F[n] = \min\{F(\lambda_+), F(\lambda_-)\}\,. \tag{9}$$

The energies $F(\lambda_+) = F_-$ and $F(\lambda_-) = F_+$ are just the extreme points in Fig. 1 and are identical to the eigenvalues for the two-state linear variational problem. Thus,

$$F_{\pm}[\phi] = \bar{F}[\phi] \pm \sqrt{(\Delta F[\phi]/2)^2 + F_{12}^2[\phi]}\,, \tag{10}$$

where $\bar{F} = (F_{22}+F_{11})/2$. The energy functional contains three different energies generated from the same orbital, that in turn determine the ground-state density.

This functional form is difficult to achieve from conventional forms of $F[n]$ particularly because of the quantum interference term F_{12}. Its analysis begins by interchanging between VB and MO wavefunctions [34]. Denote the *gerade* (g) or bonding and *ungerade* (u) or anti-bonding MOs as $\phi_{\rm g}(\cdot) = (\phi_L(\cdot) + \phi_R(\cdot))/\sqrt{2}$ and $\phi_{\rm u}(\cdot) = (\phi_L(\cdot) - \phi_R(\mathbf{1}\cdot))/\sqrt{2}$, respectively, where $\cdot$ denotes either one of the spatial coordinates. Now the MO wavefunctions are simply $\psi_{\rm g}(\mathbf{1},\mathbf{2}) = \phi_{\rm g}(\mathbf{1})\phi_{\rm g}(\mathbf{2})$ and $\psi_{\rm u}(\mathbf{1},\mathbf{2}) = \phi_{\rm u}(\mathbf{1})\phi_{\rm u}(\mathbf{2})$. The VB wavefunctions may be expressed as the linear combinations of MO wavefunctions, $\psi_1 = (\psi_{\rm g} - \psi_{\rm u})/\sqrt{2}$ and $\psi_2 = (\psi_{\rm g} + \psi_{\rm u})/\sqrt{2}$, respectively. Expanding F_{12} in the MO wavefunctions, one then obtains

$$2F_{12} = F_{\rm gg} - F_{\rm uu} = \Delta F_{\rm gu}\,. \tag{11}$$

Again, because $v_{\rm ext}[n]$ is constant for a chosen fixed n, it can be added and subtracted from the contributions in $\Delta F_{\rm gu}$, permitting the identification $\Delta F_{\rm gu} = \Delta H_{\rm gu} = H_{\rm gg} - H_{\rm uu}$, where $H_{ii} = \langle \psi_i | \hat{H} | \psi_i \rangle$ for $i =$ g or u. $\Delta H_{\rm gu}$ can also be identified as the *negative* of the "HOMO-LUMO" gap. With the appropriate substitution into Eq. (10), one obtains

$$F_{\pm}[\phi] = \bar{F}[\phi] \pm 1/2\sqrt{\Delta F^2[\phi] + \Delta F_{\rm gu}^2[\phi]}\,. \tag{12}$$

While $F_-[\phi]$ represents the universal $F[n]$,

$$F[n] = \bar{F}[\phi] - 1/2\sqrt{\Delta F^2[\phi] + \Delta F_{\rm gu}^2[\phi]}\,. \tag{13}$$

as formulated in this miniscule corner of Hilbert space, determined here within the confines of an orbital-dependent *ansatz*, it does depend on three "subsidiary" functionals specialized to the properties of the basis states used to construct it. These subsidiary functionals compete in a manner comparable to how electron-electron repulsion and electron hopping energies compete in the Hubbard models [37, 38, 40]. Furthermore, one observes that the second term in Eq. (13) precludes one from cleanly separating kinetic, exchange and correlation components. This feature comes about from application of the constraint in Eq. (7).

Finally, because of the restricted number of states in the model, the present functional is an upper bound to the true functional. By continuity of the functional, the error in this functional from the true functional becomes smaller as dissociation is approached asymptotically. When approaching dissociation, and assuming that we are close to an optimized ϕ, the HOMO-LUMO gap closes. Thus

$$F_{\pm}[\phi] \;\rightarrow\; \bar{F}[\phi] \pm 1/2|\Delta F[\phi]|\,. \tag{14}$$

Interference from the ionic state ceases as a result of the closure process, if the ionic contributions to $\bar{F}[\phi]$ and $\Delta F[\phi]$ cancel precisely. If gradient approximations are viewed from this perspective [8, 10–12, 17], it is not clear how well this sort of mechanism is accounted for. In contrast, the gap between the ionic and covalent states ΔH approaches the chemical hardness, $I - A$ [20, 41], the difference between the ionization potential I and electron affinity A for the hydrogen atom. Therefore it never closes.

