

Spectroscopic constants of diatomic molecules computed correcting Hartree-Fock or general-valence-bond potential-energy curves with correlation-energy functionals

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The Kohn-Sham energy with exact exchange [using the exact Hartree-Fock (HF) exchange but an approximate correlation-energy functional] may be computed very accurately by adding the correlation obtained from the HF density to the total HF energy. Three density functionals are used: local spin density (LSD), LSD with self-interaction correction, and LSD with generalized gradient correction. This scheme has been extended (Lie-Clementi, Colle-Salvetti, and Moscardo-San-Fabian) to be used with general-valence-bond (GVB) energies and wave functions, so that the extra correlation included in the GVB energy is not counted again. The effect of all these approximate correlations on HF or GVB spectroscopic constants (R_e , ω_e , and D_e) is studied. Approximate relations showing how correlation affects them are derived, and may be summarized as follows: (1) the effect on R_e and ω_e depends only on the correlation derivative at R_e , and (2) the effect on D_e depends mainly on the correlation difference between quasidissociated and equilibrium geometries. A consequence is that *all* correlation corrections tested here give larger ω_e and D_e and shorter R_e than the uncorrected HF or GVB values. This trend is correct for D_e for both HF and GVB. For R_e and ω_e , it is correct in most cases for GVB, but it often fails for the HF cases. A comparison is made with Kohn-Sham calculations with both exchange and correlation approximated. As a final conclusion, it is found that, within the present scheme, a qualitatively correct HF or GVB potential-energy curve, together with a correlation-energy approximation with correct dissociation behavior, is crucial for obtaining good estimates of spectroscopic constants.

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I. INTRODUCTION

The main subject of atomic and molecular physics is, no doubt, the computation of potential-energy surfaces. In these last years, some methods from the density-functional theory (DFT) have become increasingly popular, combining together a rigorous formalism [1,2] with efficient schemes for computations [3,4] (some complete reviews have appeared recently [5–11]). In this context, diatomic molecules are frequently used as a benchmark for newly developed functionals, to test their behavior for predicting potential-energy curves or spectroscopic constants, before applying them to larger systems. The present work is one such benchmark within the Kohn-Sham scheme with exact exchange, in which we will study the effect of some correlation-energy functionals on Hartree-Fock (HF) or general-valence-bond (GVB) spectroscopic constants for first-row hydrides and dimers.

In Sec. II we will review briefly the Kohn-Sham equations with exact exchange, and will present some currently used approximations for the correlation-energy functional. We will also explain how some special functionals, depending on the natural orbitals or on the second-order reduced density matrix, may be used together with GVB calculations, so that double counting of the correlation energy is avoided. In Sec. III, the technical details of our calculations will be explained (basis sets used, numerical integration techniques, fitting procedure for computing the spectroscopic constants). In Sec. IV we will explain the effect of an arbitrary correlation correction on HF or GVB equilibrium distances, vibrational fre-

quencies, and dissociation energies. In Sec. V we will study the effect of correlation on our specific molecules, and will try to find the rationale behind the facts observed. A comparison will be made with Kohn-Sham calculations (from the literature) with both exchange and correlation approximated. Finally, some concluding remarks will be given in Sec. VI.

II. METHOD

The Kohn-Sham [2] version of DFT is the most widely used in practical calculations. Within this version, the density of a system with N electron is expressed as the sum of the densities of a set of N orbitals:

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2. \quad (1)$$

The set of N orbitals is obtained solving the system of mono-electronic equations:

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \varphi(\mathbf{r}) + \mu_{xc}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \quad (2)$$

where $v(\mathbf{r})$ is the external potential, $\varphi(\mathbf{r})$ is the Coulomb potential

$$\varphi(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (3)$$

and $\mu_{xc}(\mathbf{r})$ is the *exchange-correlation potential*. This potential is the functional derivative of the *exchange-correlation-energy functional* with respect to the density:

$$\mu_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho}. \quad (4)$$

The exchange-correlation-energy functional or $E_{xc}[\rho]$ was first defined in the paper of Kohn and Sham [2] and its explicit form remains unknown to date. The whole expression of $E_{xc}[\rho]$ is usually split into two parts: an *exchange-energy functional* $E_x[\rho]$ and a *correlation-energy functional* $E_c[\rho]$:

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho]. \quad (5)$$

$E_x[\rho]$ is defined as the exchange energy of a Hartree-Fock system with density $\rho(\mathbf{r})$ [2,12]. The remaining part $E_c[\rho]$ will be called here the *Hartree-Fock correlation energy*. At this point it is convenient to note that there are other definitions of the exchange functional [13–16].

Usually, both exchange and correlation functionals are approximated when solving the Kohn-Sham equations for a given system. However, in this work, we will approximate $E_c[\rho]$ only, while $E_x[\rho]$ will be calculated exactly using its definition. The exchange-correlation potential $\mu_{xc}(\mathbf{r})$ can also be split into two components:

$$\mu_{xc}(\mathbf{r}) = \frac{\delta E_x[\rho]}{\delta \rho} + \frac{\delta E_c[\rho]}{\delta \rho}, \quad (6)$$

but the functional derivative of $E_x[\rho]$ is just the exchange operator $\hat{\mathcal{H}}$ of Hartree-Fock theory (the proof is immediate as a consequence of the definition given to $E_x[\rho]$ [2,12]). This allows us to rewrite the Kohn-Sham equations (2) as

$$\left[-\frac{1}{2} \nabla^2 + v(\mathbf{r}) + \varphi(\mathbf{r}) + \hat{\mathcal{H}} + \frac{\delta E_c[\rho]}{\delta \rho} \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \quad (7)$$

and recalling the definition of the Fock operator $\hat{\mathcal{F}}$ we get

$$\left[\hat{\mathcal{F}} + \frac{\delta E_c[\rho]}{\delta \rho} \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad (8)$$

or, expressed in words, when the exact exchange functional is used, the Kohn-Sham equations take the form of Hartree-Fock equations, but with a perturbative term due to the correlation energy. These are the Kohn-Sham equations with *exact exchange* (also called the Hartree-Fock–Kohn-Sham equations [11]). They have been used by several authors [12,17–19] for calculations on atoms and small molecules.

To obtain the total energy from this form of the Kohn-Sham equations we will use a simple but very accurate approximation. This approach, due to Stoll, Pavlidou, and Preuss [20], supposes that the correlation term is small enough to have a very little effect on the Fock operator, so that the Kohn-Sham orbitals are nearly equal to the Hartree-Fock orbitals. As a consequence, if we designate $\rho_{KS}(\mathbf{r})$ and $\rho_{HF}(\mathbf{r})$ to be, respectively, the Kohn-Sham and Hartree-Fock densities, we have

$$\rho_{KS}(\mathbf{r}) \approx \rho_{HF}(\mathbf{r}), \quad (9)$$

so that the Kohn-Sham functionals for total energy and

correlation energy can be approximated by

$$E_{KS}[\rho_{KS}] \approx E_{KS}[\rho_{HF}] = E_{HF} + E_c[\rho_{HF}], \quad (10)$$

$$E_c[\rho_{KS}] \approx E_c[\rho_{HF}], \quad (11)$$

where E_{HF} is the total Hartree-Fock energy. It should be noted that the Kohn-Sham density and total energy would be equal to the exact ones only if the *unknown* exact correlation-energy functional were used. Approximation (9) has been tested for atoms and small molecules and it holds quite accurately [21,19,6] for currently used functionals. Since the total Kohn-Sham energy with exact exchange is found variationally, the error in using approximation (10) can be expected to be very small, because it is second order with respect to the error in the density [21,22]. This has been confirmed for several systems and functionals [21,19,6,22], with errors always within a few millihartrees (above). A similar error is found [6,23] for (11), and, furthermore, it has been seen that some currently used $E_c[\rho]$ are quite insensitive to changes in the density (as basis-set improvement [24,23], or the use of the exact or a more accurate density instead of the Hartree-Fock one [23,25,26]).

