Molecular exchange-correlation Kohn-Sham potential and energy density from ab initio first- and second-order density matrices: Examples for XH (X=Li, B, F)
Gritsenko, Oleg V.; van Leeuwen, Robert; Baerends, Evert Jan

Published in:
Journal of Chemical Physics

DOI:
10.1063/1.471602

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1996

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment.

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.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
Molecular exchange-correlation Kohn–Sham potential and energy density from ab initio first- and second-order density matrices: Examples for XH (X=Li, B, F)

Oleg V. Gritsenko, Robert van Leeuwen, and Evert Jan Baerends
Afdeling Theoretische Chemie, Vrije Universiteit, De Boelelaan 1083, 1081 HV, Amsterdam, The Netherlands

(Received 25 January 1996; accepted 1 March 1996)

The molecular Kohn–Sham exchange-correlation potential \( v_{xc} \) and the energy density \( \epsilon_{xc} \) have been constructed from ab initio first- and second-order density matrices for the series XH (X=Li, B, F). The way various effects of electronic structure and electron correlation manifest themselves in the exchange-correlation hole and the potential \( v_{xc} \) has been analyzed by their decomposition into various components: the potential of the exchange-correlation hole, the kinetic component and (in the case of \( v_{xc} \)) the ‘‘response’’ component. The kinetic energy of noninteracting particles \( T_s \), the kinetic part of the exchange-correlation energy \( T_c \), and the energy of the highest occupied molecular orbital \( \epsilon_N \) have been obtained with reasonable accuracy and the effect of bond formation on these functionals has been studied.

© 1996 American Institute of Physics. [S0021-9606(96)03021-8]

I. INTRODUCTION

Key ingredients of the density functional theory (DFT) (Refs. 1, 2) are the exchange-correlation energy functional \( E_{xc}[\rho] \) of a many-electron system,

\[
E_{xc}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}(\rho, \mathbf{r}) d\mathbf{r},
\]

and the corresponding exchange-correlation Kohn–Sham (KS) potential \( v_{xc}[\rho, \mathbf{r}] \),

\[
v_{xc}[\rho, \mathbf{r}] = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})},
\]

the latter represents the local effect of electron exchange and Coulomb correlation in the one-electron KS equations (Hartree atomic units will be used throughout the paper)

\[
\left\{ -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{H}(\mathbf{r}) + v_{xc}(\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}),
\]

\[
\sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2 = \rho(\mathbf{r}).
\]

\( E_{xc}[\rho] \) is expressed in Eq. (1) as an integral of the exchange-correlation energy density per particle \( \epsilon_{xc}(\rho, \mathbf{r}) \), while \( v_{xc}[\rho, \mathbf{r}] \) is defined in Eq. (2) as a functional derivative of \( E_{xc}[\rho] \) with respect to the electron density \( \rho(\mathbf{r}) \). In Eq. (3) \( v_{\text{ext}} \) is the external potential, \( v_{H} \) is the Hartree potential of the electrostatic electron repulsion, \( N \) is the number of electrons in the system, and the occupied KS orbitals \( \phi \) yield \( \rho \) via Eq. (4).

The exact functional form of \( v_{xc} \) and \( \epsilon_{xc} \) is not known. However, several methods have been proposed\(^3-10\) to construct \( v_{xc} \) numerically using an essentially accurate \( \rho \) from ab initio calculations. Hitherto, all these methods have been applied to few-electron atomic systems and only recently the first example of a \( v_{xc} \) has been obtained with the method of Ref. 9 for a molecular system with \( N>2 \), namely, the LiH molecule.\(^11\)

For the analysis of electron interaction and for efficient DFT approximation of \( v_{xc} \) it is useful to decompose \( v_{xc} \) into various components related to the electronic structure. In particular, one can decompose \( v_{xc} \) into the ‘‘energy’’ and ‘‘response’’ components.\(^12\) The former, namely, the potential of the exchange-correlation hole \( v_{xc}^{\text{hole}} \) and the potential \( v_{c,\text{kin}} \), representing the effect of Coulomb correlation on the kinetic functional, contribute also to the exchange-correlation energy functional. The latter represent ‘‘response’’ effects on \( v_{xc}^{\text{hole}} \) and \( v_{c,\text{kin}} \) and do not contribute to \( E_{xc}[\rho] \). Such a decomposition has been carried out\(^12\) for the atomic exchange-only potentials of the optimized potential model (OPM) (Refs. 13–15) and also for \( v_{xc} \) of the two-electron He atom and H\(_2\) molecule.\(^16\) However, to our best knowledge, \( v_{xc} \) for systems with \( N>2 \) have never been analyzed in this way.

Unlike \( v_{xc} \), which is defined uniquely (up to a constant) for a given system with Eq. (2), \( \epsilon_{xc} \) is not defined uniquely with Eq. (1), since the same \( E_{xc} \) can be obtained with different functions \( \epsilon_{xc}(\mathbf{r}) \) and \( \epsilon_{xc}'(\mathbf{r}) = \epsilon_{xc}(\mathbf{r}) + f(\mathbf{r}) \) whose difference \( f(\mathbf{r}) \) integrates to zero

\[
\int \rho(\mathbf{r}) f(\mathbf{r}) d\mathbf{r} = 0.
\]

Nevertheless, in order to perform a consistent analysis of correlation effects and to provide a physically reasonable modeling of \( \epsilon_{xc} \) one can choose some suitable definition of \( \epsilon_{xc}(\mathbf{r}) \). In particular, one can express \( \epsilon_{xc} \) as a combination of \( v_{xc}^{\text{hole}} \) and \( v_{c,\text{kin}} \) (Ref. 17). (See also the next section for this definition.) A procedure to construct \( \epsilon_{xc} \) from ab initio first- and second-order density matrices has been proposed in Ref. 17 and examples of the correlation energy density \( \epsilon \) have been obtained for the two-electron systems He and H\(_2\).

This paper presents molecular $v_{xc}$ and $\epsilon_{xc}$ constructed from \textit{ab initio} first- and second-order density matrices for the closed-shell monohydrides of elements of the second period Li, H, B, and F. The corresponding KS energy characteristics such as the kinetic energy of noninteracting particles $T_e$, the kinetic part of the correlation energy $T_c$ and the energy of the highest occupied molecular orbital (HOMO) $\epsilon_{xc}$ are also calculated and discussed. The relation between the form of $v_{xc}$ and the molecular electronic structure is analyzed via the decomposition of $v_{xc}$ into $v_{xc}^{\text{hole}}$, $v_{c,\text{kin}}$ and the response potential.

