Exchange and correlation energy in density functional theory. Comparison of accurate DFT quantities with traditional Hartree-Fock based ones and generalized gradient approximations for the molecules Li2, N2, F2.
Gritsenko, O.V.; Schipper, P.R.T.; Baerends, E.J.

published in
Journal of Chemical Physics
1997

DOI (link to publisher)
10.1063/1.474864

document version
Publisher's PDF, also known as Version of record

Link to publication in VU Research Portal

citation for published version (APA)

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

E-mail address:
vuresearchportal.ub@vu.nl

Download date: 02. Jun. 2021
Exchange and correlation energy in density functional theory: Comparison of accurate density functional theory quantities with traditional Hartree–Fock based ones and generalized gradient approximations for the molecules Li$_2$, N$_2$, F$_2$

O. V. Gritsenko, P. R. T. Schipper, and E. J. Baerends
Scheikundig Laboratorium der Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

(Received 31 March 1997; accepted 24 June 1997)

The density functional definition of exchange and correlation differs from the traditional one. In order to calculate the density functional theory (DFT), quantities accurately, molecular Kohn–Sham (KS) solutions have been obtained from ab initio wave functions for the homonuclear diatomic molecules Li$_2$, N$_2$, F$_2$. These afford the construction of the KS determinant $\Psi$, and the calculation of its total electronic energy $E^{\text{KS}}$ and the kinetic, nuclear-attraction and Coulomb repulsion components $T_s$, $V$, $W_H$ as well as the (DFT) exchange energy $E_x$ and correlation energy $E_c$. Comparison of these DFT quantities has been made on one hand with the corresponding Hartree–Fock (HF) quantities and on the other hand with local density approximation (LDA) and generalized gradient approximation (GGA). Comparison with HF shows that the correlation errors in the components $T$, $V$, and $W_H$ of the total energy are much larger for HF than KS determinantal wave functions. However, the total energies $E^{\text{KS}}$ and $E^{\text{HF}}$ appear to be close to each other, as well as the exchange energies $E_x$ and $E_x^{\text{HF}}$ and correlation energies $E_c$ and $E_c^{\text{HF}}$. The KS determinantal wave function and the KS orbitals therefore correspond to much improved kinetic and Coulombic energies, while having only a slightly larger total correlation energy. It is stressed that these properties of the Kohn–Sham orbitals make them very suitable for use in the molecular orbital theories of chemistry. Comparison of the accurate Kohn–Sham exchange and correlation energies with LDA and GGA shows that the GGA exchange energies are consistently too negative, while the GGA correlation energies are not negative enough. It is argued that the GGA exchange functionals represent effectively not only exchange, but also the molecular non-dynamical correlation, while the GGA correlation functionals represent dynamical correlation only. © 1997 American Institute of Physics. [S0021-9606(97)00337-1]

I. INTRODUCTION

The exchange-correlation energy $E_{xc}$ of a many-electron system is the key quantity of density functional theory (DFT).$^{1–3}$ Within the Kohn–Sham (KS) theory,$^4$ $E_{xc}$ is defined as a functional of the electron density $\rho$ in the KS expression for the total electronic energy $E[\rho]$, $^{13}$

$$E[\rho] = T_\rho[\rho] + V[\rho] + W_H[\rho] + E_{xc}[\rho]$$

(1.1)

where $T_\rho$ is the kinetic energy of a noninteracting particle system with density $\rho$, $V$ is the energy of electron–nuclear attraction, and $W_H$ is the Coulomb or Hartree energy. $E_{xc}$ can be further subdivided into the exchange $E_x$ and correlation $E_c$ energies

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho].$$

(1.2)

Accurate values of the exchange and correlation energies obtained for chemically interesting systems are essential for analysis of the effect of electron correlation within KS theory and in order to test and calibrate various DFT approximations. We emphasize that the DFT quantities $E_x$ and $E_c$ are not the traditional exchange and correlation energies of quantum chemistry, whose definition is tied to the Hartree–Fock (HF) model (see below).

Since the exact functional form of $E_{xc}$ is not known, one can, in principle, determine accurate values of $E_x$ and $E_c$ from highly accurate ab initio wave functions, for example, from extensive configuration interaction (CI) calculations. From the accurate density $\rho$ the Kohn–Sham orbitals $\phi_i$ corresponding uniquely to that density have to be determined in order to calculate $E_x$ and $E_c$ (see the next section for the corresponding formulas). The determination of the accurate KS orbitals $\phi_i(\mathbf{r})$ and the potential $V_i(\mathbf{r})$ from a given density $\rho$ appears to be a complicated problem which was treated in a number of papers.$^5–11$ The systematic KS solutions for atoms from Li to Ar have been obtained relatively recently$^{12}$ followed by the first examples of molecular KS solutions.$^{13–16}$

Because of the lack of accurate KS solutions, traditional Hartree–Fock based exchange and correlation energies have been used in DFT to obtain reference $E_x$ and $E_c$ values. In particular, $E_x$ is approximated with the corresponding HF exchange energy $E_x^{\text{HF}}$,

$$E_x \approx E_x^{\text{HF}},$$

(1.3)

while $E_c$ of DFT is approximated with the difference $E_c^{\text{HF}}$. 

between the empirical total nonrelativistic electronic energy of a system $E$ obtained from the spectroscopic data\textsuperscript{17–19} and the HF electronic energy $E_{\text{HF}}$

\[ E_c \approx E_{\text{c}}^{\text{HF}} = E - E_{\text{HF}}. \]  

(1.4)

As has been pointed out before\textsuperscript{20,21} (see also the next section) the definition of $E_c$ in DFT differs conceptually from the definition of $E_{\text{c}}^{\text{HF}}$ of traditional quantum chemistry. However, the HF method yields rather accurate electron densities for most atoms, and in those cases $E_c$ and $E_{\text{c}}^{\text{HF}}$ as well as $E_c$ and $E_{\text{c}}^{\text{HF}}$ are actually very close to each other.\textsuperscript{22} In case of strong near-degeneracy correlation, such as in dissociating molecules, the HF and exact densities may differ strongly and the difference between the conventional and DFT definitions of exchange and correlation energies becomes relevant.\textsuperscript{23,24}

For molecules at the equilibrium geometry the question whether the DFT and traditional definitions produce close values of the exchange and correlation energies remains open.

In this paper the KS orbitals $\phi_i$ and energies such as $T_s$, $E_c$, $E_x$, and others are obtained from \textit{ab initio} wave functions for the homonuclear diatomic closed-shell molecules Li$_2$, N$_2$, F$_2$ at the equilibrium and elongated bond distances. These molecules are considered as prototype systems with truly covalent bonds and they are included into any representative set of molecules to check the accuracy of approximations in DFT. They represent rather different cases of covalent bonding, ranging from the weakly bonded Li$_2$ with a single 2$s$-based $\sigma$ bond, to the very strongly bonded N$_2$ with one $\sigma$ and two $\pi$ bonds, to the weakly bonded F$_2$ with one 2$p$-based $\sigma$ bond and Pauli repulsion between two 2$p$ lone pairs on each F atom. A comparative analysis of the exchange and correlation energies of DFT and traditional quantum chemistry is performed using a partitioning of the KS and HF electronic energies $E_{\text{KS}}$, $E_{\text{HF}}$ and correlation energies $E_c$, $E_{\text{c}}^{\text{HF}}$ into various components. The values of the DFT exchange and correlation energies obtained are compared with those calculated with the GGA models of Becke,\textsuperscript{25} and of Perdew and Wang,\textsuperscript{26–28} for exchange and of Perdew and Wang,\textsuperscript{26–28} and of Lee, Yang, and Parr\textsuperscript{29} for Coulomb correlation. As will be shown below, based on this comparison and on qualitative physical considerations one can arrive at the conclusion that for molecules the GGA exchange functionals take effectively into account also a part of the correlation energy corresponding to nondynamical correlation, while the GGA correlation functionals lack this part, thus representing the effect of dynamical correlation.