The computational simplicity of this procedure [Eq. (10)] is one of the reasons why we have chosen to treat exchange exactly and to approximate the correlation energy only. Another reason is that, treating exchange exactly, we can study the quality of several approximations currently used for $E_c[\rho]$ in their purest form, that is, without contamination from an approximate $E_x[\rho]$. Approximating both exchange and correlation together can give an erroneous measure of their respective quality, because in some current approximations (for instance, the local approximation) exchange is underestimated while correlation is overestimated, which results in a fortuitous cancellation of errors.

For the correlation-energy functional, we have selected some widely used expressions. Our first choice has been the local spin density (LSD) approximation [2,27], which supposes that the correlation energy of a system of N electrons with ground-state spin densities ρ_+ (up) and ρ_- (down) is equal to

$$E_c^{\text{LSD}}[\rho_+, \rho_-] = \int [\rho_+(\mathbf{r}) + \rho_-(\mathbf{r})] \varepsilon_c(\rho_+, \rho_-) d\mathbf{r}, \quad (12)$$

where the function $\varepsilon_c(\rho_+, \rho_-)$ is the correlation energy per electron of a uniform gas of spin densities ρ_+ and ρ_- . To date, the most exact expressions for $\varepsilon_c(\cdot)$ are those of Vosko, Wilk, and Nusair [28] and of Perdew and Zunger [29]. Both of them have been obtained by fitting a suitable function to very accurate quantum Monte Carlo data for the electron gas [30]. The results reported in this paper have been computed with the Perdew-Zunger formula. By construction, the LSD approximation is exact for a homogeneous electron gas, but, when applied to systems with fewer electrons, such as atoms and molecules, it suffers from one well-known defect: it severely overestimates the correlation energy by approximately a factor of 2 [31,32,17,29]. Specifically, LSD gives nonzero correlation energies for one-electron systems [33]. To correct these defects, two different types of approaches have been

developed: self-interaction corrections (SIC) and generalized gradient corrections (GGC).

The correlation energy is caused by the interaction of each electron of the system with all the other electrons, excluding of course interaction with itself or self-interaction. There is a SIC procedure, developed by Stoll, Pavlidou, and Preuss [20], based on the reasonable physical assumption that, although the correlation between electrons with the same spin is important in an electron gas, it should be rather small in finite systems such as atoms and molecules. The corrected functional is

$$E_c^{\text{SIC}}[\rho_+, \rho_-] = E_c^{\text{LSD}}[\rho_+, \rho_-] - E_c^{\text{LSD}}[\rho_+, 0] - E_c^{\text{LSD}}[0, \rho_-] . \quad (13)$$

Obviously, this SIC functional fails when applied to a homogeneous gas, but gives zero correlation energy in single-electron systems. For atoms and molecules, where the assumption that is made is reasonable, remarkably good results are obtained for the correlation energy [20,34,23]. It should be noted here that there is another SIC procedure, the *orbital related* SIC of Perdew and Zunger [29]. Both of the procedures have been tested with some atoms and their results are very similar, the scheme of Stoll, Pavlidou, and Preuss being slightly better [21,6,35].

Gradient expansion corrections to LSD are used to take into account the inhomogeneity of the electronic density in atoms and molecules. They have been in use since the early days of DFT [2,36], but the results provided by these corrections when applied to real systems of interest were disappointing or even disastrous. Langreth, Perdew, Mehl, and co-workers developed a *generalized gradient correction* to LSD for exchange and correlation [37,38,14,39,40]. This correction was improved later by Perdew [41], making the natural separation between exchange and correlation. As our choice for a GGC, we have selected Perdew's formula. Its author recommends that it be used together with the present Kohn-Sham scheme with exact exchange. The form of this functional is

$$E_c^{\text{GGC}}[\rho_+, \rho_-] = E_c^{\text{LSD}}[\rho_+, \rho_-] + \int \frac{e^{-\Phi} C(\rho) |\nabla \rho|^2}{d \rho^{4/3}} d\mathbf{r} , \quad (14)$$

where Φ , $C(\rho)$, and d are taken from Perdew's paper [41]. It should be used together with the Perdew-Zunger LSD [29]. The gradient term vanishes for a constant density, so that the functional recovers the LSD behavior and is still exact for a homogeneous gas. It has been tested for mono-electronic systems and gives a nearly zero correlation energy [41], so that it is accurately self-interaction-free for such systems. Furthermore, it gives good correlation energies for atoms and molecules [41,23]. Here we will point out that there is another gradient expansion functional, which has been developed by Becke [42], in a context other than the GGC, that yields very similar results [42,25]. However, all the results reported here have been computed using Perdew's functional.

Once we have selected some approximations for $E_c[\rho]$ there is the question of which Hartree-Fock scheme should be used, a *restricted* (RHF) or an *unrestricted* (UHF) method. For systems such as homogeneous electron gases, atoms, or many molecules at equilibrium distance the question is a rather academic one, because RHF energies and spin densities are very similar or equal to UHF ones. However, for molecules at large internuclear distances, the well known *size-consistence* problem appears: energies and total densities of a quasidissociated molecule—that is, with its atoms far apart a large distance—computed with a given method, are different from energies and total densities computed for the isolated atoms using the same method. This may result in substantial errors for some spectroscopic constant, like dissociation energies. As is well known, the UHF method is size-consistent, while the RHF method is not. For this reason, when it is possible, we have used UHF calculations for the molecules reported here. Furthermore, methods like the SIC and GGC selected here have been recommended by their authors [34,41] for use in an unrestricted context.

It should be noted that for a quasidissociated molecule, the UHF method gives the same energies, the same total densities, and the *same spin densities* as those of the isolated atoms. That means that, for the approximations selected here, the correlation energy of a quasidissociated molecule is equal to the correlation energy computed from the isolated atoms, or, in other words, that the *Kohn-Sham energy* with exact unrestricted exchange is *size consistent*. On the other hand, it also implies that this scheme yields the wrong spin symmetry.

Despite the previous discussion, there are cases when neither restricted nor unrestricted treatments are suitable; for instance, the potential-energy curve of the fluorine molecule, in which the RHF curve is not size-consistent, while UHF calculations give a dissociation curve without a minimum. Traditionally, quantum chemistry has solved such problems using more sophisticated wave functions than the single Hartree-Fock determinant description, as, for instance, a general-valence-bond [43] wave function. It would be highly desirable to have a similar solution within DFT for treating such cases as the fluorine molecule, where the Kohn-Sham equations with exact exchange (both restricted and unrestricted) give poor results, because a small correlation term is unable to correct the wrong Hartree-Fock behavior. This GVB-Kohn-Sham formalism should be started by splitting the exchange-correlation functional in a different manner than the way it was done in Eq. (5), now defining a GVB correlation-energy functional $E_c^{\text{GVB}}[\rho]$ as the difference between the exact and the GVB energy functionals:

$$E_c^{\text{GVB}}[\rho] = E[\rho] - E^{\text{GVB}}[\rho] . \quad (15)$$

Once the GVB correlation-energy functional has been defined, it should be approximated, and then a GVB-Kohn-Sham formalism with *exact GVB exchange* can be developed analogously, as has been done for the Kohn-Sham formalism with *exact HF exchange*. Now, there is the problem of finding reliable approximations for

$E_c^{\text{GVB}}[\rho]$. It is clear that the previous LSD, SIC, and GGC approximations for $E_c[\rho]$ cannot work very well for $E_c^{\text{GVB}}[\rho]$ because they have been developed within a Hartree-Fock correlation-energy definition, yielding an overestimation of $E_c^{\text{GVB}}[\rho]$ or *double counting* of the correlation energy: the extra correlation included in the GVB energy is counted again when computing $E_c[\rho]$. Furthermore, with these approximations, our description of molecular systems will no longer be size consistent, because the GVB method yields correct spin symmetry, and the spin densities of the quasidissociated molecule are different from those of the isolated atoms. Despite these drawbacks, we will test LSD, SIC, and GGC functionals with GVB wave functions and densities, in the hope of finding some improvements or new physical insights (a simple approach to avoid the double counting of these functionals has been recently proposed [44]).

