Universal on-top description of electron correlation in the ground and excited many-electron states with correlon quasiparticles

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On-top conditional correlation functions of many-electron theory are rearranged into a set of correlon quasiparticles representing the local effect of electron correlation in the ground and excited states. An individual correlon is characterized with a one-particle wave function, the imaginary part of which (or covalent correlon) gives the amplitude of the on-top depletion of the (conditional electron) charge (ODC) due to (strong) electron correlation. In its turn, the real part (ionic correlon) gives the amplitude of the on-top accumulation of the (electron) charge (OAC) due to the ionic squeezing of electrons. The proposed correlon theory is applied to analyze the local correlation effects in the ground and first excited states of the hydrogen molecule as well as of the equidistant and alternate linear hydrogen chains from H_4 to H_{12}. The covalent and ionic correlons obtained at the multiconfigurational self-consistent-field level of correlated functions are demonstrated to be the robust descriptors of the covalency of the ground and the ionicity of the excited H_n states.

I. INTRODUCTION

A full description of ground and excited states in many-electron theory requires knowledge of a set $\{\Psi_N^P(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)\}$ of the N-electron wave functions (x stays for the combination of the spatial $\boldsymbol{r}$ and spin s electron coordinates) [1]. The diagonal part $\rho_N^P(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)$ of the corresponding N-order density matrix for the Pth state

$$\rho_N^P(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) = \left| \Psi_N^P(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) \right|^2 \qquad (1)$$

gives the density probability of the electron configuration, in which the ith electron has the coordinate $\boldsymbol{x}_i$ [2]. In particular, comparing the ground-state (G) correlated quantities $\Psi_N^G(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)$ and $\rho_N^G(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)$ with their Hartree-Fock (HF) counterparts $\Psi_N^{G(\mathrm{HF})}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)$ and $\rho_N^{G(\mathrm{HF})}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)$, one can, in principle, analyze and evaluate the effect of the electron Coulomb correlation in the ground state. In this way, however, we encounter the involved task of the direct operation with the above-mentioned complicated N-electron objects. Furthermore, for excited states of a manifestly multiconfigurational nature the very notion of the HF approximation becomes ambiguous.

A promising way to efficiently resolve these problems is the on-top one-electron description of electron correlation. It is based on the on-top pair density $\Pi^P(\boldsymbol{r})$, which is defined as the pair density function $\rho_2^P(\boldsymbol{r}_1, \boldsymbol{r}_2)$ evaluated at the electron coalescence point $\boldsymbol{r}_1 = \boldsymbol{r}_2 = \boldsymbol{r}$ [3]

$$\Pi^P(\boldsymbol{r}) = \rho_2^P(\boldsymbol{r}, \boldsymbol{r}) = N(N-1) \int \ldots \int \left| \Psi_N^P(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_n) \right|^2$$
$$\times \, d\sigma_1 \ldots d\sigma_N d\boldsymbol{r}_3 \ldots d\boldsymbol{r}_N |_{\boldsymbol{r}_1 = \boldsymbol{r}_2 = \boldsymbol{r}}, \qquad (2)$$

where σ_i denotes a spin coordinate. The considered on-top approach naturally separates out the leading effect of the Coulomb correlation of electrons with the opposite spins. Indeed, due to the antisymmetry of the fermionic wave function, the same-spin component of the on-top pair density is zero, $\Pi^{P(\uparrow\uparrow)}(\boldsymbol{r}) = 0$, so $\Pi^P(\boldsymbol{r})$ is identically equal to its opposite-spin component $\Pi^{P(\uparrow\downarrow)}(\boldsymbol{r})$

$$\Pi^P(\boldsymbol{r}) \equiv \Pi^{P(\uparrow\downarrow)}(\boldsymbol{r}). \qquad (3)$$

Then, one can unambiguously define for both ground and excited singlet states the correlation on-top pair-density function $\Pi_c^{P(\uparrow\downarrow)}(\boldsymbol{r})$

$$\Pi_c^{P(\uparrow\downarrow)}(\boldsymbol{r}) = \Pi^{P(\uparrow\downarrow)}(\boldsymbol{r}) - \tfrac{1}{2}[\rho^P(\boldsymbol{r})]^2, \qquad (4)$$

where the second term, the half of the square of the electron density $\rho^P(\boldsymbol{r})$, is the (explicitly) uncorrelated counterpart of $\Pi^{P(\uparrow\downarrow)}(\boldsymbol{r})$. The related to $\Pi_c^{P(\uparrow\downarrow)}(\boldsymbol{r})$ on-top correlation functions can be efficiently used for the reduced description of the electron correlation of the opposite-spin electrons. Note that the pair-density functions $\Pi^P(\boldsymbol{r})$ and $\Pi_c^{P(\uparrow\downarrow)}(\boldsymbol{r})$ are employed to connect wave-function theory (WFT) [1] and density functional theory (DFT) [4–7] in the ongoing development of effective combined methods of the electronic structure calculations [8–12].