II. DEFINITION OF THE EXCHANGE AND CORRELATION ENERGIES IN DFT

In order to subdivide the exchange-correlation energy of DFT into the exchange $E_x$ and correlation components [Eq. (1.2)], the determinantal wave function $\Psi$, built from the KS orbitals $\phi_i$ is used as a reference function. By definition, these orbitals yield the true ground state density $\rho$

\[ \rho(r) = \sum_{\mu=1}^{N} |\phi_{\mu}(r)|^2 \]  

(2.1)

so the energy $E_{\text{KS}}$ of $\Psi$

\[ E_{\text{KS}} = \langle \Psi | \hat{H} | \Psi \rangle = T_s + V + W_{\text{HF}} + E_c \]  

(2.2)

($\hat{H}$ is the Hamiltonian of the system) includes the first three terms of Eq. (1.1). The fourth term in the right-hand side of Eq. (2.2) is the DFT definition for the exchange energy $E_x$,

\[ E_x = -\frac{1}{2} \sum_{\sigma} \sum_{i,j=1}^{N_{\sigma}} \int dr_1 dr_2 \phi_{\mu}^\sigma(r_1) \phi_{\mu}^\sigma(r_2) \phi_{\mu}^\sigma(r_1) \phi_{\mu}^\sigma(r_2) \frac{\Delta \rho(r_1) \Delta \rho(r_2)}{|r_1 - r_2|}, \]  

(2.3)

where $\sigma$ is the spin index. Actually, $E_x$ has the same form, as a functional of the orbitals, as the Hartree–Fock (HF) exchange energy $E_{\text{HF}}$, but $E_x[\rho]$ is defined with the KS orbitals $\phi_i$ related to the exact density $\rho(r)$, while $E_{\text{HF}}$ is defined with the HF orbitals related to the HF density $\rho_{\text{HF}}(r)$.

The DFT and traditional definitions of the correlation energy differ much more markedly. In DFT the correlation energy $E_c$ is defined as the remainder when the exchange energy $E_x$ defined above is subtracted from $E_{\text{xc}}$, which implies that $E_c$ is simply the difference between the exact energy $E$ of Eq. (1.1) and $E_{\text{KS}}$ of Eq. (2.2).

\[ E_c = E_{\text{xc}} - E_x = E - E_{\text{KS}}, \]  

(2.4)

so the KS determinantal wave function plays a role as reference wave function here in the same way as the HF determinantal wave function does in the conventional definition. Since the HF determinant is by definition the one with the lowest possible energy, the DFT correlation energy $E_c$ is necessarily more negative (larger in an absolute sense) than the traditional correlation energy\textsuperscript{30}

\[ E_c \leq E_{\text{c}}^{\text{HF}}. \]  

(2.5)

$E_c$ can be subdivided into the kinetic $T_c$ and the potential $W_c$ components,

\[ E_c = [T - T_s] + [W_{\text{xc}} - E_c] = T_c + W_c, \]  

(2.6)

where $W_{\text{xc}}$ is the exchange-correlation part of the exact electron–electron interaction energy $W$, $W_{\text{xc}} = W - W_{\text{HF}}$. On the other hand, according to the traditional definition, the correlation energy $E_{\text{c}}^{\text{HF}}$ is the difference between $E$ and the Hartree–Fock energy,

\[ E_{\text{c}}^{\text{HF}} = E - E_{\text{HF}}, \]  

(2.7)

\[ = T - T_{\text{HF}} + \int \Delta \rho(r) \nu(r) dr + \int \frac{\Delta \rho(r_1) \rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 + \frac{1}{2} \int \frac{\Delta \rho(r_1) \Delta \rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 + W_{\text{xc}} - E_{\text{c}}^{\text{HF}} = T_{\text{c}}^{\text{HF}} + V_{\text{HF}} + W_{\text{c}}^{\text{HF}} + W_{\text{c}}^{\text{HF}}. \]  

The definitions (2.4) and (2.7) differ conceptually from each other, since the DFT correlation energy is a functional of the
exact density \( \rho \), while the traditional one involves the difference \( \Delta \rho = \rho - \rho_{HF} \). Therefore correlation terms like \( \rho_{HF} \), the correlation correction to the electron–nuclear attraction energy, and \( W_{HF} \), the correlation correction to the Hartree energy of the electrostatic electron repulsion, do not enter \( E_c \). Moreover, the terms \( T_{HF} \) and \( W_{HF} \) of \( E_{HF} \) will be different from the corresponding terms \( T_c \) and \( W_c \) of \( E_c \). Note that \( W_{HF} \), according to

\[
W_{HF} = W_{c}\nu - E_{HF} = E_c + W_c - E_{HF} = \Delta E_{HF} + W_c, \tag{2.8}
\]

differ from \( W_c \) only in the difference \( \Delta E_{HF} \), between the KS and HF exchange energies.

In the next section the procedure employed to obtain the KS quantities will be outlined.

### III. CALCULATION OF THE KS QUANTITIES

The procedure used in this paper to obtain the Kohn–Sham orbitals and energies from \textit{ab initio} wave functions has been already presented and discussed in Refs. 31,14. To obtain the correlated wave functions, the HF and subsequent CI calculations have been performed for the ground states by means of the ATML package\(^{32} \) at the bond distances \( R_c \) = 5.05, \( R = 6.0 \), and \( R = 7.0 \) a.u. for \( \text{Li}_2 \); \( R_c = 2.074, R = 3.0, \) and \( R = 3.5 \) a.u. for \( \text{N}_2 \); \( R_c = 2.668, R = 3.0, \) and \( R = 3.5 \) a.u. for \( \text{F}_2 \). A basis of contracted Gaussian functions has been used for the calculations. For \( \text{Li} \) a basis\(^{33} \) with eight \( s \)- and four \( p \)-type functions has been used, which has been augmented with extra \( p \) and \( d \) polarization functions. For \( \text{N} \) and \( \text{F} \) the correlation-consistent polarized-valence triple zeta added (cc-pCVTZ) basis sets\(^{34} \) have been used.