The "LDA+U" model is perhaps the closest analog [39] to Eq. (13). In the present context, ΔF plays the role of the Hubbard U. Indeed the present study could be viewed as being related to the lattice DFT models of López-Sandoval and Pastor [40], and specifically to the side note in their Reference 22. There a lattice of fermions is treated within a Hubbard model framework, but the optimum orbitals, for a given gap parameter U and hopping integral t and for a given one-particle density matrix, are determined by a constrained search process [3]. Because ΔF and $\Delta F_{\rm gu}$ depend on n, they are determined self-consistently with other energies in the model, in contrast to the constant values of U typical of most Hubbard models. Mechanistically, the different gap energies are engaged in an essential competition to determine the optimum density and energy.

One may also calculate the Euler-Lagrange equation for the ground state of this system, which is F_- in this specialized case, with respect to variations in ϕ, the orbital that determines the electron density. Including a constraint through Lagrange multiplier ϵ_- that ϕ is normalized, the effective one-electron hamiltonian is

$$\epsilon_- \phi = \hat{v}_{\rm ext}\phi + \frac{\delta F[n]}{\delta \phi}\,. \tag{15}$$

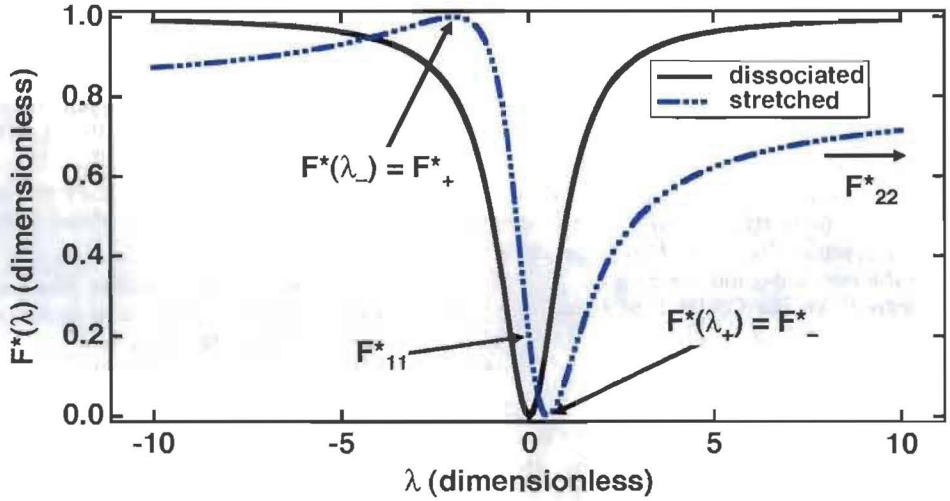

FIG. 1: The shifted and scaled energy $F^*(\lambda) = (F(\lambda) - F_-)/(F_+ - F_-)$ as a function of the ionicity or state mixing parameter λ. F_+ and F_- are the eigenvalues from Eq. (9). The starred values of F_{11} and F_{22} are defined in an analogous way: F^*_{11} corresponds to $F^*(0)$, while F^*_{22} corresponds to $F^*(\infty)$. The curve labeled as "stretched" corresponds to a value of $\lambda_+ = 0.5$. It is for illustration purposes only and does not correspond to literal values from the model wavefunction and molecule. The assignment of roots is based on the assumptions that $\Delta F > 0$ and $F_{12} < 0$.

where

$$\frac{\delta F[n]}{\delta\phi} \equiv \frac{\delta\bar{F}}{\delta\phi} + \frac{\frac{\delta\Delta F}{\delta\phi} - \frac{\Delta F_{\rm gu}}{\Delta F}\frac{\delta\Delta F_{\rm gu}}{\delta\phi}}{2\sqrt{1+\left(\frac{\Delta F_{\rm gu}}{\Delta F}\right)^2}}$$
$$= \frac{\delta F_{11}}{\delta\phi} + \frac{\left(\sqrt{1+\left(\frac{\Delta F_{\rm gu}}{\Delta F}\right)^2} - 1\right)\frac{\delta\Delta F}{\delta\phi} - \frac{\Delta F_{\rm gu}}{\Delta F}\frac{\delta\Delta F_{\rm gu}}{\delta\phi}}{2\sqrt{1+\left(\frac{\Delta F_{\rm gu}}{\Delta F}\right)^2}}. \quad (16)$$

The second equality comes from the identity $\bar{F} = F_{11} + \Delta F/2$, followed by additional algebraic manipulations. The Euler-Lagrange equation in terms of the universal functional and its components is nonlocal through the appearance of functionals for the gaps, in addition to the more familiar nonlocal exchange and correlation contributions within each subsidiary functional. Nevertheless, size consistency is achieved via cancellation and the structure of the F_{11} functional to be discussed later.