II. PARTITIONING OF $v_{xc}$ AND $\epsilon_{xc}$

To define $\epsilon_{xc}$ and to provide a partitioning for $v_{xc}$, we use the following expression for $E_{xc}[\rho]$:

$$E_{xc}[\rho] = W_{xc}[\rho] + T_e[\rho],$$  \hspace{1cm} (6)

$$W_{xc}[\rho] = \frac{1}{2} \int |\nabla \rho(r)|^2 v_{xc}(r) dr,$$  \hspace{1cm} (7)

$$T_e[\rho] = \int \rho(r) [v_{xc}(\rho(r)) - v_{c,\text{kin}}(\rho(r))] dr.$$  \hspace{1cm} (8)

The first term of Eq. (6) is the potential (i.e., electron–electron interaction) contribution $W_{xc}$ to $E_{xc}$ with $v_{xc}^{\text{hole}}$ in Eq. (7) being the potential of the exchange-correlation-hole,

$$v_{xc}^{\text{hole}}(\mathbf{r}_1) = \int \frac{\rho_2(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|^2} d\mathbf{r}_2.$$  \hspace{1cm} (9)

In Eq. (9) $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ and $g(\mathbf{r}_1, \mathbf{r}_2)$ are the diagonal part of the second-order density matrix and the pair-correlation function with the electron interaction $\lambda/|\mathbf{r}_1 - \mathbf{r}_2|$ at full strength, $\lambda = 1$. The second term of Eq. (6) is the kinetic contribution $T_e$ to $E_{xc}$ with the local potential $v_{c,\text{kin}}(\rho)$ being defined as follows:

$$v_{c,\text{kin}}(\mathbf{r}_1) = \frac{1}{2} \int |\nabla \Phi(s_1, x_2, \ldots, x_N|\mathbf{r}_1)|^2 ds_1 dx_2 \cdots dx_N,$$  \hspace{1cm} (10)

$$= \frac{\nabla^2 v_{c,\text{kin}}(\rho(\mathbf{r}_1))}{2\rho(\mathbf{r}_1)}.$$  \hspace{1cm} (11)

In Eq. (10) $\Phi(s_1, x_2, \ldots, x_N|\mathbf{r}_1)$ is the conditional probability amplitude of the total wave function $\Psi(x_1, x_2, \ldots, x_N|h(x)|\{s_1, \ldots, s_j\})$ (the space and $\{s_j\}$ are the spin variables),

$$\Phi(s_1, x_2, \ldots, x_N|\mathbf{r}_1) = \frac{\Psi(x_1, \ldots, x_N)}{\sqrt{\rho(\mathbf{r}_1)}},$$  \hspace{1cm} (12)

and $\rho(\mathbf{r}_1)$ is the first-order density matrix for $\lambda = 1$. $\Phi(s_1, x_2, \ldots, x_N|\mathbf{r}_1)$ embodies all effects of electron correlation (exchange as well as Coulomb) in that its square is the probability distribution of the remaining $N - 1$ electrons associated with positions $x_2, \ldots, x_N$ when one electron is known to be at $\mathbf{r}_1$. $v_{c,\text{kin}}$ can be interpreted as a measure of how strongly the motion of the reference electron at $\mathbf{r}_1$ is correlated with other electrons in the system, in the sense that it reflects the magnitude of change in $\Phi$ with changing $\mathbf{r}_1$ (so it is a measure of the change in correlation hole with reference position $\mathbf{r}_1$). $v_{s,\text{kin}}$ is defined analogously to $v_{\text{kin}}$ in terms of the Kohn–Sham functions.

$$v_{s,\text{kin}}(\mathbf{r}_1) = \frac{1}{2} \int |\nabla \Phi(s_1, x_2, \ldots, x_N|\mathbf{r}_1)|^2 ds_1 dx_2 \cdots dx_N,$$  \hspace{1cm} (13)

$$= \frac{1}{2} \sum_{i=1}^{N} |\nabla \phi(r_i)|^2 \rho(\mathbf{r}_i)/\rho(\mathbf{r}_1).$$  \hspace{1cm} (14)

From Eqs. (1), (6), (7), (8) one can define $\epsilon_{xc}$ as follows:

$$\epsilon_{xc}(\mathbf{r}) = \frac{1}{2} v_{xc}^{\text{hole}}(\mathbf{r}) + v_{c,\text{kin}}(\mathbf{r}),$$  \hspace{1cm} (15)

where

$$v_{c,\text{kin}}(\mathbf{r}) = v_{\text{kin}}(\mathbf{r}) - v_{s,\text{kin}}(\mathbf{r}).$$  \hspace{1cm} (16)

Note that this definition of $\epsilon_{xc}$ is in terms of unique potentials that enter the Kohn–Sham equations and the effective potential for the density amplitude $\sqrt{\rho}$, and that have a clear physical interpretation. In the DFT literature an alternative definition of $\epsilon_{xc}$ is often used, in which it is expressed via an integral over the coupling parameter $\lambda$.

$$\epsilon_{xc}(\mathbf{r}_1) = \frac{1}{2} \int_0^\lambda \int_0^\lambda \rho(\mathbf{r}_1)|g^\lambda(\mathbf{r}_1, \mathbf{r}_2) - 1| d\lambda d\mathbf{r}_2$$  \hspace{1cm} (17)

In this paper, however, we choose definition (14) as more convenient for our purpose, since in this case one does not need to know the dependence of $g^\lambda$ on $\lambda$.

Equation (14) provides also a partitioning of $v_{xc}$. Taking the functional derivative Eq. (2) of Eq. (6) leads to the following expression for $v_{xc}$:

$$v_{xc}(\rho; \mathbf{r}) = v_{xc}^{\text{hole}}(\rho; \mathbf{r}) + v_{c,\text{kin}}(\rho; \mathbf{r}) + v_{\text{resp}}(\rho; \mathbf{r}),$$  \hspace{1cm} (18)

where

$$v_{\text{resp}}(\rho; \mathbf{r}) = v_{xc}^{\text{hole,resp}}(\rho; \mathbf{r}) + v_{c,\text{kin}}^{\text{resp}}(\rho; \mathbf{r}).$$  \hspace{1cm} (19)

Here the potential $v_{xc}^{\text{hole,resp}}(\rho; \mathbf{r})$ is an integral of the linear “response” of $g(\rho; \mathbf{r}_1, \mathbf{r}_2)$ to the change $\delta(\rho; \mathbf{r}_1, \mathbf{r}_2)$ in the density $\rho(\mathbf{r})$.

$$v_{xc}^{\text{hole,resp}}(\rho; \mathbf{r}) = \int \frac{(\rho(\mathbf{r}_1) \rho(\mathbf{r}_2) - \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) g(\rho; \mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1) - \rho(\mathbf{r}_2)} d\mathbf{r}_1 d\mathbf{r}_2.$$  \hspace{1cm} (20)