The basis sets cc-pCVXZ from X=D (double zeta) to X=Q (quintuple zeta) were obtained for the atoms B through Ne as an extension of the correlation-consistent polarized valence basis sets (cc-pVXZ).\(^{35} \) This extension allows us to represent adequately the correlated electron density \( \rho \) in all regions and to treat uniformly core, core–valence, and valence correlation effects when performing the multireference CI calculations with the cc-pCVXZ basis. This goal is achieved by the inclusion of a large number of basis functions, so that the gap between the core and valence exponents is rather small.\(^{36} \) The exponents were optimized in atomic MRCI calculations. In order to describe properly effects of angular core and valence electron correlation, higher angular momentum polarization functions were included with both high exponents (corelike) and intermediate exponents (valence size). In particular, the cc-pCVTZ basis chosen in this paper includes \( p \)- and \( d \)-type polarization functions of typical angular core extent and \( d \)- and \( f \)-type polarization functions with typical valence exponents. In a similar way, in order to describe properly the angular correlation, we have augmented the basis of Ref. 33 for \( \text{Li} \) with polarization \( p \)- and \( d \)-type functions of both core and valence extent.

The performance of MRCI with the combined cc-pCVXZ basis sets as well as with the original cc-pVXZ sets was tested in Refs. 34, 36, 37 in atomic calculations and with benchmark calculations on the \( \text{H}_2 \), \( \text{C}_n\text{H} \) \((n = 2–7)\), \( \text{OH} \), \( \text{HF} \), \( \text{N}_2 \) molecules. MRCI calculations in the cc-pCVXZ basis have proven to provide the same good description of the valence correlation effects as the corresponding calculations in a basis of atomic natural orbitals (ANO).\(^{38} \) In general, the quality of the results appreciably improves when going from cc-pCVDZ to cc-pCVTZ basis, while further extension of the basis produces relatively little improvement. The test MRCI calculations in the cc-pCVTZ basis reproduce well the state separation energies, equilibrium geometry, harmonic frequencies, and anharmonicities, as well as the dipole and quadrupole moments, which is indicative of the good quality of the corresponding wave function and the correlated density \( \rho \).

In this paper the MRCI calculations have been carried out within the direct CI approach with 106 reference configurations for \( \text{Li}_2 \) and \( \text{N}_2 \) and 36 reference configurations for \( \text{F}_2 \). The reference configurations were selected within the internal space of eight lowest energy Hartree–Fock molecular orbitals (MO) for \( \text{Li}_2 \) and 10 orbitals for \( \text{N}_2 \) and \( \text{F}_2 \). For \( \text{N}_2 \) and \( \text{F}_2 \) the internal space includes, apart from the occupied orbitals of the main (Hartree–Fock) configuration, also the orbitals, which are essential for a proper dissociation limit of the molecule. These are the 2\( p^2 \)-MO of \( \text{F}_2 \) and 2\( p^2 \)-\( s^2 \)-\( p^2 \)-MOs of \( \text{N}_2 \). For \( \text{Li}_2 \), apart from \( 1s^2 \sigma, 1s^2\pi_0, 2s_\sigma, \) and \( 2s_\pi \)-MOs (the inclusion of the latter MO is essential for a proper dissociation limit), three more \( \sigma \)-type and two \( \pi \)-type orbitals have been included into the internal space. This choice of the internal space for the reference configurations together with the use of the cc-pCVTZ basis is expected to provide a reliable description of the correlated \( \rho \) at both equilibrium and larger bond distances \( A–A \).

All single and double excitations from each reference configuration to either internal or external subspaces have been included in the MRCI, which have also been augmented with the configurations obtained by single excitation from a reference configuration to the internal subspace with subsequent single excitation to the external subspace. The MRCI calculations performed at \( R_c \) recover 86% of the total Coulomb correlation energy \( E_{HF} \) for \( \text{Li}_2 \) and \( \text{N}_2 \), and 84% of \( E_{HF} \) for \( \text{F}_2 \).

The KS orbitals \( \phi_i(r) \) and potential \( \nu_i(r) \) of the one-electron KS equations,

\[
-\frac{1}{2} \nabla^2 + \nu_i(r) \phi_i(r) = e_i \phi_i(r) \tag{3.1}
\]

have been obtained with an iterative procedure,\(^{11} \) which has been used previously to calculate the exchange-correlation potentials and energy densities for the monohydrides \( \text{LiH}, \text{BH}, \text{HF} \).\(^{13,14} \) The KS orbitals \( \phi_i \) are represented in the same basis of MO’s as has been used for the MRCI calculations. The accuracy of the resultant KS solution can be characterized with the values of the integrated difference between the calculated and target densities (absolute integral error of the iterative procedure) \( \Delta \rho = 0.0035 \) \( e \) for \( \text{N}_2 \), \( \Delta \rho = 0.007 \) \( e \) for \( \text{F}_2 \), and \( \Delta \rho = 0.04 \) \( e \) for \( \text{Li}_2 \) obtained at \( R_c \) after 100 iterations. The relatively large error for \( \text{Li}_2 \) appears, probably, because for this molecule with its diffuse electron density the region of density tails (where both the Gaussian basis set representation and the potential construction procedure are
TABLE I. Kohn–Sham energy characteristics (a.u.) for Li2 and their differences from the Hartree–Fock characteristics.

<table>
<thead>
<tr>
<th>R(Li–Li)</th>
<th>5.05</th>
<th>6.0</th>
<th>7.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_s</td>
<td>14.902</td>
<td>14.840</td>
<td>14.817</td>
</tr>
<tr>
<td>ΔT_s^HF</td>
<td>0.011</td>
<td>0.015</td>
<td>0.036</td>
</tr>
<tr>
<td>T_c</td>
<td>0.083</td>
<td>0.084</td>
<td>0.079</td>
</tr>
<tr>
<td>ΔT_c^HF</td>
<td>0.094</td>
<td>0.099</td>
<td>0.115</td>
</tr>
<tr>
<td>V</td>
<td>-38.062</td>
<td>-37.392</td>
<td>-36.880</td>
</tr>
<tr>
<td>ΔV^HF = V_c^HF</td>
<td>-0.048</td>
<td>-0.044</td>
<td>-0.064</td>
</tr>
<tr>
<td>W_H</td>
<td>10.079</td>
<td>9.729</td>
<td>9.450</td>
</tr>
<tr>
<td>ΔW_H^HF = W_{H,c}^HF</td>
<td>0.045</td>
<td>0.032</td>
<td>0.037</td>
</tr>
<tr>
<td>E_s</td>
<td>-3.565</td>
<td>-3.541</td>
<td>-3.521</td>
</tr>
<tr>
<td>ΔE_s^HF</td>
<td>-0.002</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>W_c</td>
<td>-0.194</td>
<td>-0.190</td>
<td>-0.192</td>
</tr>
<tr>
<td>ΔE_c^HF</td>
<td>-0.111</td>
<td>-0.106</td>
<td>-0.113</td>
</tr>
<tr>
<td>E_c</td>
<td>-0.105</td>
<td>-0.103</td>
<td>-0.104</td>
</tr>
<tr>
<td>ΔE_c^HF</td>
<td>-0.006</td>
<td>-0.003</td>
<td>-0.009</td>
</tr>
<tr>
<td>E_{emp}</td>
<td>-0.128</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE II. Kohn–Sham energy characteristics (a.u.) for N2 and their differences from the Hartree–Fock characteristics.