Over the years, there have been a number of correlation-energy functionals developed according to the GVB correlation-energy definition (or analogous definitions for more complex wave functions); for instance, the works of Lie and Clementi [45,46], Savin [47,48], Colle and Salvetti [49,50], Gritsenko and co-workers [51,52], or Moscardo and San-Fabian [53]. Here, we will report results computed with the methods of Lie and Clementi, Colle and Salvetti, and Moscardo and San-Fabian, which we are going to review briefly.

Lie and Clementi take an earlier local-density functional from Gombas [54],

$$E_c^{\text{LC}}[\rho] = \int \left[a_1 \frac{\rho^{1/3}}{a_2 + \rho^{1/3}} + b_1 \ln(1 + b_2 \rho^{1/3}) \right] \rho d\mathbf{r}, \quad (16)$$

and then they replace the density $\rho(\mathbf{r})$ by a modified density $\rho_m(\mathbf{r})$, depending upon natural orbital densities $\rho_i(\mathbf{r})$ and occupation numbers n_i ,

$$\rho_m(\mathbf{r}) = \sum_i n_i e^{-(2-n_i)^2/2} \rho_i(\mathbf{r}). \quad (17)$$

As a consequence, a single occupied orbital ($n_i=1$) should not contribute to the total correlation energy as heavily as a paired electron ($n_i=2$), and so a double counting of the correlation energy is avoided in some way. It should be noted that, as this functional does not depend on spin densities, it is size consistent. Finally, the constants in Eq. (16) were reparametrized empirically to the values $a_1=b_1=0.02096$, $a_2=1.2$, and $b_2=2.39$ (results in a.u.). Lie and Clementi used $E_c^{\text{LC}}[\rho_m]$ to correct multiconfiguration self-consistent field (MCSCF) potential-energy curves for second-row hydrides [45] and dimers [46], and then, from the corrected curves, they obtain *correlated* spectroscopic constants. In this work, we recompute these spectroscopic constants from UHF and GVB wave functions, using their method, to compare it with the other methods tested here.

Colle and Salvetti [49,50] write the exact wave function of the system as the product of an approximate one Ψ_0 (better than or equal to the HF determinant Ψ_{HF} ; for instance, a GVB wave function) multiplied by a correlation factor. After a great deal of manipulation and some approximations they got for the correlation energy the following expression (in a.u.):

$$E_c^{\text{CS}}[\rho, \Gamma_0, \Gamma_{\text{HF}}] = -0.37588\pi \int \frac{\Gamma_0(\mathbf{R}, \mathbf{R}; \mathbf{R}, \mathbf{R})}{(\beta + 0.8)\beta^2} \left[1 + 0.173K \frac{e^{-0.58/\beta}}{\beta^2} \right] d\mathbf{R} \quad (18)$$

where K and β are defined as

$$K = \left. \frac{\nabla_r^2 \Gamma_0 \left[\mathbf{R} - \frac{\mathbf{r}}{2}, \mathbf{R} + \frac{\mathbf{r}}{2}; \mathbf{R} - \frac{\mathbf{r}}{2}, \mathbf{R} + \frac{\mathbf{r}}{2} \right]}{\Gamma_0 \left[\mathbf{R} - \frac{\mathbf{r}}{2}, \mathbf{R} + \frac{\mathbf{r}}{2}; \mathbf{R} - \frac{\mathbf{r}}{2}, \mathbf{R} + \frac{\mathbf{r}}{2} \right]} \right|_{\mathbf{r}=0} \quad (19)$$

and

$$\beta = q \left[1 + \frac{a}{2} \left(\frac{(\nabla_1^2 + \nabla_2^2) \Gamma_0(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)}{\Gamma_0(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)} - \frac{(\nabla_1^2 + \nabla_2^2) \Gamma_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)}{\Gamma_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)} \right) \right]_{\substack{\mathbf{r}'_1 = \mathbf{r}_1 \\ \mathbf{r}'_2 = \mathbf{r}_2 \\ \mathbf{r} = 0}} \rho(\mathbf{R})^{1/3} \quad (20)$$

and $q=2.29$ and $a=7.0$. \mathbf{R} is expressed as $(\mathbf{r}_1 + \mathbf{r}_2)/2$ and \mathbf{r} as $\mathbf{r}_2 - \mathbf{r}_1$.

This correlation-energy formula depends on three entities: the spin-free reduced density matrices of second order from Ψ_{HF} and Ψ_0 [$\Gamma_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)$ and $\Gamma_0(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)$, respectively] and the density from Ψ_0 or $\rho(\mathbf{r})$. When Ψ_0 is the Hartree-Fock wave function, β

simplifies to $q\rho^{1/3}$, so that the whole functional reduces to a simpler formula [49] that gives quite good correlation energies for a broad variety of systems [55–60, 24, 61–64]. This simplest form has been reparametrized lately by Carravetta and Clementi [65,66]; and Lee, Yang, and Parr [67] have modified it to obtain a true density functional, depending only on the

spin densities. It is interesting to point out that for $\Psi_0 = \Psi_{\text{HF}}$, a full optimization of $E_{\text{HF}} + E_c^{\text{CS}}[\rho, \Gamma_{\text{HF}}, \Gamma_{\text{HF}}]$ with respect to the Hartree-Fock orbitals has little effect on the total energy [68], as happens for the others correlation-energy functionals [approximation (10)]. As better Ψ_0 are used, β becomes greater, and Eq. (18) gives less correlation energy. When Ψ_0 is the exact wave function, Colle and Salvetti show that β has an infinite value everywhere, so that no correlation energy at all is recovered. A drawback of this method is the computational complexity of the expressions for K and β (useful relations for them have been derived [69]). We have taken Ψ_{HF} to be the first determinant in the GVB wave function (this approximation would be exact for a configuration-interaction expansion). As a consequence, our results are *not size consistent*, because the β for the quasidissociated molecule is not $q\rho^{1/3}$, as it should be for the free atoms. We want to remark that Colle and Salvetti have developed a new formula to be used with MCSCF wave functions [70].

Finally, the last method to estimate the correlation energy, which we have used here, is that of Moscardo and San-Fabian [53], which was derived within the correlation factor method also. It depends on $\rho(\mathbf{r})$, but, unlike the Colle-Salvetti method, it depends only on the diagonal part of $\Gamma_0(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)$:

$$E_c^{\text{MSF}}[\rho, \Gamma_0] = (N-1) \int \varepsilon_c[\rho, t, \beta] d\mathbf{r}, \quad (21)$$

where N is the number of electrons,

$$t(\mathbf{r}) = \pi^{-1} \left[\frac{(N-1)\rho(\mathbf{r})^2}{\Gamma_0(\mathbf{r})} \right]^{2/3}, \quad (22)$$

and β is taken as in Eq. (20), but with $q = 1.8$ and $a = 1.5$ (there are other options for β [53]). $\varepsilon_c[\rho, t, \beta]$ is given elsewhere [53] and has a form such that, when Ψ_0 is the exact wave function ($\beta = \infty$), the correlation recovered from (22) is zero also. Again, we have replaced Ψ_{HF} by the first determinant from the GVB wave function, so that this method is not size consistent either. Furthermore, its explicit dependence on N yields a correlation energy for a quasidissociated system that is different from the sum of the correlation energies of its isolated constituents. Fortunately, these effects tend to cancel each other.