It is a measure of the sensitivity of the pair-correlation function to density variations. These density variations may be understood in the following way. If the density changes to $\rho + \delta \rho$, then according to the Hohenberg–Kohn theorem this changed density corresponds uniquely to an external potential $v_{\text{ext}} + \delta v_{\text{ext}}$. For the system with external potential $v_{\text{ext}} + \delta v_{\text{ext}}$ we have the corresponding Kohn–Sham system and the pair-correlation function $g(\rho + \delta \rho; \mathbf{r}_1, \mathbf{r}_2)$. So the derivative occurring in the response
III. CONSTRUCTION OF $v_{xc}$ AND $\epsilon_{xc}$

To construct $v_{xc}$, $\epsilon_{xc}$ and their components, the first-order density matrix $p(r'|r)$, its diagonal part $\rho(r)$ and the diagonal part $p_2(r_1, r_2)$ of the second-order density matrix from \textit{ab initio} calculations are used as the input functions. In our actual implementation, these functions are represented as matrices in the basis of the Hartree–Fock MO's. A scheme for the numerical construction consists of the following steps: \cite{11}

1. For a given grid $\{r\}$, the Hartree potential $\rho(r)$ is calculated from the correlated density $\rho(r)$, $\epsilon_{kin}(r)$ is calculated from $\rho(r')$, $\rho(r)$ via Eq. (10) and $v_{xc}^{hole}(r)$ is calculated from $\rho(r)$ and $p_2(r_1, r_2)$ via Eq. (9). $\epsilon_{kin}$ and $v_{xc}^{hole}$ are used for the analysis of $v_{xc}$ and for the construction of $\epsilon_{xc}$, while $v_{H}$ and $v_{xc}^{hole}$ are used in the procedure of $v_{xc}$ construction as components of the starting potential of electron interaction $v_{el}^{0}$.

2. The set of KS orbitals $\{\phi_i(r)\}$ are obtained from the correlated $\rho(r)$ with an iterative procedure, \cite{9} starting from some initial guess $\rho_0^{el}$ for $v_{el}^{0}$,

$$v_{el}^{0}(r) = v_{H}(r) + v_{xc}(r).$$

At the $n$th iteration the KS equations (3) are solved with the potential $\rho_n^{el}$,

$$\rho_n^{el}(r) = f_m(r) v_{el}^{n-1}(r),$$

from which the previous iteration with the correction factor $f_m$, the latter being the ratio of the density $\rho^{m-1}$ from the $(m-1)$th iteration and the given $\rho$,  \begin{equation}
0 = \frac{(\rho(r)) = \rho^{m-1}(r)}{\rho(r)}.
\end{equation}

Then, $\rho^{m-1}$ in Eq. (24) is replaced with $\rho^{m}$ obtained at the $m$th iteration and this procedure continues until further iterations cease lowering the difference $|\rho^{m}(r) - \rho^{m}(r)|$ in the region of nonvanishing densities. Finally, $v_{xc}(r)$ is obtained by subtracting $v_{H}(r)$ from the resulting potential (22). As was pointed out in Ref. 9, this iterative procedure is not guaranteed to converge. However, if it converges then its limit is unique as guaranteed by the Hohenberg–Kohn theorem applied to a noninteracting electron system. \cite{22}

In the calculations we have used a slightly modified form Eq. of (24),

$$f_m(r) = \frac{\rho^{m-1}(r) + a}{\rho(r) + a},$$

with $a=0.5$, which smooths out the effect of the remote exponential density tails on the procedure.

3. $v_{xc}(r)$ is calculated from $\rho_0^{el}(r)$, $\rho(r)$ and $\{\phi_0(r)\}$ via Eqs. (12)–(15) and $v_{xc}^{0}(r)$ is calculated by subtracting $v_{xc}^{0}(r)$ from the constructed $v_{xc}(r)$.

4. $\epsilon_{xc}(r)$ is obtained according to Eq. (14). Implementation of this scheme for the monohydrides LiH, BH, HF will be discussed in the next sections.

IV. DETAILS OF CALCULATIONS FOR LH, BH, HF

The monohydrides XH (X=Li, B, F) have been chosen because they form the simplest series of closed-shell molecules. For those molecules accurate empirical estimates of the Coulomb correlation energies $E^c_r$ are available. \cite{23} The correlated wave functions for XH have been obtained with singly and doubly excited configuration interaction (SDCI) calculations of the ground states at equilibrium distances $R(Li-H)=3.015$ a.u., $R(B-H)=2.330$ a.u., $R(H-F)=1.733$ a.u.. Calculations have been performed within the direct CI approach by means of the ATOML package. \cite{24}

A basis of contracted Gaussian functions \cite{25} has been used with five $s$- and two $p$-type functions for H, seven $s$- and four $p$-type functions for Li, and seven $s$-, four $p$- and two $d$-type functions for B and F. For H an extra valence polarization $d$-function with the exponent $\alpha=1.0$ and for Li two such functions with the exponents $\alpha=0.36$ and $\alpha=0.15$ have been used. In order to better take into account the correlation effects for core electrons, this basis has been augmented for X with two localized polarization $p$- and two $d$-functions of the core size, whose exponents were set equal to those of the second most localized contracted $s$-function of the basis. \cite{25}

The increase in the absolute value of the correlation energy due to inclusion of core polarization functions amounts to 6% of $E^c_r$ for LiH, 14% for BH, and 8% for HF, so that the SDCI calculations recover 93% of $E^c_r$ for LiH, 90% for BH, and 78% for HF.

Calculation of $\rho(r', r)$ and $p_2(r_1, r_2)$ from the SDCI wave functions with the subsequent construction of $v_{xc}$, $\epsilon_{xc}$ and their components has been performed in the same basis of MO’s as the SDCI calculations by means of a special density functional extension of the \textit{ab initio} ATOML package. Matrix elements of $v_{el}^{m}$ in this basis have been calculated using a numerical integration with grids according to Ref. 27.