<table>
<thead>
<tr>
<th>R(N–N)</th>
<th>2.074</th>
<th>3.0</th>
<th>3.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_s</td>
<td>109.070</td>
<td>108.095</td>
<td>108.223</td>
</tr>
<tr>
<td>ΔT_s^HF</td>
<td>0.296</td>
<td>0.692</td>
<td>0.903</td>
</tr>
<tr>
<td>T_c</td>
<td>0.329</td>
<td>0.328</td>
<td>0.313</td>
</tr>
<tr>
<td>ΔT_c^HF</td>
<td>0.625</td>
<td>1.020</td>
<td>1.216</td>
</tr>
<tr>
<td>V</td>
<td>-303.628</td>
<td>-288.260</td>
<td>-283.780</td>
</tr>
<tr>
<td>ΔV^HF = V_c^HF</td>
<td>-0.558</td>
<td>-1.330</td>
<td>-1.759</td>
</tr>
<tr>
<td>W_H</td>
<td>75.068</td>
<td>67.858</td>
<td>65.666</td>
</tr>
<tr>
<td>ΔW_H^HF = W_{H,c}^HF</td>
<td>0.274</td>
<td>0.716</td>
<td>0.980</td>
</tr>
<tr>
<td>ΔE_s^HF</td>
<td>-0.006</td>
<td>-0.040</td>
<td>-0.067</td>
</tr>
<tr>
<td>W_c</td>
<td>-0.804</td>
<td>-0.969</td>
<td>-1.063</td>
</tr>
<tr>
<td>ΔE_c^HF</td>
<td>-0.475</td>
<td>-0.641</td>
<td>-0.750</td>
</tr>
<tr>
<td>E_c</td>
<td>-0.469</td>
<td>-0.603</td>
<td>-0.687</td>
</tr>
<tr>
<td>ΔE_c^HF</td>
<td>-0.006</td>
<td>-0.038</td>
<td>-0.063</td>
</tr>
<tr>
<td>E_{emp}</td>
<td>-0.552</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE III. Kohn–Sham energy characteristics (a.u.) for F2 and their differences from the Hartree–Fock characteristics.

<table>
<thead>
<tr>
<th>R(F–F)</th>
<th>2.668</th>
<th>3.0</th>
<th>3.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_s</td>
<td>198.922</td>
<td>198.754</td>
<td>198.726</td>
</tr>
<tr>
<td>ΔT_s^HF</td>
<td>0.356</td>
<td>0.436</td>
<td>0.545</td>
</tr>
<tr>
<td>T_c</td>
<td>0.556</td>
<td>0.454</td>
<td>0.454</td>
</tr>
<tr>
<td>ΔT_c^HF</td>
<td>0.806</td>
<td>0.890</td>
<td>0.999</td>
</tr>
<tr>
<td>V</td>
<td>-537.656</td>
<td>-530.896</td>
<td>-523.252</td>
</tr>
<tr>
<td>ΔV^HF = V_c^HF</td>
<td>-0.493</td>
<td>-0.653</td>
<td>-0.890</td>
</tr>
<tr>
<td>W_H</td>
<td>129.566</td>
<td>126.286</td>
<td>122.529</td>
</tr>
<tr>
<td>ΔW_H^HF = W_{H,c}^HF</td>
<td>0.122</td>
<td>0.215</td>
<td>0.363</td>
</tr>
<tr>
<td>E_s</td>
<td>-19.935</td>
<td>-19.841</td>
<td>-19.760</td>
</tr>
<tr>
<td>ΔE_s^HF</td>
<td>0.024</td>
<td>0.022</td>
<td>0.014</td>
</tr>
<tr>
<td>W_c</td>
<td>-1.082</td>
<td>-1.122</td>
<td>-1.181</td>
</tr>
<tr>
<td>ΔE_c^HF</td>
<td>-0.632</td>
<td>-0.668</td>
<td>-0.727</td>
</tr>
<tr>
<td>E_c</td>
<td>-0.623</td>
<td>-0.649</td>
<td>-0.695</td>
</tr>
<tr>
<td>ΔE_c^HF</td>
<td>-0.009</td>
<td>-0.019</td>
<td>-0.032</td>
</tr>
<tr>
<td>E_{emp}</td>
<td>-0.755</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

less adequate) plays a more important role. The errors Δρ increase with increasing bond distance R(A–A). Finally, using ab initio energies and densities as well as the obtained KS orbitals, the exchange and correlation energies and their components have been calculated. They will be presented and discussed in the next section.

IV. CORRELATION CORRECTIONS TO THE KINETIC ENERGY AND VARIOUS POTENTIAL ENERGY TERMS FOR THE KOHN–SHAM AND HARTREE–FOCK DETERMINANTAL WAVE FUNCTIONS

Tables I–III present various Kohn–Sham energy characteristics of Li₂, N₂, and F₂ calculated for three different bond distances R(A–A). The components T_s, V, W_H, and E_s of the total electronic energy EKS, all calculated with the KS determinant ΨKS, and the KS correlation energy E_c = T_c + W_c [Eq. (2.6)] are compared with those calculated with the Hartree–Fock determinant and the corresponding differences ΔE_c^HF are presented. The HF determinant differs markedly from the KS determinant, in particular for N₂ and F₂, as can be judged from the large differences ΔT_s^HF, ΔV^HF, ΔW_s^HF in the kinetic energy, electron–nuclear and Hartree part of the electron–electron potential energy, respectively. The magnitude of these terms may be put in perspective when comparing them to the dissociation energies of these molecules which range from a few hundreds of an a.u. (Li₂ and F₂) to ~0.37 a.u. (N₂). The explanation of the large differences between these KS and HF quantities is the diffuse nature of the HF orbitals and electron density.39,24 The Coulomb correlation leads to a considerable contraction of the correlated density ρ around the nuclei as compared with the HF one, ρHF. Because of this contraction, the corresponding differences of the electron–nuclear attraction energies ΔV_c^HF = V_c^HF − V_c^HF are in all cases negative, while those of the kinetic energy, ΔT_s^HF = T_s^HF − T_s^HF, and the Hartree energy, ΔW_s^HF = W_s^HF − W_s^HF, are positive. Obviously, since the KS density is exact, there are no correlation corrections to the KS V and W_H, and ΔV_s^HF and ΔW_s^HF also represent the HF correlation corrections V_c^HF and W_{H,c}^HF to V and W_H. The large ΔW_s^HF and ΔV_s^HF in the tables demonstrate the large correlation corrections in the electron–electron and in particular in the electron–nuclear Coulombic energies in the case of HF. They are as a matter of fact of the same order of magnitude as W_c and W_c^HF, which represent the change in the electron–electron interaction energy due to the Coulomb hole. W_c is purely an effect of the correlation between the electrons, but it is not significantly larger than the “secondary” effects of the correlation induced changes in the one-electron density matrix and diagonal density, T_c, V_c, and W_{H,c}^HF, respectively. The T_s and T_c values are given explicitly in the tables and show that these correlation corrections to the kinetic energies are modest as a percentage of T, but they are large in an absolute sense, and they differ significantly (about a factor 2 for N₂ and F₂) between KS and HF.