The functional derivatives $\delta\bar{F}/\delta\phi$ and $\delta\Delta F/\delta\phi$ are relatively familiar, although the gap energy is somewhat rare in density functional theory at the present time. Since ΔH is a nonzero gap in this sytem, Eq. (15) may be expanded in powers of $\Delta F_{\rm gu}/\Delta F$. Asymptotically then

$$\frac{\delta F}{\delta\phi} \to \frac{\delta F_{11}}{\delta\phi} + \frac{\Delta F_{\rm gu}}{2\Delta F}\frac{\delta\left(\Delta F - \Delta F_{\rm gu}\right)}{\delta\phi}, \quad (17)$$

which is correct and analogous to Eq. (14). The approach of the Euler-Lagrange equation to this functional form at dissociation is controlled by the rate of closure of the HOMO-LUMO gap. If instead one relies on the first part of Eq. (15), a careful cancellation of contributions between $\bar{F}$ and ΔF is required. Any residual contamination from incomplete cancellation will lead to a residual error in the ground-state energy.

III. EXCHANGE-CORRELATION FUNCTIONAL

To further analyze the functional, we focus on the exchange-correlation energy and functional. For this purpose, note that, expressed in terms of the MO wavefunctions, $\bar{F} = (F_{\rm gg} + F_{\rm uu})/2$. From this form, it is clear that $F_{\rm gg}$ can be identified as the sum of Hartree-Fock kinetic $T_{\rm HF}[n] = \langle\psi_{\rm gg}| - 1/2\,\Delta|\psi_{\rm gg}\rangle$ and electron-electron repulsion energy functionals. The Hartree-Fock electron-electron repulsion energy consists of the classical coulomb energy $J[n] = 1/2\int d\mathbf{r}_1 d\mathbf{r}_2 n(\mathbf{r}_1)n(\mathbf{r}_2)/|\mathbf{r}_1 - \mathbf{r}_2|$ and exact exchange functional $K[n] = -1/2\int d\mathbf{r}_1 d\mathbf{r}_2 |\gamma_1^{(\rm g)}(\mathbf{r}_1,\mathbf{r}_2)|^2/|\mathbf{r}_1 - \mathbf{r}_2|$, where $\gamma_1^{(\rm g)}(\mathbf{r}_1,\mathbf{r}_2) = N\int d\mathbf{r}'_2\ldots d\mathbf{r}'_N \psi_{\rm g}(\mathbf{r}_2,\mathbf{r}'_2,\ldots,\mathbf{r}'_N)\psi_{\rm g}(\mathbf{r}_1,\mathbf{r}'_2,\ldots,\mathbf{r}'_N)$. Note too that $\bar{F} = F_{\rm gg} - \Delta F_{\rm gu}/2$.

With these identifications in hand, Eq. (13) may be

reformulated as

$$\begin{aligned} F[n] &= (F_{gg}[n] + F_{uu}[n])/2 - 1/2\sqrt{\Delta F^2[n] + \Delta F^2_{gu}[n]} \\ &= T_{HF}[n] + J[n] + K[n] \\ &- 1/2\left(\Delta F_{gu}[n] + \sqrt{\Delta F^2[n] + \Delta F^2_{gu}[n]}\right). \end{aligned} \tag{18}$$

Since the first three terms represent Hartree-Fock contributions, the correlation energy is

$$E_{corr}[n] = -1/2\left(\Delta F_{gu}[n] + \sqrt{\Delta F^2[n] + \Delta F^2_{gu}[n]}\right). \tag{19}$$

It contains differences in kinetic, exchange, and correlation energies among the states pertinent to this system. Specifically it is a functional of two different energy gaps related to the *same* density.