To obtain $v_{xc}$ and $\{\phi\}$ via the procedure (22)–(25), two alternative initial potentials $v_{el}^{0}$,

$$v_{el}^{0}([\rho];r) = v_{H}([\rho];r) + v_{xc}^{0}([\rho];r),$$

$$v_{el}^{0}([\rho];r) = v_{H}([\rho];r) + v_{xc}^{0}([\rho];r) + v_{resp}^{0}([\rho];r),$$

have been employed. In Eqs. (26), (27) $v_{H}$ and $v_{xc}^{0}$ are the rigorous Hartree potential and exchange-correlation hole potential calculated from the correlated $\rho(r)$ and $p_2(r_1, r_2)$, while $v_{xc}^{0}$ and $v_{resp}^{0}$ are the following approximations: \cite{28}
\[ v_{\alpha}^0(\rho; r) = v_{X\alpha}(\rho; r) + 2 \epsilon_i^B(\rho; r) \nabla \rho(\rho; r) + 2 \epsilon_c^{\text{VWN}}(\rho; r), \]

(28)

\[ v_{\text{res}}^0(\rho; r) = 0.382 \sum_{i=1}^N \sqrt{\mu - \epsilon_i} |\phi_i(r)|^2 \rho(r). \]

(29)

In Eq. (28) \( v_{X\alpha} \) is the exchange-correlation X\( \alpha \) potential,\(^{29} \) \( \epsilon_i^B \) is the exchange energy density gradient correction of Becke,\(^{30} \) and \( \epsilon_c^{\text{VWN}} \) is the local density approximation (LDA) of Vosko, Wilk, and Nusair\(^{31} \) for the correlation energy density. The parameter \( \alpha \) of \( v_{X\alpha} \) is chosen from the following fitting condition:

\[ -\frac{1}{2} \nabla^2 + v_{\text{ex}}(r) + v_{\text{res}}^0(r) \phi_N(r) = -I_p \phi_N(r), \]

(30)

where \( \phi_N \) is the highest occupied Kohn–Sham molecular orbital (HOMO) and \( I_p \) is the experimental ionization energy of the molecule. The Kohn–Sham calculation with this optimized potential may also be used to construct \( v_{\text{res}}^0 \) of Eq. (29), which is the KS orbital dependent approximation\(^{28} \) for \( v_{\text{res}} \) with \( \epsilon_i \) being the energy of the KS orbital \( \phi_i \) and \( \mu \) being the Fermi level of a given system, which is equal to the energy of the HOMO \( \mu = \epsilon_N \). Both potentials (26) and (27) have a proper long-range Coulombic asymptotics \( v_{\alpha}^0 \rightarrow -(Z-1)/|r| \).

For the lighter monohydrides LiH and BH the results obtained depend only slightly on the type of the initial guess used, with Eq. (26) providing a somewhat better final HOMO energy. This is probably due to the fact that for this property “perfect” starting potential (cf. Eq. (30)). After 45–50 iterations the procedure (22)–(25) has reached its saturation state, with no further discernible change of results. The densities obtained agree with the correlated \( \rho \) within 0.1% in the region of nonvanishing densities. Similar accuracy for \( \epsilon_N \) (and \( \rho \)) may probably be obtained with the starting potential of Eq. (27) by varying the constant in \( v_{\text{res}}^0 \) [Eq. (29)] so as to start with the accurate \( \epsilon_N = -I_p \), but we are satisfied with the solution obtained with the initial guess (26). The results obtained with this starting potential will be presented in the next section.

For the heavier HF system the initial potential (26) appears to overestimate substantially the attractive character of \( v_{xc} \) near the F nucleus. The subsequent iterative procedure has not been able to remove this defect and it has not reached its saturation state even after 100 iterations. The resulting \( v_{xc} \) appears to be very close to \( v_{\text{hole}} \) near the F nucleus. Since it is known\(^{12,28} \) that the response potential \( v_{\text{res}} = v_{xc} - v_{\text{hole}} \) is fairly large and positive in the \( 1s \) region (see Fig. 8 below), and \( v_{\text{kin}} \) is much smaller (cf. Fig. 7), \( v_{xc} \) is obviously somewhat deficient. On the other hand, with the initial guess (27) for HF, which does build in correctly this repulsive term in the \( 1s \) region (cf. Eq. (29)) from the start, the procedure did approach its saturation state with the resulting \( v_{xc} \) being appreciably less attractive than \( v_{\text{hole}} \) near the F nucleus. The results for HF obtained with the initial guess (27) will be presented in the next sections.

### V. Kohn–Sham Energy Characteristics

Table I presents various energy characteristics for the KS orbitals \{\( \phi_i(r) \}\), which have been obtained with the procedure (22)–(25). The first is the HOMO energy \( \epsilon_N \). According to Refs. 33–36, an accurate HOMO energy \( \epsilon_N \) is equal to the minus the ionization potential of the system \( I_p \) and \( \epsilon_N \) values obtained for XH are indeed close to the experimental \( -I_p \) values (see Table I). In this respect it is informative to consider the evolution we observed of \( \epsilon_N \) calculated for LiH and BH during the cycles of the iteration procedure. Starting from the value \( \epsilon_N = -I_p \) [because of the fitting condition (30)], \( \epsilon_N \) departs from \( -I_p \) at the first few iterations with simultaneous lowering of the calculated KS kinetic energy \( T_s \) and then goes back to the value \( -I_p \) at the subsequent iterations.

Table I also presents the kinetic energy of the KS system \( T_s \).

\[ T_s = -\frac{1}{2} \sum_{i=1}^N \int \phi_i^*(r) \nabla^2 \phi_i(r) d^3r \]

(31)

and the kinetic part of the exchange-correlation energy \( T_c \), where we indicate the fact that we are dealing with an approximation to this quantity by a CI calculation by way of the superscript CI,

\[ T_c^{CI} = T_c - T_s = \int \rho(r) v_{\text{kin}}(r) d^3r. \]

(32)

Since the DFT definition of correlation energy deviates from the conventional one, which is always with respect to the Hartree–Fock energy as the reference, we will denote the conventional quantities with the subscript HF:

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

\[ T_{c,\text{HF}} = T - T_{\text{HF}}. \]

(33)

Due to the virial theorem these exact quantities are equal

\[ T_{c,\text{HF}} \frac{E_{c,\text{HF}}}{E_{\text{HF}}} = -1. \]

(34)

The approximation to the exact conventional correlation energy that we obtain from our SDCI calculation, \( E_{c,\text{HF}}^{CI} \), may

---

**Table I.** Kohn–Sham energy characteristics (a.u.).

<table>
<thead>
<tr>
<th></th>
<th>LiH</th>
<th>BH</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \epsilon_{\text{HOMO}} )</td>
<td>-0.284</td>
<td>-0.359</td>
<td>-0.585</td>
</tr>
<tr>
<td>( -I_p )</td>
<td>-0.283</td>
<td>-0.359</td>
<td>-0.589</td>
</tr>
<tr>
<td>( T_s )</td>
<td>7.993</td>
<td>25.119</td>
<td>100.027</td>
</tr>
<tr>
<td>( T_{\text{HF}}^{CI} )</td>
<td>8.058</td>
<td>25.252</td>
<td>100.309</td>
</tr>
<tr>
<td>( T_{\text{CI}} )</td>
<td>0.057</td>
<td>0.099</td>
<td>0.237</td>
</tr>
<tr>
<td>( T_{c,\text{HF}}^{CI} )</td>
<td>0.061</td>
<td>0.110</td>
<td>0.304</td>
</tr>
<tr>
<td>( \Delta T_s )</td>
<td>0.061</td>
<td>0.093</td>
<td>0.102</td>
</tr>
<tr>
<td>( \Delta T_c )</td>
<td>0.023</td>
<td>0.012</td>
<td>0.050</td>
</tr>
</tbody>
</table>
be compared to the known exact values,\textsuperscript{23,32} to obtain improved estimates from the CI approximations to $T_{c,\text{HF}}$ and to $T_c$.