In view of the considerable differences between various
HF and KS energy terms, it is quite remarkable to note that in a number of cases there is close agreement. To begin with, the exchange energies $E_x$ and $E_x^{\text{HF}}$ are quite close for $R_s(A-A)$ (note the small $\Delta E_x^{\text{HF}}$ in the tables) except for $F_2$. As a consequence $W_c$ and $W_{\text{HF}} = \Delta E_x^{\text{HF}} + W_c$ are quite close. Since on the other hand $T_c$ and $T_c^{\text{HF}}$ differ quite a bit, one would expect $E_c = T_c + W_c$ to differ from $E_{\text{HF}}$, but remarkably the remaining terms $V_{\text{HF}}$ and $W_{\text{HF}}$, in $E_{\text{HF}}$ [see Eq. (2.7)] are not only individually large but also cancel the difference in $T_c$ and $T_c^{\text{HF}}$, so that ultimately $E_c$ and $E_{\text{HF}}$ are very close. The difference $\Delta E_c^{\text{HF}}$ between $E_c$ and $E_c^{\text{HF}}$ is simply the difference between the energies $E_{\text{HF}}$ and $E_{\text{KS}}$, as follows immediately from Eqs. (2.4) and (2.7),

$$\Delta E_c^{\text{HF}} = E_c - E_c^{\text{HF}} = E_{\text{HF}} - E_{\text{KS}} \quad (4.1)$$

and $E_{\text{HF}}$ and $E_{\text{KS}}$ are probably close due to the stationarity of the HF determinant energy against orbital variation. As was noted before, the HF determinant is by definition the one with the lowest possible energy [cf. Eq. (2.5)], and $\Delta E_c^{\text{HF}}$ is always negative (see Tables I–III).

We use the calculated $\Delta E_c^{\text{HF}}$ values to estimate the true correlation energies $E_c$ of DFT for Li$_2$, N$_2$, F$_2$. In order to do this, we add the difference $\Delta E_c^{\text{HF}}$ to the empirical value for the traditional correlation energy $E_{\text{HF,emp}}^{\text{emp}}$ obtained by using an empirical estimate for the exact total energy $E$ in the equation below,

$$E_c^{\text{emp}} = (E^{\text{emp}} - E_{\text{HF}}^{\text{emp}}) + (E_{\text{HF}} - E_{\text{KS}}) = E_c^{\text{HF,emp}} + \Delta E_c^{\text{HF}}. \quad (4.2)$$

As follows from the previous discussion, the resulting empirical $E_c^{\text{emp}}$ values presented in Tables I–III are close to the corresponding $E_{\text{HF,emp}}$ ones. One can conclude that the present results for $R_s(A-A)$ justify (at least, for the case of the second row dimers) the current practice to approximate the DFT quantities $E_c$ and $E_c^{\text{HF}}$ with the traditional $E_{\text{HF}}$ and $E_{\text{KS}}$ ones.

However, for larger bond distances $R(A-A)$ this conclusion does not hold true. The quality of the HF density $\rho_{\text{HF}}$ deteriorates with increasing bond distance and it becomes progressively less contracted than the correlated density $\rho$. This is due to the ionic configurations present in the covalent bonds described by the RHF wave function. The Hartree–Fock effective field is therefore too repulsive around the nuclei, an effect that is particularly strong at large bond lengths and if there are ionic configurations with multiple charge, as is inevitable in case of multiple bonds. As a result, the differences $\Delta T_r^{\text{HF}}, \Delta V^{\text{HF}}, \Delta W_h^{\text{HF}}$ increase, quite significantly so for N$_2$ and F$_2$, and moderately for Li$_2$ [\Delta W_h^{\text{HF}} for Li$_2$ actually slightly decreases for larger distances $R$(Li–Li) = 6.0 and 7.0 a.u.]. Compensation of the differences in the various terms which have opposite sign again takes place in these cases to a high degree, yet the resulting $\Delta E_c^{\text{HF}}$ values are distinctly more negative than those for $R_s(A-A)$, so that the DFT correlation energy $E_c$ becomes progressively more negative than the traditional $E_c^{\text{HF}}$.

Left–right correlation is treated fundamentally differently in KS and HF calculations, (it is not treated at all in the latter case). The progressively larger $V_h^{\text{HF}}$ and $W_h^{\text{HF}}$ values upon bond lengthening reflect the increasingly more diffuse nature of the HF orbitals due to the presence of ionic configurations. There are no corresponding correlation errors in $V$ and $W$ in the KS case. A similar important difference between HF and KS is apparent in the kinetic energies. Tables I–III present the kinetic part of the DFT exchange-correlation energy $T_c$ as well as that of the traditional correlation energy $T_c^{\text{HF}}$. The $T_c$ and $T_c^{\text{HF}}$ values are evaluated as the difference between the CI kinetic energy $T_c^{\text{CI}}$ and the corresponding independent-particle kinetic energies,

$$T_c \approx T_c^{\text{CI}} - T_s, \quad (4.3)$$

$$T_c^{\text{HF}} \approx T_c^{\text{CI}} - T_{\text{HF}}. \quad (4.4)$$

The diffuse nature of the HF orbitals makes $T_{\text{HF}}$ increasingly lower than $T_c$, i.e., $T_c^{\text{HF}}$ increases strongly upon bond elongation, in particular in the triply bonded N$_2$, for which $T_c^{\text{HF}}$ increases from 0.625 hartree at $R$(N–N) = 2.074 a.u. to 1.216 hartree at $R$(N–N) = 3.5 a.u. The kinetic energy of the KS system does not suffer such an error, and in fact $T_c$ hardly changes as a function of bond distance. In the dissociation limit $T_c$ approaches to the sum of the $T_c$ contributions of the atomic fragments, which does not appear to be much different from $T_c$ at $R_c$.

To sum up, the results of this section show that for the dimers Li$_2$, N$_2$, F$_2$ at the equilibrium bond distances the DFT and the traditional definitions of the exchange and correlation energies produce close numerical values. However, these close values emerge from the nearly precise cancellation of large differences $\Delta T_r^{\text{HF}}, \Delta V^{\text{HF}}, \Delta W_h^{\text{HF}}$ of the corresponding individual contributions. In other words, in spite of the abovementioned difference of the HF and KS electron densities, the electronic energy of the molecules A$_2$ calculated at the equilibrium bond distances in the exchange-only approximation (i.e., from the one-determinantal wave functions) remains practically the same for both HF and KS approaches. However, for the dissociating molecules, and in general for weak-interaction situations, the typical Hartree–Fock error of neglect of left–right correlation becomes more serious and the DFT and traditional definitions yield increasingly different exchange and correlation energies. The traditional exchange and correlation energies can no longer be taken as reference values for molecular DFT applications.

V. KS AND GGA EXCHANGE AND CORRELATION ENERGIES

The KS exchange energies $E_x$ and the empirical estimate $E_x^{\text{emp}}$ of the DFT correlation energies for Li$_2$, N$_2$, F$_2$ presented in the previous section are compared in Table IV with those calculated with the current functionals of the generalized gradient approximation (GGA) and also with the corresponding values obtained with the local density approximation (LDA). In the last column of the table the exchange-correlation energy $E_x + E_x^{\text{emp}}$ (row labeled KS) is compared with the sum of the exchange $E_x^{\text{PW}}$ and correlation $E_x^{\text{PW}}$ functionals of Perdew and Wang (row PW/PW), the sum of the exchange $E_x^{\text{B}}$ functional of Becke (row PW/BP), and the sum of $E_x^{\text{B}}$ and the correlation functional $E_x^{\text{LYP}}$ of Perdew and Wang.
Lee, Yang and Parr\textsuperscript{29} (row BLYP). In the first and second columns the KS $E_1$ and $E_{1\text{emp}}$ respectively, are compared with the corresponding individual components of PW/PW, BPW, and BLYP. All LDA and GGA values are calculated at the equilibrium bond distances with the same \textit{ab initio} density \(\rho\), which has been used to obtain the KS solution.