III. CALCULATIONS

Potential-energy curves of the following molecules in their ground states have been studied: $\text{H}_2(^1\Sigma_g^+)$, $\text{LiH}(^1\Sigma^+)$, $\text{BH}(^1\Sigma^+)$, $\text{FH}(^1\Sigma^+)$, $\text{Li}_2(^1\Sigma_g^+)$, $\text{B}_2(^3\Sigma_g^-)$, $\text{C}_2(^1\Sigma_g^+)$, $\text{N}_2(^1\Sigma_g^+)$, and $\text{F}_2(^1\Sigma_g^+)$. If possible, we have calculated both unrestricted Hartree-Fock and general-valence-bond (perfect-pairing) [43] energies and wave functions. There are two cases (C_2 and N_2), where neither UHF nor GVB wave functions can describe a pure ground state, so that we have used a minimal configuration interaction from the GVB orbitals instead of the GVB wave function. UHF results for F_2 are not included because this curve does not have a minimum. Due to its electronic configuration, a GVB (perfect-

pairing) description of the valence electrons of the B_2 molecule is not possible (fortunately, the UHF curve has a correct dissociation behavior).

For these systems, we have built up a series of *correlated* potential-energy curves by first calculating the UHF (or GVB) energy at a given set of internuclear distances, and then correcting these energies with an estimation of the correlation energy from UHF (or GVB) densities and wave functions, according to Eq. (10) [or (15)].

6.311G** basis sets [71] have been used for all the molecules. Because of the good quality of these sets, it is expected that when computing spectroscopic constants, errors due to the basis sets are smaller than the effect of any correlation approximation. Furthermore, spectroscopic constants are only dependent on the shape of the potential-energy curve rather than on its absolute value. The UHF and GVB energies and wave functions have been computed with standard quantum-chemistry packages [72,73].

The correlation energy is computed by numerical integration following the efficient scheme of Becke [74], used together with Clenshaw-Curtis quadrature formulas [75,76] for automatic numerical integration. A more detailed description of the procedure has been given elsewhere [77]. Simultaneously, we integrate also the total charge of the molecules, and take the difference between this value and the number of electrons as a measure of the error in the correlation energy. This error is in any case greater than 0.0001 a.u.

For each molecule, we have computed the energy at the same set of distances as that used by Lie and Clementi [45,46], because these authors give also estimations of the exact total energy at those points, values that we have used here as a reference. Lie and Clementi make their estimations using the Hulburt-Hirschfelder potential [78] with experimental values of the spectroscopic constants (for the hydrogen molecule, the accurate theoretical values of Kolos and Wolniewicz [79] were used instead).

From the potential-energy curves at the set of internuclear distances (R 's), we have computed several spectroscopic constants (the *equilibrium distance* or R_e , the *vibrational frequency* or ω_e , and the *dissociation energy* or D_e), in order to study how they are affected by different correlation-energy approximations. Spectroscopic constants are often computed by a least-squares fitting of these points to a polynomial in $1/R$ [4,80–83], and, from this polynomial, R_e (the minimum), ω_e (related to the second derivative at R_e), and D_e (the difference between the energy of the quasidissociated molecule and the fitted polynomial at R_e) are readily computed. Because the correlation correction is rather small, special care has been taken in such calculations, in order to be sure that their error is smaller than the effect of correlation. The whole process may be outlined as follows.

(i) First we have to select a set of points to be fitted and the order of the polynomial in $1/R$ to be used. We assign an error or standard deviation $\sigma = 0.0001$ a.u. to the energy of each point (the error of the numerical integration). Then we take a set of n points and fit them to a polynomial of order m using a χ^2 fit [84]. We check the goodness-of-fit with the value [84]

$Q = 1 - P(0.5(n - m), 0.5\chi^2)$, where $P(\cdot)$ is the incomplete Γ function [85], and χ^2 is the quantity to be minimized in the χ^2 fit. We repeat for some values of n and m and finally we choose those that give the maximum Q . The procedure is applied to each curve to be fitted.

(ii) We fit the UHF or GVB curves and the UHF or GVB curves corrected by all the correlation estimations, and from them we compute their respective spectroscopic constants.

(iii) We take as the errors of our constants their standard deviation, computed from the *covariance matrix* of their respective fit [84].

IV. EFFECTS OF CORRELATION ON HF OR GVB SPECTROSCOPIC CONSTANTS

In the section we will study the effect of a *smooth* correlation correction on HF (or GVB) spectroscopic constants of diatomic molecules. Let us suppose that we are dealing with a diatomic molecule with a reduced mass μ and that $U(R)$ is the HF (or GVB) potential-energy curve of the molecule. R_e , ω_e , and D_e are spectroscopic constants computed from $U(R)$. We will assume that such a curve is to be corrected with a given correlation estimation $E_c(R)$ to give a correlated potential-energy curve $U_c(R)$:

$$U_c(R) = U(R) + E_c(R). \quad (23)$$

Both $U(R)$ and $U_c(R)$ have been shifted to give zero energy for $R \rightarrow \infty$. From this correlated curve, we can obtain a new set of correlated spectroscopic constants that will be named R_e^c , ω_e^c , and D_e^c .

Now, we will suppose that near the equilibrium distance $U(R)$ can be approximated as a Taylor series on $1/R$ to second order:

$$U(R) \approx -D_e + \frac{\mu\omega_e^2 R_e^4}{2} \left[\frac{1}{R} - \frac{1}{R_e} \right]^2. \quad (24)$$

It is easy to see that this expression has a minimum at $R = R_e$, that $U(R_e) = -D_e$, and that $U''(R_e) = \mu\omega_e^2$, as should be for the true potential-energy curve.

For $E_c(R)$, we will take only a first-order Taylor expansion on $1/R$, provided that the correlation curve is a smooth one,

$$E_c(R) \approx \Delta\varepsilon_c - \varepsilon'_c R_e^2 \left[\frac{1}{R} - \frac{1}{R_e} \right], \quad (25)$$

$$\Delta\varepsilon_c = E_c(R_e) - \lim_{R \rightarrow \infty} E_c(R), \quad (26)$$

where ε'_c is the first derivative of $E_c(R)$ at R_e .

Using approximations (24) and (25), we can find the minimum R_e^c of $U_c(R)$, taking the first derivative of Eq. (23),

$$U'_c(R) = \varepsilon'_c \frac{R_e^2}{R^2} - \frac{\mu\omega_e^2 R_e^4}{R^2} \left[\frac{1}{R} - \frac{1}{R_e} \right]; \quad (27)$$

and then, equating to zero and solving for $R = R_e^c$, it results in

$$\frac{1}{R_e^c} - \frac{1}{R_e} = \frac{\varepsilon'_c}{\mu\omega_e^2 R_e^2}. \quad (28)$$

This last equation is the one we are looking for. It relates the change in the equilibrium distance due to a correlation correction with the derivative of $E_c(R)$ at R_e .

For seeing how $E_c(R)$ changes the vibrational frequency from ω_e to ω_e^c , we take the next derivative of (27) and, then, using the known relation between the second derivative and the vibrational frequency, $U''_c(R_e^c) = \mu\omega_e^{c2}$, we have

$$\mu\omega_e^{c2} = \frac{-2\varepsilon'_c R_e^2}{R_e^{c3}} - \mu\omega_e^2 R_e^4 \left[\frac{-2}{R_e^{c3}} \left(\frac{1}{R_e^c} - \frac{1}{R_e} \right) - \frac{1}{R_e^{c4}} \right]. \quad (29)$$

Then, substituting $1/R_e^c - 1/R_e$ by its value [Eq. (28)] we finally obtain the relation between changes in the vibrational frequency and correlation:

$$\omega_e^c = \omega_e \left[\frac{R_e}{R_e^c} \right]^2. \quad (30)$$

For the dissociation energy, we have that $D_e^c = -U_c(R_e^c)$. Taking $U_c(R)$ from (23)–(25) and replacing $1/R_e^c - 1/R_e$ by (28), we have

$$D_e^c - D_e \approx -\Delta\varepsilon_c + \frac{\varepsilon_c'^2}{2\mu\omega_e^2}. \quad (31)$$

The results of this section are summarized by Eqs. (28), (30), and (31). Correlation acts on equilibrium distances and vibrational frequencies only through ε'_c [the derivative of $E_c(R)$ at the uncorrelated R_e]. The effect on dissociation energies depends also on $\Delta\varepsilon_c$ (the difference in correlation between the system at equilibrium and at quasidissociation distances).