$$T_{c,\text{HF}}^\prime = T_{c,\text{CI}}^\prime \frac{E_{c,\text{HF}}}{E_{c,\text{CI}}},$$

$$T_c^\prime = T_c^\prime \frac{E_{c,\text{HF}}}{E_{c,\text{CI}}}. \quad (35)$$

The correction factors are 1.075, 1.11, and 1.28 for LiH, BH, and FH, respectively. The extrapolated values for $T_c$, denoted with a superscript $\prime$ (cf. Table I), are still approximations for two reasons. In the first place, applying the correction factor deduced from the correlation energies (exact and CI) to just the kinetic part of the correlation energy is only allowed if the virial theorem would also hold for the approximate CI, whereas it will only hold exactly for a full CI. In the second place, the correction factor is not necessarily equal for $T_{c,\text{CI}}^\prime$ and $T_c^\prime$. In particular, the extrapolation of $T_c$ will be dubious in systems that are not good Hartree–Fock cases, i.e., where a single determinant is not a good first order approximation to the wave function, such as a dissociating molecule. In such a case $T_c$ may differ strongly from $T_{c,\text{HF}}$, cf. Table II in Ref. 16.

It is interesting to consider in the present series of molecules, where Hartree–Fock is a reasonable first approximation, what actually the difference is between $T_c$ and $T_{c,\text{HF}}$. The KS kinetic functional $T_c[\rho]$ minimizes the kinetic energy for a Kohn–Sham determinant with the density constrained to the correlated density $\rho$. It is well known that the correlated density is more contracted around the nuclei than the Hartree–Fock density, which is extremely so in poor Hartree–Fock cases like dissociating $H_2$.\textsuperscript{16,46} Due to this contraction effect of correlation, the minimal energy $T_c$ is still higher than $T_{c,\text{HF}}$. Although the difference is not large percentage wise (see Table I), it is not negligible on the scale of the difference between $T_{c,\text{CI}}$ and $T_c$, i.e., $T_c$. As a result, the ratio $T_{c,\text{CI}}^\prime/T_{c,\text{HF}}^\prime$ is consistently lower than 1 for $XH$ ranging from 0.75 for BH to 0.88 for LiH. We may expect this ratio to be closer to 1 in the corresponding atoms, since the atoms $X$ are closer to the limiting case of tightly bound, good Hartree–Fock systems.

One can study the effect of bond formation on the kinetic functionals by comparison of $T_c$ and $T_c^\prime$ values obtained at the equilibrium $X–H$ distance with the sum of atomic values for $X$ and $H$. For the one-electron $H$ atom $T_c(H)=0$ and the KS system coincides with the exact one, so that, according to the virial theorem, $T_c(H)$ is equal to minus the total energy of the H atom $T_c(H)=0.5$ a.u. Taking $T_c(X)$ values from Ref. 37 and extracting $T_c^\prime(X)$ values from the data reported in this reference, we obtain the differences

$$\Delta T_c = T_c(XH) - T_c(X) - 0.5, \quad (36)$$

$$\Delta T_c^\prime = T_c^\prime(XH) - T_c^\prime(X), \quad (37)$$

which are presented in Table I. We note that the atomic data in Ref. 37 are approximate since the atoms are open shell systems that have been treated using shell averaging.

For the series $XH$ ($X=\text{Li, B, F}$) the difference $\Delta T_c$ is a positive quantity, which increases monotonically from 0.061 a.u. for LiH to 0.093 a.u. for BH and to 0.102 a.u. for FH. The positive sign of $\Delta T_c$ is in line with the positive sign of the exact as well as Hartree–Fock values for the kinetic energy change upon bond formation. It reflects contraction of the KS orbitals occurring at bond distances close to $R_e$. This can be understood, if we rewrite the expression (31) for $T_c$ in the gradient form,\textsuperscript{1}

$$T_c = \frac{1}{\pi} \sum_{i=1}^{N} \int |\nabla \phi_i(\mathbf{r})|^2 d\mathbf{r}. \quad (38)$$

The more localized the KS orbitals are, the higher are their gradients, which leads, according to Eq. (38) to increase of $T_c$. The energetical effect of the orbital contraction increases with increasing nuclear charge of the $X$ atom. The kinetic energy effects due to bond formation, in particular the lowering of the kinetic energy at long distances and the orbital contraction and concomitant kinetic energy rise at $R=\infty$ have been studied in the classical papers by Ruedenberg \textit{et al.} on $H_2^+$ and $H_2$.\textsuperscript{38,39} An analysis of kinetic energy effects for individual Kohn–Sham orbitals describing various bond types ($\sigma$ and $\pi$) at long and short distances has been given in Ref. 40.

The difference $\Delta T_c$ reflects the effect of bond formation on the kinetic part of the correlation functional. Unlike $\Delta T_c$, it changes nonmonotonically in the series $XH$: $\Delta T_c$ is minimal for BH (0.012 a.u.), it is larger for LiH (0.023 a.u.), and it has the largest value 0.050 a.u. for FH. Note the same trend for the difference $\Delta E_{c,\text{HF}} = E_{c,\text{HF}}(XH) - E_{c,\text{HF}}(X)$ of the conventional total correlation energies,\textsuperscript{23} which have the values 0.038, 0.028, and 0.064 a.u. for LiH, BH, and HF, respectively. This is not surprising, because the conventional exact quantities $T_{c,\text{HF}}$ and $E_{c,\text{HF}}$ are equal on account of the virial theorem, and $T_c$ is roughly proportional to $T_{c,\text{HF}}$ for both atomic and molecular systems considered.

VI. POTENTIALS AND ENERGY DENSITIES

In Figs. 1–3 the molecular Kohn–Sham exchange-correlation potentials $v_{\text{xc}}$ constructed for the series $XH$ ($X=\text{Li, B, F}$) are compared with the potentials of the exchange-correlation hole $v_{\text{xc}}^{\text{hole}}$. The potentials are plotted along the bond axis, as functions of the distance $z$ from the bond midpoint. In all cases $v_{\text{xc}}$ is everywhere less attractive than the corresponding $v_{\text{xc}}^{\text{hole}}$. This is an anticipated trend since, according to Eq. (17), $v_{\text{xc}}$ can be obtained by addition of $v_{\text{resp}}$ and $v_{c,\text{kin}}$ to $v_{\text{xc}}^{\text{hole}}$, and the former potentials are expected\textsuperscript{12,16,42} to be mainly repulsive.