For the LDA functionals the trend for all three molecules is rather uniform. The correlation functional of LDA tends to overestimate the molecular electron correlation by \(\sim 100\%\) and \(E_{1\text{LDA}}\) values are consistently too negative. This is due to the well-known difference in correlation between the homogeneous electron gas model (which is represented by the LDA) and finite inhomogeneous atomic and molecular systems\textsuperscript{44} (the overestimation is correctly performed in the GGA correlation functionals). However, this overestimation is overcompensated by underestimation of the atomic and molecular exchange in LDA, so that \(E_{1\text{LDA}}\) and the total \(E_{1\text{xc}}\) values are significantly higher (less negative) than the corresponding KS ones.

The gradient corrections of GGA bring the corresponding exchange and correlation energies much closer to the KS ones as compared to LDA. In particular, for Li\(_2\) the exchange energy \(E_1\) and the correlation energies \(E_{1\text{PW}}\) and \(E_{1\text{LYP}}\) are only a few millihartrees off their KS counterparts, with the difference between \(E_{1\text{PW}}\) and \(E_1\) being somewhat larger. As a result, the corresponding GGA exchange-correlation energies are also close to the KS ones.

However, for \(N_2\) and \(F_2\) appreciable differences between the individual GGA and KS exchange and correlation components of the exchange-correlation energy are observed. Here, both GGA exchange functionals yield consistently too negative values as compared with the KS $E_1$. The largest difference is between $E_1^B$ and $E_1^\tau$ for $N_2$ amounting to \(-0.094\) hartrees for $N_2$ and to \(-0.166\) hartrees for $F_2$. On the other hand, the GGA correlation functionals yield consistently too high values as compared with $E_{1\text{emp}}$. For $N_2$ the largest difference of 0.068 hartrees is for $E_{1\text{LYP}}$ and for $F_2$ the largest difference of 0.086 hartrees is for $E_{1\text{PW}}$. These differences of opposite signs compensate each other to a large extent in the resulting GGA exchange-correlation energies. For $N_2$ the PW value $E_{1\text{PW}} = -13.67$ hartrees practically coincides with the corresponding KS value $E_1 + E_{1\text{emp}} = -13.666$ hartrees and the PW and BLYP values are not very far from $E_1 + E_{1\text{emp}}$. For $F_2$ there is also considerable compensation of errors of opposite sign in $E_1$ and $E_\tau$, but a somewhat larger difference between the KS and GGA values for $E_{1\text{xc}}$ remains (see Table IV).

Note, that according to Ref. 45, the deviation of the atomization energy of the $N_2$ molecule calculated with the PW approximation from the empirical atomization energy is 0.021 hartrees. Its sign indicates relative overestimation of the molecular total energy within the PW GGA, in agreement with the abovementioned overestimation of the exchange-correlation energy of this molecule ($E_{1\text{PW}}$ is 0.004 hartrees lower than $E_1 + E_{1\text{emp}}$), but the absolute value of the atomization energy error of PW is larger than that of the molecular exchange-correlation energy error. A possible reason for this might be a slight relative underestimation of the total energy of the $N$ atom with the PW GGA. Another reason is that calculations with the PW functional have been carried out in this paper and in Ref. 45 with different densities $\rho$. While in Ref. 45 $\rho$ obtained with the local spin density approximation has been used, in this paper the MRCI $\rho$ has been employed to calculate $E_{1\text{xc}}$.

We have observed in a study of the correlation energy density $e_\tau(r)$ Ref. 31 for dissociating $H_2$ that the GGA lacks the left-right correlation. This is also evident from the large error in $W_{1\text{PW}}$ as compared to the exact $W_1$ in the same case\textsuperscript{33} (\(-0.057\) instead of \(-0.207\) at $R = 5.0$ bohr). The trouble stems from the fact that the LDA and GGA approximations do not properly describe exchange and correlation separately. This may be understood from the exchange (Fermi) and correlation (Coulomb) hole functions $\rho_1(r_2|\mathbf{r}_1)$ and $\rho_\tau(r_2|\mathbf{r}_1)$ from which the corresponding energies may be obtained:

\begin{equation}
E_1 = \frac{1}{2} \int \frac{\rho_1(\mathbf{r}_1)\rho_\tau(\mathbf{r}_2|\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 d\mathbf{r}_2,
\end{equation}

\begin{equation}
W_\tau = \frac{1}{2} \int \frac{\rho_1(\mathbf{r}_1)\rho_\tau(\mathbf{r}_2|\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 d\mathbf{r}_2.
\end{equation}

\begin{table}[h]
\centering
\begin{tabular}{|l|ccc|}
\hline
 & $E_1$ & $E_\tau$ & $E_{1\text{xc}}$ \\
\hline
Li\(_2\) & $-3.084$ & $-0.330$ & $-3.414$ \\
PW/PW & $-3.537$ & $-0.137$ & $-3.674$ \\
BPW & $-3.555$ & $-0.137$ & $-3.692$ \\
BLYP & $-3.555$ & $-0.134$ & $-3.699$ \\
KS & $-3.565$ & $-0.128$ & $-3.693$ \\
\hline
N\(_2\) & $-11.873$ & $-0.942$ & $-12.815$ \\
BPW & $-13.208$ & $-0.490$ & $-13.698$ \\
BLYP & $-13.208$ & $-0.484$ & $-13.692$ \\
KS & $-13.114$ & $-0.552$ & $-13.666$ \\
\hline
H\(_2\) ($R = 1.401$) & $-0.569$ & $-0.095$ & $-0.664$ \\
PW & $-0.658$ & $-0.046$ & $-0.704$ \\
BPW & $-0.661$ & $-0.039$ & $-0.700$ \\
BLYP & $-0.662$ & $-0.038$ & $-0.700$ \\
KS & $-0.423$ & $-0.083$ & $-0.506$ \\
\hline
H\(_2\) ($R = 5.0$) & $-0.521$ & $-0.032$ & $-0.544$ \\
PW & $-0.512$ & $-0.032$ & $-0.544$ \\
BPW & $-0.410$ & $-0.186$ & $-0.596$ \\
BLYP & $-0.524$ & $-0.072$ & $-0.661$ \\
\hline
\end{tabular}
\caption{Kohn–Sham, LDA, and GGA exchange and correlation energies (a.u.). The KS entries in the $E_1$ and $E_{1\text{xc}}$ columns refer to the empirical estimates $E_{1\text{emp}}$ and $E_{1\text{xc}} = E_1 + E_{1\text{emp}}$.}
\end{table}
If the reference position \( \mathbf{r}_1 \) is close to nucleus \( A \) of a diatomic \( AB \), the exchange and correlation holes will be delocalized over both centers, irrespective of their distance. This delocalization is unphysical, and in fact the exchange and correlation holes on center \( B \) have opposite sign and cancel each other. They are both negative at \( A \) and build together a localized hole at \( A \) around the reference position \( \mathbf{r}_1 \). (We refer to Ref. 39 for an extensive discussion of the shape and behavior of exchange and correlation holes.) The electron gas does not contain the phenomenon of left–right correlation, the holes are always localized around the reference electron. The exchange and correlation functionals developed from the homogeneous or inhomogeneous electron gas cannot be expected to be able to describe the corresponding delocalized holes in molecules. However, it is an old notion\(^46\) that the exchange functional, since it mimicks a localized hole, might be hoped to be describing in molecules the combined effect of exchange and left–right correlation, which also leads to a localized hole (cf. also Ref. 47).