Important qualitative conclusions may be inferred from these approximations. From Eq. (28) it follows that a *positive* ε'_c means a *shorter* equilibrium distance, which in turn, due to Eq. (30), means a *larger* vibrational frequency, or, as has been pointed out by Kemister and Nordholm [19], if a correlation correction *decreases* the equilibrium distance, then it *increases* the vibrational frequency.

For the dissociation energy, one may expect that correlation energies should be larger (more negative) at equilibrium distance (density ρ_{AB}) than at quasidissociation distance (densities ρ_A and ρ_B):

$$-E_c[\rho_{AB}] > -E_c[\rho_A] - E_c[\rho_B]. \quad (32)$$

This relation may be justified if we consider that the molecule AB at R_e has more correlation energy than both atoms A and B , because for the isolated atoms, electrons on A do not interact with electrons on B and vice versa. Thus, $-\Delta\varepsilon_c$ must be positive, like the second term in the right-hand side of Eq. (31). Thus the following conclusion results: the correlated dissociation energy *should always be larger* than the noncorrelated one.

Despite the simplicity of the model used to derive

them, relations (28), (30), and (31) yield quite accurate numerical results. The errors they produce are nearly always within our error estimates for D_e^c , and for R_e^c in most cases.

V. RESULTS AND DISCUSSION

Here we will study the results obtained with the methods described in Sec. III. Six correlation corrections have been used: local spin density [29], LSD with self-interaction correction [20], LSD with generalized gradient correction [41], Lie-Clementi (LC) [45,46], Colle-Salvetti (CS) [49,50], and Moscardo-San-Fabian (MSF) [53].

In Table I the quasidissociation behaviors of all the correlation functionals is shown for UHF and GVB wave functions. By quasidissociation distance we mean that geometry with maximum internuclear distance (10, 20 or 30 a.u., depending upon the molecule; see the work of Lie and Clementi [45,46]). The sum of the correlation energy of the constituent atoms is also shown ($A + B$ rows). The values in column "Exact" are the experimental correlation energies with their relativistic contributions subtracted [86]. This table illustrates the size-consistency behavior of the different correlation-energy functionals. As expected from Sec. II, all of them are size consistent

when applied to a UHF wave function (except the MSF method, due to its explicit N dependence), while only the LC functional is truly size consistent for GVB results. GVB correlation energies (with reversed sign) at quasidissociation distance are always overestimated by the LSD, SIC, and GGC methods, and always underestimated by the CS formula. There is no clear trend for the MSF functional, because there are two effects that tend to cancel each other (as explained in Sec. II).

In Tables II–IV the spectroscopic constants R_e , ω_e , and D_e , are shown. The correlation functionals have been used to correct UHF results (UHF+LSD, . . .) and GVB results (GVB+LSD, . . .). The row "Expt." shows the experimental value of the constants, as quoted by Lie and Clementi [45,46]. The maximum standard deviation of all the results in a column is shown in the row "Error" (in Table IV this row is not shown, because errors are always smaller than 0.01 eV). Finally, in these tables we have put Kohn-Sham results from the literature [83,87,19,88–91], that have been computed approximating both exchange and correlation. We have grouped them as KS(LSD), KS(SIC), or KS(GGC) according to the kinds of functionals used for exchange and correlation (respectively, LSD, LSD with SIC, or LSD with GGC). We have tried to select results computed with functionals and computational methods that are as simi-

TABLE I. Correlation energies (in 10^{-3} a.u., with reversed sign) at quasidissociation distance (see text) from several wave functions Ψ_0 (UHF, GVB), or from the sum of the correlation energy of the constituent atoms ($A + B$).

System	Ψ_0	Exact ^a	LSD	SIC	GGC	LC	CS	MSF
$\text{H}_2(^1\Sigma_g^+)$	UHF	0.0	44.7	0.0	5.3	15.5	0.0	0.0
	GVB	0.0	83.3	43.1	33.7	15.5	0.0	0.0
	$A + B$	0.0	44.6	0.0	5.4	15.4	0.0	0.0
$\text{LiH}(^1\Sigma^+)$	UHF	45.4	172.5	70.0	55.4	76.7	51.6	63.6
	GVB	45.4	202.8	103.9	78.4	76.7	47.6	62.7
	$A + B$	45.4	172.5	70.0	55.4	76.6	51.6	58.0
$\text{BH}(^1\Sigma^+)$	UHF	125.8	309.5	142.1	127.5	136.3	124.3	136.0
	GVB	125.8	337.5	173.1	148.3	136.4	107.4	132.9
	$A + B$	125.8	309.5	142.1	127.5	136.3	124.4	131.3
$\text{FH}(^1\Sigma^+)$	UHF	347.7	656.8	319.1	327.8	318.4	317.9	331.0
	GVB	347.7	684.1	349.2	347.6	318.5	268.7	315.9
	$A + B$	347.7	656.7	319.1	327.8	318.4	317.9	326.5
$\text{Li}_2(^1\Sigma_g^+)$	UHF	90.8	300.4	140.0	105.4	137.9	103.2	139.3
	GVB	90.8	321.9	164.6	122.9	137.9	95.2	137.5
	$A + B$	90.8	300.4	140.0	105.4	137.8	103.2	116.0
$\text{B}_2(^3\Sigma_g^-)$	UHF	251.6	574.4	284.2	249.6	257.1	248.7	293.1
	$A + B$	251.6	574.4	284.2	249.6	257.2	248.8	262.6
$\text{C}_2(^1\Sigma_g^+)$	GVB	318.6	748.4	383.0	350.1	315.5	181.6	304.4
	$A + B$	318.6	707.2	337.4	319.2	315.6	320.4	322.8
$\text{N}_2(^1\Sigma_g^+)$	GVB	389.6	913.6	466.9	447.5	376.1	251.4	390.2
	$A + B$	389.6	842.6	387.0	394.2	378.0	394.8	378.0
$\text{F}_2(^1\Sigma_g^+)$	UHF	695.4	1268.8	638.2	650.3	621.4	635.7	702.1
	GVB	695.4	1284.5	655.2	661.4	621.4	537.3	669.6
	$A + B$	695.4	1268.8	638.2	650.2	621.4	635.8	653.0

^aFrom Ref. [86], with relativistic contributions subtracted from the experimental correlation energies.

lar as possible to those we have used in this work.

In Figs. 1–5, correlation-energy curves $E_c(R)$ are shown. All of them have been shifted to give zero correlation energy at quasidissociation distances. The vertical lines are at the uncorrelated equilibrium distance. Exact curves have been obtained from the curves given by Lie and Clementi [45,46].

We will discuss separately the results obtained from UHF and GVB wave functions. For each series, we first comment on the dissociation energy, which depends on $\Delta\epsilon_c$ and $\epsilon'_c{}^2$ [Eq. (31)], and after that we analyze the constants R_e and ω_e , which depend only on ϵ'_c , through Eqs. (28) and (30). Finally, we compare our UHF series (computed within a Kohn-Sham scheme with exact exchange) with the Kohn-Sham calculations with approximate exchange.

A. UHF plus correlation energy

From Tables II–IV we can extract the following conclusions.