The form of $v_{\text{xc}}$ resembles that of $v_{\text{xc}}^{\text{hole}}$, for instance, both potentials have a deep well around the nucleus $X$. This is simply due to the fact that at positions $r$ within the 1$s$ shell the exchange hole surrounding $r$ is very close to minus the 1$s$ density, leading to a strongly attractive potential. Still, there exists a significant difference between $v_{\text{xc}}$ and $v_{\text{xc}}^{\text{hole}}$; while $v_{\text{xc}}^{\text{hole}}$ is a rather smooth potential, $v_{\text{xc}}$ displays a characteristic structure. The most visible features of $v_{\text{xc}}$ are the local maxima (intershell peaks) between the core and valence

regions. One can see them most clearly on the outer sides of the B and F atoms with the maxima of the peaks being placed at \( z = -1.90 \) a.u. and \( z = -1.22 \) a.u., respectively. The outer-side intershell peak is more pronounced in the case of the F atom in the HF molecule, while it is less pronounced for B and it completely disappears for Li in the LiH molecule. The same trend is observed for the intershell peaks of individual atoms X~ see Figs. 2 and 3 of Ref. 37~. Analogous peaks are displayed on the inner, bonding sides of X in BH and HF with the maxima at \( z = 0.45 \) a.u. and \( z = 0.50 \) a.u., respectively. \( v_{\text{xc}} \) for LiH also exhibits a peak in the bonding region, but its maximum \( z = -0.22 \) is closer to the bond midpoint and this peak seems to be caused by a combination of various correlation effects (see the discussion below).

\( v_{\text{xc}} \) displays also features in the valence region, which can be related to the heteropolar nature of the diatomic bonds, leading to anionic atoms F~ and H~ in HF and H~ in LiH. Local wells in \( v_{\text{xc}} \) are discernable that ‘attract’ electrons to the electronegative atom. For HF this well surrounds the F core just beyond the intershell peak and where the bond axis intersects with the well local minima in \( v_{\text{xc}} \) are visible in Fig. 3 at \( z = -1.39 \) a.u. and \( z = -0.31 \) a.u. For LiH, this well spans the region of the H atom (see Fig. 1) with the minimum placed at the H nucleus (we neglect the small wiggle at the H nucleus, which probably is an artefact of the iterative procedure of \( v_{\text{xc}} \) construction). These wells favor accumulation of the electron density on the more electronegative atoms F (in HF) and H (in LiH), thus providing the ionic patterns of the electron distribution H~F~ and Li~F~. For BH, a molecule with a more covalent type of bonding, \( v_{\text{xc}} \) exhibits a more ‘covalent’ pattern, having a flat shape in the bonding region (see Fig. 2).

In Figs. 4–6 the exchange-correlation energy density \( E_{\text{xc}} \) [as defined in Eq. (14)] is plotted for the series XH together with its potential \( \frac{1}{2}v_{\text{xc}}^{\text{hole}} \) and kinetic \( v_{\text{c,kin}} \) components. It is not surprising, that the form of \( E_{\text{xc}} \) is determined primarily by that of its potential component. While \( v_{\text{c,kin}} \) represents a Coulomb correlation effect, \( v_{\text{xc}}^{\text{hole}} \) represents also the exchange, a dominating part of the total electronic exchange-correlation. Still, a proper account of the pure Coulomb correlation effect on both potential and kinetic functionals, embodied in the Coulomb hole potential \( v_{\text{c,kin}} \) and in \( v_{\text{c,kin}} \), is important for an adequate description of molecular systems, especially for one-electron properties of valence electrons and for bonding properties.

In all cases \( E_{\text{xc}} \) has a deep and rather sharp well around the X nucleus, caused by \( \frac{1}{2}v_{\text{xc}}^{\text{hole}} \), i.e., by the exchange hole in the 1s shell, see above. However, the form of \( E_{\text{xc}} \) in the region of the H atom changes substantially within the series XH. For LiH \( E_{\text{xc}} \), just as its dominating component \( \frac{1}{2}v_{\text{xc}}^{\text{hole}} \), has a distinct well around the H nucleus, while for BH such a well becomes very shallow and for HF it completely dis-
appears. This trend reflects the above-mentioned effect of a different ionicity of the H atom on \( v_{xc}^{\text{hole}} \), which is also the dominating component of \( v_{xc} \).

The kinetic part \( v_{c,\text{kin}} \) of the exchange-correlation energy density is small compared to \( \epsilon_{xc} \), due to the large exchange contribution to that quantity. Nevertheless, addition of \( v_{c,\text{kin}} \) to \( v_{xc}^{\text{hole}} \) produces some structure in \( \epsilon_{xc} \). One may mention the distinct peak of \( \epsilon_{xc} \) in the bond midpoint region of LiH (see Fig. 4) or its small intershell peak on the outer side of the B atom in BH (see Fig. 5).

In Figs. 7(a) and 7(b) the potentials \( v_{c,\text{kin}} \) are presented. In order to make the comparison more clear, in Fig. 7(a) the plot of \( v_{c,\text{kin}} \) vs the scaled coordinate \( z' = 1.29z \) (1.29 is the bond length ratio for LiH and BH) for BH is compared with \( v_{c,\text{kin}(z)} \) for LiH, so that the nuclear positions in both plots coincide. Analogously, in Fig. 7(b) the plot \( v_{c,\text{kin}}(z') \), \( z' = 1.34z \) for HF is compared with \( v_{c,\text{kin}}(z) \) for BH.

Figures 7(a) and 7(b) show that \( v_{c,\text{kin}} \) is an oscillating function in the region of the atom X, the oscillations tend to become more contracted with increasing atomic number of X. Apart from this contraction, \( v_{c,\text{kin}} \) displays some characteristic patterns. Its most visible features are the positive peaks in the intershell regions. One can see them, for example, on the inner, bonding side of the X atom with the maxima of the peaks being placed at \( z = -0.27 \) for LiH and \( z' = -0.65 \) for BH in Fig. 7(a), and at \( z = -0.50 \) for BH and \( z' = -0.74 \) for HF in Fig. 7(b). The peaks are higher and closer to the nucleus for the heavier X, the latter feature illustrates the abovementioned contraction of the \( v_{c,\text{kin}} \) oscillations. Note, that scaling of the \( z \) coordinate reduces the visual effect of contraction, so that for the real, unscaled coordinate \( z \) the contraction of oscillations is stronger.

Closer to the X nucleus, the peaks of \( v_{c,\text{kin}} \) are replaced with negative wells of a lower amplitude (except for the sharp peak at the nucleus mentioned before). In the bonding region \( v_{c,\text{kin}} \) has a smoother behavior. It decreases in the direction of the H atom, passing through a small local maximum in the bonding region. In this region \( v_{c,\text{kin}} \) is somewhat reminiscent (especially for HF) of the corresponding potential for the \( H_2 \) molecule at the equilibrium distance, which has been constructed in Ref. 16.