It is the so-called nondynamical or near-degeneracy correlation that introduces left–right correlation and effects the hole localization. The LDA and GGA functionals cannot describe the exact KS exchange, since it has a delocalized hole, but it is interesting to investigate to what extent the LDA or GGA exchange functionals effectively describe, even if not by construction, the combined effect of exchange and nondynamical correlation. Dynamical correlation alone might be described by the electron-gas based correlation functionals. The energy of nondynamical correlation \( E_{c}^{\text{nd}} \) can be estimated with the assumption that simple CI wave functions constructed in Ref. 33, which provide the proper dissociation limit (PDL) for the dimers \( A_2 \), take into account the effect of nondynamical correlation and neglect dynamical correlation. With this assumption the energy \( E_{c}^{\text{nd}} \) can be estimated as the difference between the electronic energies of the PDL and HF functions, \( E_{c}^{\text{nd}} = E_{\text{PDL}} - E_{\text{HF}} \). This yields \( E_{c}^{\text{nd}} \) values of \(-0.009, -0.076, \) and \(-0.079 \) hartrees for \( \text{Li}_2 \), \( \text{N}_2 \), and \( \text{F}_2 \), respectively. Thus, the energy effect of nondynamical correlation at \( R(J) \) is small for \( \text{Li}_2 \), while it is appreciable for \( \text{N}_2 \) and \( \text{F}_2 \). Bearing this in mind, we present in Table IV the energy of dynamical correlation \( E_{c}^{\text{d}} \) estimated as the difference \( E_{c}^{\text{d}} = E_{c}^{\text{em}} - E_{c}^{\text{em}} \) and the sum \( (E_{c} + E_{c}^{\text{em}}) \) of the exchange energy and \( E_{c}^{\text{em}} \). The energies \( E_{c}^{\text{d}} \) appear to be close to the GGA correlation energies,

\[
E_{c}^{\text{GGA}} \approx E_{c}^{\text{d}}. 
\]

Thus, we arrive at the conclusion that the GGA correlation functionals \( E_{c}^{\text{GGA}}(\rho) \) (\( E_{c}^{\text{PW}} \) or \( E_{c}^{\text{LYP}} \)) effectively model the dynamical correlation of electrons in \( \text{N}_2 \) and \( \text{F}_2 \). Similarly, the GGA “exchange” energies are actually much closer to the sum of exchange and nondynamical correlation energies,

\[
E_{x}^{\text{GGA}} \approx E_{x} + E_{c}^{\text{nd}}. 
\]

The localized hole corresponding to \( E_{x}^{\text{GGA}}(\rho) \) simulates the abovementioned combined effect of exchange and nondynamical correlation which produces a localized exchange-correlation hole. For \( \text{N}_2 \) the GGA exchange energies (especially, the PW one) are close to the sum \( (E_{x} + E_{c}^{\text{nd}}) \) (see Table IV). For \( \text{F}_2 \) the energies \( E_{x}^{\text{GGA}} \) are still too negative, but they are clearly much closer to \( (E_{x} + E_{c}^{\text{nd}}) \) than to the bare exchange energy \( E_{x} \). For \( \text{Li}_2 \), as was shown above, the effect of nondynamical correlation is small at \( R(J) \) and Eq. (5.4) reduces effectively within GGA to \( E_{c}^{\text{GGA}} \approx E_{c} \), while Eq. (5.3) reduces to \( E_{c}^{\text{GGA}} \approx E_{c} \). At elongated distances \( E_{c}^{\text{GGA}} \) is expected to become much larger, but no \( E_{c}^{\text{emp}} \) is available. We have therefore added to Table IV entries for the well-studied case of \( \text{H}_2 \) at both equilibrium distance and at \( R = 5.0 \) bohr, where we may rely on full-CI calculations to obtain accurate correlation energies. Full-CI results and \( E_{c}^{\text{GGA}} \) from a proper-dissociation CI involving just the configurations \((\sigma_J)^2 \) and \((\sigma_K)^2 \) have been obtained from Ref. 39. \( E_{c}^{\text{GGA}} \) is very small \((-0.001 \) a.u.) at \( R \), but at \( R = 5 \) bohr it is of course large \((-0.114 \) a.u.) for this prototype case of left–right correlation. There is a striking discrepancy at \( R = 5 \) bohr between the PW estimate of \( E_{c} \) \((-0.032) \) and the accurate KS value \((-0.186) \). In this case the near-degeneracy part of \( E_{c} \) is large, and \( E_{c}^{\text{PW}} \) is clearly much closer to \( E_{c} - E_{c}^{\text{nd}} \). Also \( E_{c} + E_{c}^{\text{nd}} \) is closer to the Becke exchange energy than the bare KS exchange energy is. Since \( T_{c} \) is small at this large distance, \( T_{c} \) is close to \( W_{c} \), and we note that the large discrepancy observed in Ref. 23 between \( W_{c} \) and \( W_{c}^{\text{PW}} \) may be similarly explained by \( W_{c}^{\text{PW}} \) lacking the near-degeneracy part.

Summarizing, GGA appears to provide approximately the partitioning

\[
E_{xc}^{\text{GGA}} = E_{x}^{\text{GGA}} + E_{c}^{\text{GGA}} = (E_{x} + E_{c}^{\text{nd}}) + E_{c}^{\text{d}}
\]

for the exchange-correlation energy.

VI. CONCLUSIONS

In this paper the difference between the DFT definition of exchange and correlation and the traditional Hartree–Fock based one is stressed. In particular we have noted that the components \( T_{c} \), \( V \), and \( W_{\alpha} \) of the KS energy differ significantly from their HF counterparts. The conceptual difference of the DFT and traditional definitions of the correlation energy is illustrated by the markedly different dependence of the corresponding kinetic components \( T_{c} \) and \( T_{c}^{\text{HF}} \) on the bond distance \( R(N–N) \). While \( T_{c}^{\text{HF}} \) rapidly increases with increasing \( R(N–N) \), \( T_{c} \) remains practically constant for the distances considered (cf. Ref. 48). However, at the equilibrium bond distances, due to compensation of differences of opposite sign, the total energies \( E^{\text{KS}} \) and \( E^{\text{HF}} \) of the KS and HF one-determinantal wave functions are close to each other, as are the corresponding exchange energies \( E_{x} \) and \( E_{x}^{\text{HF}} \). As a result, \( E_{c} \) and \( E_{c}^{\text{HF}} \) values are also close to each other. These results justify for the equilibrium geometry the existing practice to assess the performance of approximate DFT exchange and correlation functionals for molecules by comparing to conventional \( E_{x}^{\text{HF}} \) and \( E_{c}^{\text{HF}} \) values. For elongated bond distances the difference between \( E_{c} \) and \( E_{c}^{\text{HF}} \) increases somewhat. For \( \text{N}_2 \), a molecule with a triple bond and strong Coulomb correlation effects, the difference between \( E_{c} \) and \( E_{c}^{\text{HF}} \) has increased to 10% at 3.5 bohr. It is therefore worthwhile to take into account the difference between the DFT
and traditional definitions of correlation if one tries to develop DFT functionals capable to calculate accurately full molecular potential energy surfaces.