At dissociation, $\delta F_{11}/\delta\phi$ is the surviving functional. To further analyze the Euler-Lagrange equation, our desire is to observe how the ionic terms of the MO wavefunctions are cancelled. The 2-matrix for the covalent state, in terms of the MO functions, may be expressed as

$$\begin{aligned} \gamma_2^{(1)}(\mathbf{1},\mathbf{2}) &= D_2^{(g)}(\mathbf{1},\mathbf{2}) + 1/2\Big(D_2^{(u)}(\mathbf{1},\mathbf{2}) - D_2^{(g)}(\mathbf{1},\mathbf{2}) \\ &- 1/2\, D_1^{(g)}(\mathbf{1},\mathbf{2}) D_1^{(u)}(\mathbf{2},\mathbf{1})\Big). \end{aligned} \tag{20}$$

Superscript "(1)" denotes the covalent state (ψ_1) terms. Reduced matrices denoted by a "D" indicate that they originate from single-determinant wavefunctions. The "g" states are what would appear as the ground-state with spin-restricted states in a Hartree-Fock calculation. The remainder comprises the correlation 2-matrix. One can observe here how carefully the ionic terms in the "g" and "u" states must cancel each other in order to prevent dissociation to an unphysical state. This situation is the counterpart to the one that arises in the cancellation of self-interaction contributions between classical and exchange parts of the Hartree-Fock 2-matrix.

The electron-electron repulsion energy V_{ee} for the covalent state and its various contributions may be expressed from the 2-matrix and its components. For any 2-matrix γ_2, in the Löwdin normalization,

$$V_{ee} = \langle \gamma_2(\mathbf{r}_1,\mathbf{r}_2)/|\mathbf{r}_1 - \mathbf{r}_2|\rangle. \tag{21}$$

Each contribution from Eq. (20) has this form. These will be labeled as $V_{ee}^{(g)}$, $V_{ee}^{(u)}$, and $V_{ee}^{(gu)}$, respectively. Recall too that $V_{ee}^{(g)} = J[n] + K[n]$, since the canonical Hartree-Fock term originates from $D_2^{(g)}$, as it must. The remaining terms define $V_c[n]$, the electron-electron repulsion correlation energy. Substituting into Eq. (21) leads to

$$\begin{aligned} V_{ee}[n] &= J[n] + K[n] \\ &+ 1/2\left(V_{ee}^{(u)}[n] - V_{ee}^{(g)}[n] - 1/2\, V_{ee}^{(gu)}[n]\right). \end{aligned} \tag{22}$$

Again the last term $1/2\,(V_{ee}^{(u)}[n] - V_{ee}^{(g)}[n] - 1/2\, V_{ee}^{(gu)}[n])$ represent the correlation energy from the electron-electron repulsion at dissociation. These contributions go to zero because of cancellations among the various components. By contrast, in terms of the VB orbitals, V_{ee} goes to zero at dissociation because the VB orbitals do not overlap.

Similarly, for the kinetic energy,

$$\begin{aligned} \gamma_1^{(1)}(\mathbf{1},\mathbf{1}') &= D_1^{(g)}(\mathbf{1},\mathbf{1}') \\ &+ 1/2\,(D_1^{(u)}(\mathbf{1},\mathbf{1}') - D_1^{(g)}(\mathbf{1},\mathbf{1}')). \end{aligned} \tag{23}$$

The off-diagonal component from $\gamma_2^{(1)}$ rigorously vanishes. The uncorrelated contributions come from the first term. Thus, the correlation kinetic energy T_c come from the difference of $D_1^{(u)}$ and $D_1^{(g)}$. Again cancellation is required in order to achieve an accurate result.

IV. CONCLUSIONS

In summary, the present study on the stretched H_2 molecule within the framework of constrained search DFT provides insights into the coupling of contributions from different configurational wavefunctions. The coupling is introduced through the constraint from the configurational wavefunctions having the same density. These states were designed from valence bond theory to achieve size consistency and correct dissociative limits. Quantum interference effects within this coupling, even near dissociation, plays a central role. Here, it is expressed as a HOMO-LUMO gap, and constitutes a subsidiary functional. Another gap representing ionization and electron attachment processes appears as a second subsidiary functional. Interference from the ionic components of the trial wavefunction are eliminated by closure of the HOMO-LUMO gap. The correlation energy is a explicit functional of these two gaps. In total, these results constitute an asymptotically correct form of the (orbital-dependent) density functional of the stretched H_2 molecule.

The asymptotically-correct form of the universal density functional is shown to depend on these three subsidiary functionals. The formulation of the model in terms of 1-particle density matrices depends not only on exact cancellation of self-interaction contributions, but also, ionic ones. A second type of cancellation involves correct closure of the HOMO-LUMO gap. This analysis suggests that an advanced functional might need to orchestrate a variational competition among three or more *different* functionals for the *same* electron density. The general strategic sense of the model points toward finding at least two states within the subset of wavefunctions needed for a constrained search whose arbitrary combination are nearly the same in density, and allowing those states to compete to produce a ground state.

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