This complicated behavior of \( v_{c,\text{kin}} \) reflects the fact that, according to its definition (15), the relatively small \( v_{c,\text{kin}}(\mathbf{r}_1) \) is a difference of two larger potentials, \( v_{\text{kin}}(\mathbf{r}_1) \) and \( v_{s,\text{kin}}(\mathbf{r}_1) \). In its turn, the latter difference is determined according to Eqs. (10), (12) by the integrated difference of the conditional amplitude gradients \( \left| \nabla_x \Phi(s_1, \mathbf{x}_2, \ldots, \mathbf{x}_N | \mathbf{r}_1) \right|^2 \) or, in other words, by the relative sensitivity of the total exchange-correlation hole and the pure exchange (Fermi) hole in the distribution of other electrons.
to the displacement of the reference electron from \( r_1 \). If the exchange-correlation hole associated with \( \Phi(\delta_1, x_2, ..., x_N | r_1) \) has a more substantial change of its form than the Fermi hole associated with \( \Phi_c(\delta_1, x_2, ..., x_N | r_1) \), \( v_{c,\text{kin}}(r_1) \) will be positive and it will be close to zero if there is no or little Coulomb correlation or even negative if the Coulomb hole variation counteracts the Fermi hole variation so as to produce a smaller sensitivity to the reference position of the total hole than just the Fermi hole. Note, that in the exchange-only case only electrons with the same spin as that of the reference electron respond to its displacement. On the other hand, in the exchange-correlation case electrons with both the same and opposite spins change their distribution with the changing \( r_1 \). Because of this, \( v_{c,\text{kin}}(r_1) \) is positive in the main regions.

The maximum of \( v_{c,\text{kin}} \) in the \( 1s-2s \) intershell region can be interpreted in the following way. It is well known that the intershell peak in \( v_{\text{kin}} \) reflects the fact that the Fermi hole “jumps” from one shell to another accompanying the reference electron when it crosses the intershell border.\(^{43-45,16,46}\) Less is known about the Coulomb hole. From the results of Ref. 46 it is clear that when the reference position is within a shell (like the \( 1s \) in He) the hole will have a contractive shape when the \( r_{\text{ref}} \) is in the outer part; spherical, negative around \( r = |r_{\text{ref}}| \), positive closer to the nucleus. When the reference position is at intermediate positions in the shell, the hole has a polarization shape; negative around \( r_{\text{ref}} \), positive at the other side of the nucleus. When \( r_{\text{ref}} \) is close to the nucleus, the hole acquires an expansive shape; spherical, negative around the nucleus and \( r_{\text{ref}} \), positive in the outer region. When the reference position moves (e.g., in Ne) out of the \( 2s \) region into the \( 1s \) shell, the Coulomb hole almost disappears from the \( 2s \) region and becomes purely polarizationlike within the \( 1s \) shell (Fig. 3.3 of Ref. 46). This Coulomb hole behavior enhances the “jump” of the exchange hole from \( 2s,2p \) character to \( 1s \) character, which explains the positive peak in \( v_{c,\text{kin}} \) in the \( 2s-1s \) border region. When moving closer to the nucleus the hole stabilizes to a Fermi part that is just minus the \( 1s \) density, and a Coulomb part that is polarization like, and \( v_{c,\text{kin}} \) becomes small (actually somewhat negative). Moving still closer to the nucleus we observe again (smaller) peaks at both sides of the nucleus, which become larger and considerably closer to the nucleus in the series Li, B, F (in F they nearly coalesce). While the Fermi hole is stable at these reference positions, we conjecture that these peaks are related to the change in Coulomb hole from polarization to expansion shape. We have no explanation for the sharp dip at the nucleus, which may be an artefact of our procedure for constructing \( v_{xc} \), or may be caused by the unphysical Gaussian shape of our CI density at the nucleus.

The behavior of \( v_{c,\text{kin}} \) in the bonding region reflects the

FIG. 5. Exchange-correlation energy density and its kinetic and potential components for BH.

FIG. 6. Exchange-correlation energy density and its kinetic and potential components for HF.
effect of the left–right correlation of electrons of a single bond X–H. When the reference electron crosses the bond midpoint, another electron has to switch from one atom to the other due to the left–right correlation of electrons of a single bond X–H. As a consequence, a bond midpoint peak is expected in $v_{c,kin}$. Since there is no analogous exchange effect, $v_{c,kin}$ is definitely positive in this region with a small local maximum near the bond midpoint. However, as was shown in Ref. 16 for the case of the $H_2$ molecule, the effect is small at the equilibrium geometry and only for the dissociating molecule, where the left–right correlation is strengthened by the strong near-degeneracy effect, $v_{c,kin}$ develops a relatively high bond midpoint peak.

In Fig. 8 the response potentials $v_{resp}$ are plotted, which have been obtained by subtraction of $v_{c,kin}$ and $v_{xc}^{hole}$ from $v_{xc}$. Just as in the case of $v_{c,kin}$, $v_{resp}(z')$, $z' = 1.29z$ and $v_{resp}(z'')$, $z'' = 1.74z$ are plotted for BH and HF respectively. As was established in Ref. 12 within the exchange-only OPM model, the atomic $v_{x}^{hole,resp}$ is a repulsive potential, which has the characteristic form of a step function with the steps representing individual electronic shells. For example, for atoms of the second period with a 1s core $v_{x}^{hole,resp}$ has just one step with the higher plateau for the 1s electrons and with a rather steep descent to low values in the region of the 2s, 2p electrons. In Ref. 42 it has been shown within the generalization of the exchange-only Krieger–Li–Iafrate approximation that the steps of $v_{x}^{hole,resp}$ originate from the corresponding stepped structure of the derivative $\delta g_x(r_j,r_k)/\delta \rho(r_j)$ [see Eq. (19)] as a function of $r_j$ and an expression has been obtained for individual step heights in terms of the energetical characteristics of the corresponding shell.

By construction, $v_{resp}$ presented in this paper contains not only the exchange component $v_{x}^{hole,resp}$, but also the correlation components $v_{c}^{hole,resp}$ and $v_{c,kin}^{resp}$ [see Eq. (20)]. One can see from Fig. 8 that for all systems the $v_{resp}$ obtained are everywhere positive, repulsive potentials. Though far from perfect, the one-step structure can be recognized for $v_{resp}$ of BH with higher values for the core electrons and lower values for other electrons. The step pattern is disturbed, mainly, by the cusps and wiggles of $v_{resp}$ near the nuclei. In particular, $v_{resp}$ for HF has an especially deep cusp near the F nucleus. One of the possible reasons for these features can be the inclusion of the correlation effects. Another reason can be the performance of the numerical procedure of $v_{xc}$ construction. Because of the singularity of the derivative of $\rho$ at nuclei, it appears to be somewhat difficult, in general, to achieve high numerical accuracy of the KS solution in the core regions.