The HF determinant is often denoted as the “best” one-determinantal wave function (and therefore the HF orbitals as the “best” orbitals) since it yields the lowest energy. However, it is to be noted that the HF wave function makes quite large errors in important energy terms such as the kinetic energy and the electron–nuclear and electron–electron Coulomb energies. In N₂ for instance, the electron–nuclear energy is not negative enough by 15 eV at Rₐ, and by almost 50 eV at 3.5 bohr (to be compared to a bond energy of 10 eV and to a zero error in this term for the KS determinant). HF is making this error, which results from a too diffuse density, since it can lower the kinetic energy by making the density (i.e., the orbitals) diffuse. However, this increases the error in the kinetic energy; the HF error in the kinetic energy is at Rₐ twice the error of the kinetic energy of the KS orbitals, and at 3.5 bohr the HF error is four times as large (more than 33 eV too low, whereas Tₓ is only 8.5 eV too low). In short, HF is only trying to minimize the total energy, and it will make large errors in individual energy components if it can lower the total energy, even if only barely. It has been noticed that this “freedom” of HF to distort the density and the orbitals, if only the energy decreases, may lead to a distorted picture of chemical bonding, for instance to localized orbitals (ionic bonds) whereas more accurate wave functions (CASSCF) yield a covalent picture.⁴⁰⁴⁹ One can turn the above argument about the “distortion” effected by HF around and note that the KS determinant manages to improve the kinetic energy and various Coulomb energy terms with respect to HF very much, with only a small rise of the total energy, and therefore the (total) correlation energy. If the criterion for “best determinantal wave function” would not only be based on the correlation error in the total energy, but would also take into account the correlation errors in the physically important energy components discussed above, the KS determinantal wave function is clearly “better.”

It is not useful to argue about “better or not,” since this amounts to deciding on the best criterium, which may be a matter of taste, but it is important to note that the present results hold an important message concerning the status of Kohn–Sham orbitals as compared to Hartree–Fock orbitals. The Kohn–Sham approach has endowed chemistry and physics with a new set of one-particle wave functions (orbitals). The physical meaning of these orbitals has for some time remained somewhat obscure, and it is sometimes stated that one should not look for physical meaning or usefulness, but consider these orbitals as mere mathematical constructs whose only meaning is to build the exact density. However, we wish to reiterate that on the contrary the KS orbitals do make physical sense. This is a direct consequence of the form of the local potential $\nu_\text{x}(r)$ in which the KS electrons move,

$$\nu_\text{x}(r) = \nu(r) + \nu_{\text{HF}}(r) + \nu_{\text{Coulomb}}^\text{hole}(r) + \nu_{\text{Coulomb}}^\text{emp}(r)$$

The leading terms in $\nu_\text{x}$, the external (i.e., nuclear) field $\nu(r)$, the electronic Coulomb (or Hartree) potential $\nu_{\text{HF}}(r)$, and the potential of the exchange or Fermi hole, $\nu_{\text{Coulomb}}^\text{hole}(r)$, cause the KS orbitals to be roughly similar to the Hartree–Fock orbitals, with usually a similar nodal pattern and one-electron energy distribution. However, $\nu_{\text{Coulomb}}$ also contains the potential of the Coulomb hole $\nu_{\text{Coulomb}}^\text{hole}(r)$ (we do not discuss the less important contributions $\nu_{\text{Coulomb}}^\text{kin}$ and $\nu_{\text{Coulomb}}^\text{emp}$, cf. Refs. 51, 52, 14). It is $\nu_{\text{Coulomb}}^\text{hole}(r)$ that builds the most important aspects of electron correlation (such as the left–right correlation in a two-center bond) into the effective potential of the KS electron. The HF model causes an electron, when being in an atomic region, to feel too much repulsion from the remaining electrons (HF has too much weight for “ionic configurations,” in particular at long bond distances), hence the too diffuse nature of the HF orbitals. This HF error is annihilated by $\nu_{\text{Coulomb}}^\text{hole}(r)$, making the total field correspond to a proper localized exchange-correlation hole around the reference electron.³⁹ This prevents the orbitals and density from becoming distorted, as they sometimes are in the HF model (for instance too diffuse, or unduly localized at one end of the bond⁴⁰,⁴⁹, and results in the “advantages” of the KS orbitals noted above. These properties of the KS orbitals may also lead to superior performance (as compared to HF orbitals) in perturbation theoretic approaches to the electron correlation problem, or various types of CI approaches. In this respect also the realistic nature of the KS virtual orbitals will play a role; the KS virtual orbitals do not exhibit the artificial upshift and diffuse nature of the HF virtual orbitals, the one-electron energy differences $\Delta \epsilon_a = \epsilon_a - \epsilon_i$ between a virtual orbital $a$ and an occupied orbital $i$ are closely related to excitation energies. We wish to stress that the properties of the KS orbitals make them particularly suitable for use in the molecular orbital theories of chemistry.⁵³,⁵⁴

For atoms LDA is known to underestimate the exchange energy by roughly 10% and it overestimates the correlation energy by roughly 100%. The present examples demonstrate this to be true for molecules as well. The errors do not cancel precisely, the total LDA exchange-correlation energies are consistently too high (not negative enough) as compared to the sum ($E_\text{x} + E_\text{C}^{\text{emp}}$). The gradient corrections bring the GGA exchange and correlation energies much closer to $E_\text{x}$ and $E_\text{C}^{\text{emp}}$, but for N₂ and F₂ they seem to overcorrect and the GGA exchange energies are consistently too low (too negative), while the GGA correlation energies are too high as compared to $E_\text{x}$ and $E_\text{C}^{\text{emp}}$, respectively. However, the differences of opposite sign compensate each other and the resulting GGA exchange-correlation energies are rather close (especially, in the case of N₂) to the sum ($E_\text{x} + E_\text{C}^{\text{emp}}$).

Concerning the systematic deviations between the GGA and KS exchange and correlation energies separately, we have noted that qualitative considerations concerning the difference between Fermi and Coulomb holes in molecules and in the electron gas suggest that the GGA exchange functionals represent effectively not only exchange, but also the molecular nondynamical Coulomb correlation, while the GGA correlation functionals represent the dynamical Coulomb correlation. We have demonstrated that there is semiquanti-
tative evidence for this point of view. However, since the GGA models were derived from the inhomogeneous electron gas and (at least, some of them) are fitted for atoms, their proper representation of the molecular nondynamical correlation might appear somewhat accidental and the quality of the calculated total exchange-correlation energies may vary. This, indeed, happens in the case of F$_2$ (see Table IV) for which GGA seems to overestimate nondynamical correlation.

Further improvement of the approximate DFT functionals may require the development of gradient- and Laplacian-dependent model functionals for the exchange-correlation energy, in which the exchange and correlation components are not separated from each other.