(a) D_e . Correlation always improves dissociation energies, in some cases dramatically (H_2 , LiH, BH). Nevertheless, errors with respect to experimental values are

still considerable for other molecules (FH, B_2). The reason for such improvements is that UHF D_e are severely underestimated, and, as has been discussed in the preceding section, any correlation correction should increase the dissociation energy. The six correlation functionals considered here give similar results and it is difficult to favor one of them for computing correlation corrections to D_e .

(b) R_e and ω_e . All the correlation corrections *decrease* equilibrium distances and *increase* vibrational frequencies. As the UHF equilibrium distances (or vibrational frequencies) for H_2 , BH, and FH (or H_2 , LiH, BH, and FH) are already shorter (or larger) than the experimental values, these spectroscopic constants are *worsened* rather than improved when corrected with correlation. This behavior of the Hartree-Fock spectroscopic constants is not restricted to these molecules. Pople [92] pointed out that for basis sets such as 6-31G* there is a systematic underestimation of Hartree-Fock equilibrium distances, in most cases by about 0.02–0.04 a.u. Conversely, vibrational frequencies are usually overestimated (for instance, from a set of 39 Hartree-Fock vibrational frequencies belonging to diatomic and polyatomic molecules only three were smaller than its experimental counterpart [93]).

TABLE II. Equilibrium distance R_e (in a.u.).

	H_2	LiH	BH	FH	Li_2	B_2	C_2	N_2	F_2
Expt.	1.401	3.015	2.336	1.733	5.051	3.003	2.347	2.073	2.679
Error	0.003	0.008	0.003	0.002	0.041	0.003	0.003	0.001	0.005
UHF	1.390	3.038	2.314	1.693	5.538	3.096			
UHF+LSD	1.365	2.969	2.273	1.676	4.876	3.026			
UHF+SIC	1.377	3.002	2.293	1.685	4.914	3.070			
UHF+GGC	1.386	2.996	2.301	1.680	4.968	3.042			
UHF+LC	1.373	2.996	2.285	1.681	5.186	3.046			
UHF+CS	1.382	2.973	2.285	1.684	4.891	3.034			
UHF+MSF	1.380	3.000	2.290	1.684	4.941	3.063			
GVB	1.430	3.093	2.370	1.728	5.537		2.443	2.079	2.873
GVB+LSD	1.402	3.016	2.325	1.708	5.317		2.407	2.054	2.790
GVB+SIC	1.416	3.052	2.347	1.718	5.412		2.425	2.066	2.831
GVB+GGC	1.424	3.043	2.354	1.710	5.377		2.413	2.067	2.700
GVB+LC	1.409	3.042	2.335	1.711	5.383		2.407	2.055	2.729
GVB+CS	1.413	2.987	2.344	1.708	5.096		2.348	2.007	2.704
GVB+MSF	1.411	3.028	2.330	1.708	5.230		2.397	2.051	2.753
KS(LSD)	1.45 ^a	3.0 ^b			5.12 ^a	3.03 ^a	2.35 ^a	2.07 ^a	2.61 ^a
KS(SIC)	1.423 ^c			1.791 ^c	5.22 ^d			2.113 ^c	2.802 ^c
KS(GGC)		3.033 ^e		1.757 ^e	5.22 ^f			2.07 ^f	2.699 ^e

^aFully numerical calculation from Ref. [83] using the Vosko, Wilk, and Nusair LSD functional for correlation (Ref. [28]).

^bFrom Ref. [87] with the exchange correlation functional of Rajagopal, Singhal, and Kimball. Computed using an uncontracted 6-21G with polarization functions.

^cFrom Ref. [19], with the LSD for exchange and a LSD functional (Ref. [28]) with the Stoll, Pavlidou, and Preuss SIC (Ref. [20]) for correlation. The 6-311G** basis set is used.

^dFrom Ref. [88], spin unrestricted exchange-only calculation using the SIC scheme of Perdew and Zunger (Ref. [29]). Computed using a linear combination of atomic orbitals with a fixed basis set of Gaussian-type orbitals.

^eFrom Ref. [89], with the functional of Becke and Perdew (Ref. [41]) for exchange and correlation, respectively. Uncontracted STO basis sets are used.

^fFrom Ref. [90], with the Langreth and Mehl functional for exchange and correlation (Refs. [14,39,40]). Augmented Gaussian basis sets were used.

TABLE III. Bond vibrational frequency ω_e (in cm^{-1}).

	H ₂	LiH	BH	FH	Li ₂	B ₂	C ₂	N ₂	F ₂
Expt.	4400	1406	2368	4139	351	1051	1855	2358	892
Error	43	15	19	18	6	7	8	4	9
UHF	4581	1428	2470	4498	229	939			
UHF+LSD	4738	1505	2589	4613	422	1063			
UHF+SIC	4655	1466	2530	4554	413	972			
UHF+GGC	4626	1471	2522	4609	393	1035			
UHF+LC	4686	1471	2547	4581	314	1027			
UHF+CS	4626	1492	2548	4566	402	1008			
UHF+MSF	4647	1470	2541	4566	400	981			
GVB	4208	1301	2260	4132	273		1548	2384	543
GVB+LSD	4392	1388	2383	4264	310		1628	2492	614
GVB+SIC	4299	1347	2322	4194	293		1587	2439	577
GVB+GGC	4274	1356	2322	4278	299		1624	2439	733
GVB+LC	4349	1360	2357	4256	300		1637	2497	737
GVB+CS	4380	1452	2302	4325	361		1830	2783	809
GVB+MSF	4368	1406	2359	4306	337		1679	2547	757
KS(LSD)	4190 ^a	1400 ^b			330 ^a	1030 ^a	1880 ^a	2380 ^a	1060 ^a
KS(SIC)	4290 ^c			3929 ^c	293 ^d			2281 ^c	1012 ^c
KS(GGC)		1408 ^e		4026 ^e	364 ^f			2409 ^f	1002 ^e

^aSee footnote a of Table II.^bSee footnote b of Table II.^cSee footnote c of Table II.^dSee footnote d of Table II.^eSee footnote e of Table II.^fSee footnote f of Table II.TABLE IV. Dissociation energy D_e (in eV).

	H ₂	LiH	BH	FH	Li ₂	B ₂	C ₂	N ₂	F ₂
Expt.	4.75	2.52	3.58	6.12	1.14	3.00	6.36	9.91	1.66
UHF	3.62	1.47	2.65	4.09	0.20	0.75			
UHF+LSD	4.99	2.69	3.74	5.29	0.85	1.07			
UHF+SIC	4.95	2.60	3.66	5.14	0.84	0.95			
UHF+GGC	4.75	2.46	3.61	5.42	0.82	1.56			
UHF+LC	4.18	1.95	3.25	4.95	0.41	0.90			
UHF+CS	4.64	2.38	3.53	5.16	0.75	1.26			
UHF+MSF	4.54	2.47	3.67	5.25	0.76	1.00			
GVB	4.12	1.92	3.15	4.81	0.44		2.84	7.10	0.55
GVB+LSD	4.44	2.28	3.47	5.25	0.59		3.55	8.56	0.71
GVB+SIC	4.28	2.11	3.31	5.03	0.52		3.19	7.83	0.62
GVB+GGC	4.48	2.24	3.53	5.58	0.65		3.67	8.13	1.11
GVB+LC	4.67	2.37	3.73	5.64	0.66		4.23	9.82	1.21
GVB+CS	4.74	2.59	3.93	6.25	0.94		6.89	12.34	2.48
GVB+MSF	4.79	2.66	3.91	5.88	0.91		5.64	10.64	1.46
KS(LSD)	4.9 ^a	2.2 ^b			1.0 ^a	3.9 ^a	7.3 ^a	11.6 ^a	3.4 ^a
KS(SIC)	4.84 ^c			6.56 ^c	0.28 ^d			9.44 ^c	2.61 ^c
KS(GGC)	5.0 ^e	2.4 ^e		6.2 ^e	0.60 ^f	3.3 ^e	6.1 ^e	10.1 ^e	2.2 ^e

^aSee footnote a of Table II.^bSee footnote b of Table II.^cSee footnote c of Table II.^dSee footnote d of Table II.^eSee footnote e of Table II.^fSee footnote f of Table II.