Nevertheless, Fig. 8 represents a reasonable trend for $v_{resp}$ in the series XH. For the heavier X atoms the step exhibits a definite contraction (which should be more pronounced for the real, unscaled coordinate $z$) and the height of the step $\delta e$ increases in accordance with its rough estimate.
mines the general form of \( v_{xc} \) bond midpoint regions, while the structure of \( v_{xc} \) shows the role of its various components. While \( v_{xc}^{\text{hole}} \) determines the general form of \( v_{xc} \), \( v_{resp} \) and \( v_{c,\text{kin}} \) provide an additional structure on top of that of \( v_{xc}^{\text{hole}} \). Each component of \( v_{xc} \) displays its own characteristic structure, \( v_{xc}^{\text{hole}} \) has wells around the X nuclei and around the H nucleus of the \( \text{H}^\delta-\) anionic atom of LiH \( v_{c,\text{kin}} \) has peaks in the intershell and bond midpoint regions, while \( v_{resp} \) displays steplike structure. The structure of \( v_{xc} \) and its components reflects effects of electronic structure and electron correlation, such as the ionicity of XH molecules and the variation of the form of the exchange-correlation hole in various molecular regions. \( v_{xc}^{\text{hole}} \) and \( v_{c,\text{kin}} \), the “energetical” parts of \( v_{xc} \), yield the exchange-correlation energy density, thus defining the local energetical effect of the electron correlation.

VII. CONCLUSIONS

In this paper the molecular Kohn–Sham exchange-correlation potentials \( v_{xc} \) and the energy densities \( \epsilon_{xc} \) have been constructed from \textit{ab initio} first-and second-order density matrices for the series XH (X=Li, B, F). Comparison of the molecular values of the KS kinetic functionals \( T_s \) and \( T_h \) obtained in this paper with the atomic ones obtained in Ref. 37 has revealed the effect of bond formation on these functionals. The energies of the highest occupied KS MO calculated with \( v_{xc} \) reproduce the experimental ionization energies of XH.

The structure of \( v_{xc} \) and \( \epsilon_{xc} \) has been analyzed in terms of their components \( v_{xc}^{\text{hole}}, v_{c,\text{kin}} \) and \( v_{resp} \). The form of \( v_{xc} \) and \( \epsilon_{xc} \) is determined by a combination of the characteristic features of their components, namely, the wells of \( v_{xc}^{\text{hole}} \); the peaks of \( v_{c,\text{kin}} \) and (in the case of \( v_{xc} \)) the stepped-like patterns of \( v_{resp} \). The relation of these features with various effects of electronic structure and electron correlation has been discussed. Anionic nature of atomic fragments \( \text{H}^\delta- \) in the LiH molecule and \( \text{F}^\delta- \) in the HF molecule manifests itself through the formation of local wells of \( v_{xc} \) in the corresponding regions.

The present results have shown sensitivity of the molecular KS solution obtained via the iterative procedure (22)–(25) to the starting potential \( v_{el}^0 \). This is especially true for the regions near the nuclei. The stability of the procedure also appears to decrease when going from the lighter LiH and BH molecules to the heavier HF molecule. One of the possible reasons of this is the local nature of the simple updating formula (23), (24) for the potential of electron interaction \( v_{el} \). According to this formula, the change of potential at the \( m \)th iteration \( \Delta v_{el}(r) = v_{el}^m(r) - v_{el}^{m-1}(r) \) depends explicitly only on the local density difference \( \Delta \rho(r) = \rho^{m-1}(r) - \rho(r) \) and the local ratio \( v_{m-1}(r)/\rho(r) \),

\[
\delta \epsilon = 0.38 \sqrt{\epsilon_{\text{HOMO}} - \epsilon_{1s}},
\]

where \( \epsilon_{1s} \) is the energy of the core orbital.

To sum up, the analysis of \( v_{xc} \) performed in this section shows the role of its various components. While \( v_{xc}^{\text{hole}} \) determines the general form of \( v_{xc} \), \( v_{resp} \) and \( v_{c,\text{kin}} \) provide an additional structure on top of that of \( v_{xc}^{\text{hole}} \). Each component of \( v_{xc} \) displays its own characteristic structure, \( v_{xc}^{\text{hole}} \) has wells around the X nuclei and around the H nucleus of the \( \text{H}^\delta-\) anionic atom of LiH \( v_{c,\text{kin}} \) has peaks in the intershell and bond midpoint regions, while \( v_{resp} \) displays steplike structure. The structure of \( v_{xc} \) and its components reflects effects of electronic structure and electron correlation, such as the ionicity of XH molecules and the variation of the form of the exchange-correlation hole in various molecular regions. \( v_{xc}^{\text{hole}} \) and \( v_{c,\text{kin}} \), the “energetical” parts of \( v_{xc} \), yield the exchange-correlation energy density, thus defining the local energetical effect of the electron correlation.
$v_{xc}(\mathbf{r})$ and $\epsilon_{xc}(\mathbf{r})$ constructed from the correlated $\rho(\mathbf{r}, \mathbf{r}')$ and $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ contain important information about the local effect of the electron correlation and can serve as a reference for density functional approximations. In particular, this opens new possibilities for modeling of $\epsilon_{xc}$, which became an essential part of the development of DFT.\cite{1,2} When developing a new $\epsilon_{xc}$, one can take into account not only the total $E_{xc}$ values or the scaling and asymptotic properties of the $E_{xc}$ functional, but also the local behavior of $\epsilon_{xc}(\mathbf{r})$ obtained from \textit{ab initio} wave functions for a representive set of atomic and molecular systems. A promising option is to approximate directly the potential $\frac{1}{2}v_{xc}^\text{hole}(\mathbf{r})$ and kinetic $v_{xc,kin}(\mathbf{r})$ components. Hopefully, an efficient approximation to $v_{xc}$ can be achieved with a function of the density $\rho$ and its gradient, while $v_{xc,kin}$, with its bond midpoint and intershell peaks may require a less traditional orbital-dependent approximation. The corresponding work, as well as the refinement of the procedure of $v_{xc}(\mathbf{r})$ and $\epsilon_{xc}(\mathbf{r})$ construction and its application to different types of bonding situations, is in progress.

ACKNOWLEDGMENTS

We gratefully acknowledge funding by the Netherlands Foundation for Scientific Research (NWO) and the Stichting Fundamenteel Onderzoek der Materie (FOM).