^gFrom Ref. [91], with the Langreth-Mehl functional for exchange and correlation (Ref. [14]). Computed perturbatively from fully numerical LSD densities.

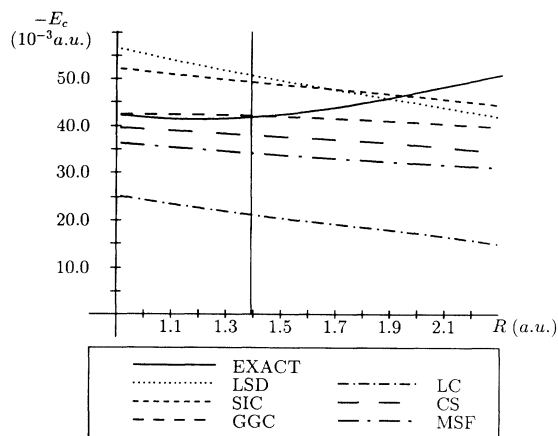


FIG. 1. H_2 molecule. Correlation energy with reversed sign ($-E_c$) vs internuclear distance (R), from the UHF wave function. All the curves have been shifted to give zero correlation energy at large R . The vertical line is at the UHF equilibrium distance.

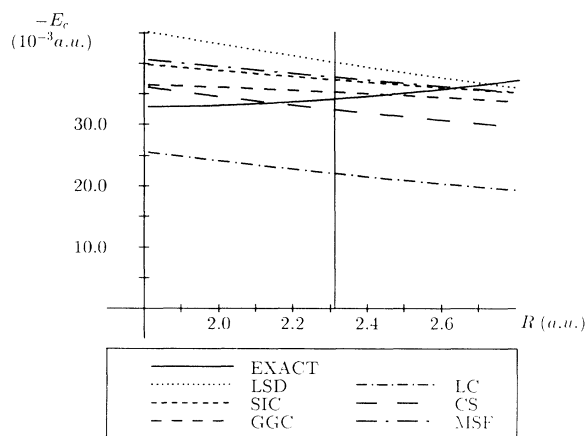


FIG. 2. BH molecule. Correlation energy with reversed sign ($-E_c$) vs internuclear distance (R), from the UHF wave function. All the curves have been shifted to give zero correlation energy at large R . The vertical line is at the UHF equilibrium distance.

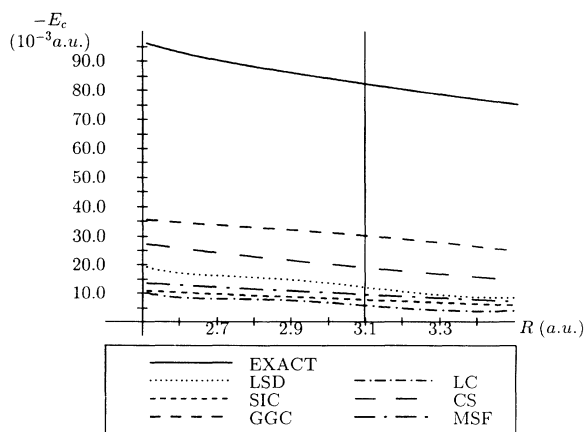


FIG. 3. B_2 molecule. Correlation energy with reversed sign ($-E_c$) vs internuclear distance (R), from the UHF wave function. All the curves have been shifted to give zero correlation energy at large R . The vertical line is at the UHF equilibrium distance.

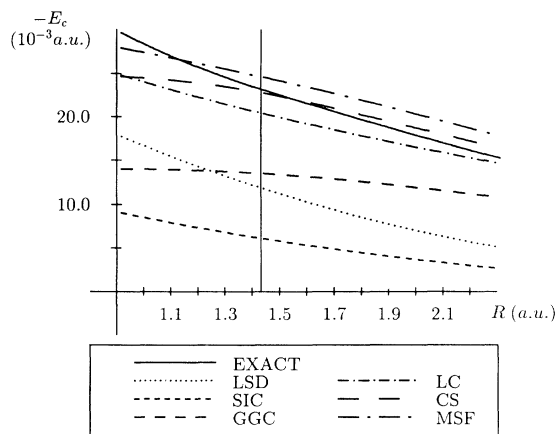


FIG. 4. H_2 molecule. Correlation energy with reversed sign ($-E_c$) vs internuclear distance (R), from the GVB wave function. All the curves have been shifted to give zero correlation energy at large R . The vertical line is at the GVB equilibrium distance.

We will study in some detail this last point, following the analysis of Cook and Karplus [94]. To simplify the discussion, we will restrict ourselves to the H_2 molecule. We are interested in the *unrestricted* Hartree-Fock potential-energy curve near the equilibrium distance, but, as has been known for many years [95], this curve is virtually identical to the *restricted* one (for distances shorter than the Coulson-Fischer point, ≈ 2.27 a.u.). So, we will discuss here the restricted case, with both electrons in the same orbital

$$\phi(\mathbf{r}) = \varphi_a(\mathbf{r}) + \varphi_b(\mathbf{r}), \quad (33)$$

where $\varphi_a(\mathbf{r})$ and $\varphi_b(\mathbf{r})$ are equivalent functions the first centered on atom A and the second on atom B . Using this orbital we form the Hartree-Fock wave function (for simplicity we will hereafter omit spin terms and normalization constants):

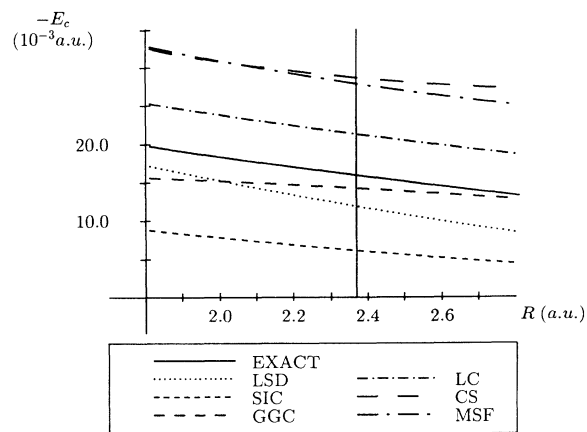


FIG. 5. BH molecule. Correlation energy with reversed sign ($-E_c$) vs internuclear distance (R), from the GVB wave function. All the curves have been shifted to give zero correlation energy at large R . The vertical line is at the GVB equilibrium distance.

$$\begin{aligned}\Psi_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) &= \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) \\ &= \varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_b(\mathbf{r}_1)\varphi_a(\mathbf{r}_2) \\ &\quad + \varphi_a(\mathbf{r}_1)\varphi_a(\mathbf{r}_2) + \varphi_b(\mathbf{r}_1)\varphi_b(\mathbf{r}_2). \quad (34)\end{aligned}$$

In a correct description of the hydrogen molecule, the relative importance of the ionic terms should decrease as R increases. However, the Hartree-Fock wave function (34) keeps this rate constant for any distance, and so, as the distance R increases, the error in the Hartree-Fock energy, $-E_c(R)$, also increases [96] (see Fig. 1). In other words, the HF correlation energy $E_c(R)$ is a decreasing curve, so that ϵ'_c is negative. This is exactly the opposite behavior of what we would expect for a correct correlation energy curve: as R increases and the H atoms fall far apart, each electron should remain bounded to a different nucleus, so that correlation between both electrons decreases, given a decreasing $-E_c(R)$. All the correlation functionals behave in this form.

For other molecules, an increasing $-E_c(R)$ is to be expected when the Hartree-Fock description of the molecular bond is qualitatively incorrect (at distances where restricted and unrestricted HF descriptions are equal). This is confirmed for the molecules H_2 , LiH , BH , FH , and Li_2 , which have not a qualitatively correct Hartree-Fock wave function (for example, Figs. 1 and 2, where it can be seen that Exact's are increasing curves for some interval of R). If the interval on which $-E_c(R)$ increases includes the UHF equilibrium distance (as for H_2 , BH , and FH), then this constant is shorter than the experimental value, and the UHF ω_e is larger. On the other hand, the B_2 molecule has a qualitatively correct Hartree-Fock curve, so that a decreasing $-E_c(R)$ is expected, as confirmed in Fig. 3. As a consequence, UHF R_e for B_2 is larger than the experimental value, and UHF ω_e is smaller. With respect to the correlation functionals, it should be stressed that they always have decreasing $-E_c(R)$ curves for all these molecules.

From the previous discussion, it becomes clear that correlation corrections to Hartree-Fock R_e or ω_e have little predictive value, unless the Hartree-Fock description of the molecular bond is qualitatively correct. The fact has already been pointed out in some recent papers [19,6].

B. GVB plus correlation energy

We can point out the following facts from Tables II–IV.

(a) D_e . Dissociation energies are increased (and improved) by all of the correlation corrections, as expected from inequality (32). GVB+LSD, GVB+SIC, and GVB+GGC dissociation energies are always smaller than GVB+LC values, and these in turn are smaller than GVB+CS and GVB+MSF dissociation energies. This ordering has to do with the size-consistency behavior of these methods (see the previous discussion of Table I). An overestimation of the correlation energy with reversed sign at quasidissociation distance (GVB+LSD, GVB+SIC, and GVB+GGC) yields a smaller dissociation

energy, while an underestimation (GVB+CS, GVB+MSF) yields larger D_e 's. The GVB+MSF series gives in general the best results, probably due to a cancellation of errors between the correlation energy at R_e and at large distance.

(b) R_e and ω_e . Equilibrium distances and vibrational frequencies are respectively decreased and increased by any correlation correction. Looking at Figs. 4 and 5 we see that $-E_c(R)$ are always decreasing curves for all correlation-energy corrections, but now, unlike the Hartree-Fock case, exact GVB correlation-energy curves are also decreasing curves, and that gives R_e (ω_e) larger (smaller) than the experimental value (this is also true for all the other molecules tested here, except perhaps the FH molecule, which has a nearly constant curve due to the goodness of its GVB description). This behavior seems to be quite general. For instance, from GVB or MCSCF calculations on a set of 14 molecules [45,46], only one had both R_e shorter and ω_e larger than its respective experimental values. As a consequence, this means an improvement of the spectroscopic constants, whatever the method we use. However, it is not clear which method is the best, although perhaps the Colle-Salvetti corrections are the most reliable.

We will illustrate the differences with the Hartree-Fock case using the H_2 molecule again. The GVB wave function for this molecule may be expressed [97,98] in a form similar to that used for the Hartree-Fock wave function, Eq. (34),

$$\begin{aligned}\Psi_{\text{GVB}}(\mathbf{r}_1, \mathbf{r}_2) &= \varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_b(\mathbf{r}_1)\varphi_a(\mathbf{r}_2) \\ &\quad + c[\varphi_a(\mathbf{r}_1)\varphi_a(\mathbf{r}_2) + \varphi_b(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)]. \quad (35)\end{aligned}$$

The parameter c allows the ionic terms to have the correct relative importance. The wrong effect due to the ionic terms in the HF wave function (34) is now corrected, so that we can expect smaller errors to the total energy for larger distances, that is, a decreasing $-E_c(R)$ or an increasing $E_c(R)$ curve (see Fig. 4). That means larger equilibrium distances and smaller vibrational frequencies than their respective experimental values [Eqs. (28) and (30)]. As a consequence, any reasonable correlation estimation (that is, one that gives smaller absolute correlation energies as the distance increases, as do all the expressions tested here) should improve (and indeed they do) the value of these spectroscopic constants.

C. Comparison with Kohn-Sham results with approximate exchange

Here we will compare our results, computed within the Kohn-Sham scheme with exact exchange and approximated correlation, with results from the literature, obtained with both exchange and correlation approximated (using the same or as similar as possible a correlation functional). The spectroscopic constants are shown in Tables II–IV. Provided that correlation approximations and computational methods are comparable for each pair of calculations [UHF+LSD–KS(LSD), UHF+SIC–KS(SIC), UHF+GGC–KS(GGC)] we believe that differences in the results may be attributed to the use of

either the exact or an approximate exchange, so that they may be useful in assessing their respective quality. The conclusions that follow should be taken cautiously, because different results have been computed with different basis sets.

In Table II (III) we see that equilibrium distances (vibrational frequencies) calculated with approximate exchange are always larger (smaller) than their respective values computed with exact exchange. This is the correct trend, because, as has been said above, correlation corrected UHF values are usually underestimated (overestimated). For explaining this trend, we will use again the same simple model for the H_2 molecule [94]. Near the equilibrium distance, restricted and unrestricted DFT calculations are also equal to each other [99,100], as they are for the Hartree-Fock case, so that only total densities rather than spin densities are needed. From a double occupied orbital like that used to build up the HF wave function (orbital 33), we get the (unnormalized) electron density:

$$\rho(\mathbf{r}) = |\varphi_a(\mathbf{r})|^2 + |\varphi_b(\mathbf{r})|^2 + 2\varphi_a(\mathbf{r})\varphi_b(\mathbf{r}). \quad (36)$$

It is clear that, as the distance R between atoms A and B increases, this density tends to the density of the isolated atoms A and B , because the term $2\varphi_a(\mathbf{r})\varphi_b(\mathbf{r})$ decreases. We would expect that any reasonable exchange functional yields smaller errors for the isolated atoms, so that the error of such an exchange functional, contrary to the Hartree-Fock exchange, is a decreasing curve with R . Thus, unlike the exact exchange case, calculations made with approximate exchange are good candidates for improvement with any reasonable [or decreasing $-E_c(R)$ curve] correlation estimation. Looking at Tables II and III we can say that R_e and ω_e computed with approximate exchange are generally of similar or better quality than those computed with exact exchange. This observation, together with the fact that reliable UHF curves cannot be obtained for some molecules such as N_2 , O_2 , or F_2 (and so prevent us from using the exact exchange scheme), seems to mean that approximate exchanges are more useful than the exact one (at least for this small set of molecules).

With respect to dissociation energies (Table IV), there is no clear trend in the reduced set of molecules we have

selected. Both kinds of calculations usually give similar results.

VI. CONCLUDING REMARKS

For Hartree-Fock or Kohn-Sham with exact exchange calculations, it seems that the size-consistency problem is the source of most troubles when computing magnitudes related with potential-energy curves such as equilibrium distances or vibrational frequencies. Those problems are still present at short distances, and despite this we use unrestricted methods, which give correct dissociation at large distance. A *qualitatively correct* description of the potential-energy curve is needed if it is to be improved with correlation energy functionals.

Paradoxically, Kohn-Sham calculations where the exact exchange is replaced by an approximate exchange give better potential-energy curves near the equilibrium distance. That means that approximated exchanges may be closer to experimental results than the exact-by-definition exchange, although Kohn-Sham dissociation energies computed with approximated exchanges are sometimes overestimated.

Finally, the troubles arising from the Hartree-Fock exchange may be removed by using a slightly more complex wave function (just to have a qualitatively correct behavior) such as a GVB or a short CI expansion. Current density-functional estimations of the correlation energy (LSD, LSDSIC, and LSDGGC) are still useful for improving the potential-energy curves, despite the double counting of correlation energy or the lack of size consistency. Better results are obtained with correlation approximations that have been specially treated to avoid the double counting, whether they are size consistent, as is the Lie-Clementi method; or not, as are the Colle-Salvetti and Moscardo-San-Fabian methods. The Moscardo-San-Fabian method gives the best dissociation energies.

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