Below, the on-top pair-density description will be employed to analyze the true physical meaning of the conventional classification of molecular electronic states as "covalent" or "ionic," according to the nature of their electron correlation. The prototype example of this classification are the covalent ground $1\,^1\Sigma_g^+$ and the ionic excited $1\,^1\Sigma_u^+$ states of the H_2 molecule. The first state is characterized with a considerable strong (nondynamic) electron correlation, which increases with the H-H bond stretching. Due to this, the
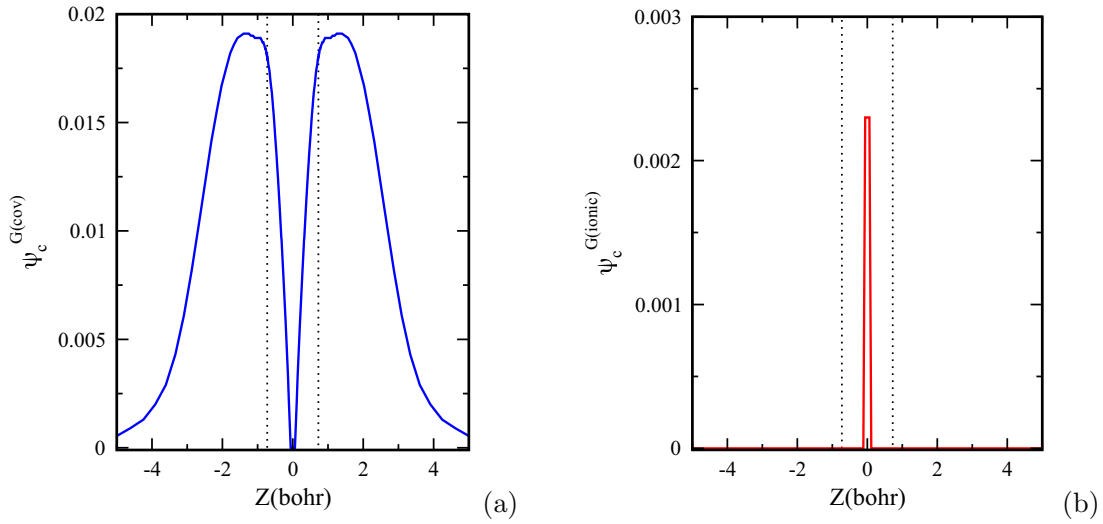
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FIG. 1. (a) Covalent and (b) ionic correlons obtained with MCSCF wave function for the H_2 molecule in the ground state. Dotted lines indicate positions of nuclei. Molecule positioned along the Z axis.

$1^1\Sigma_g^+$ state displays the covalent pattern of dissociation of the two-electron bond, according to which the electron of a particular spin is located on one H atom, while the electron of the opposite spin is located on another H atom [13]. In physics, such a pattern is represented with the paradigmatic Hubbard model [14]. At variance with this, in the excited $1^1\Sigma_u^+$ state strong electron correlation is suppressed with the ionic two-electron distribution, which is characterized with a symmetrized combination of the ionic configurations H^+ and H^- [1]. A question of the assignment of electronic states as "covalent" or "ionic" was addressed in our previous work [12]. The descriptor of the nature of the state was proposed based on the specific influence of nondynamic correlation on the energy of dynamic correlation evaluated for a given state.

In this paper, a correlon quasiparticle is proposed to describe electron correlation in a given many-electron state. The quasiparticle approach, which is widely applied in molecular theory [15] and solid state physics [16], represents various many-electron effects as particle-like entities within the one-particle approach. In general, electron excitations are described with exciton quasiparticles, the bound states of an electron and a hole [15,17,18]. The present introduction of correlons for a specialized description of electron correlation is motivated with the following features of the above-mentioned on-top approach.

(1) The function $\Pi_c^{P(\uparrow\downarrow)}(\boldsymbol{r})$ of Eq. (4) offers a one-particle picture of the local effect of electron correlation at each spatial point $\boldsymbol{r}$.

(2) The corresponding quasiparticle approach allows one to reduce the description of electron correlation with the set of the correlated many-electron states $\{\Psi_N^P(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)\}$ to that with a set of correlon quasiparticles.
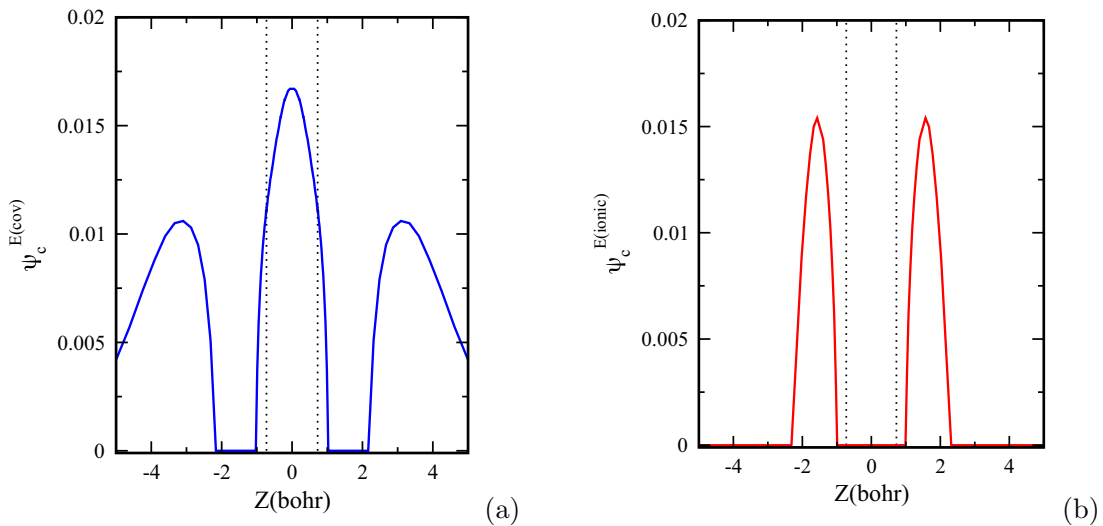

FIG. 2. (a) Covalent and (b) ionic correlons obtained with MCSCF wave function for the H_2 molecule in the excited state. Dotted lines indicate positions of nuclei. Molecule positioned along the Z axis.
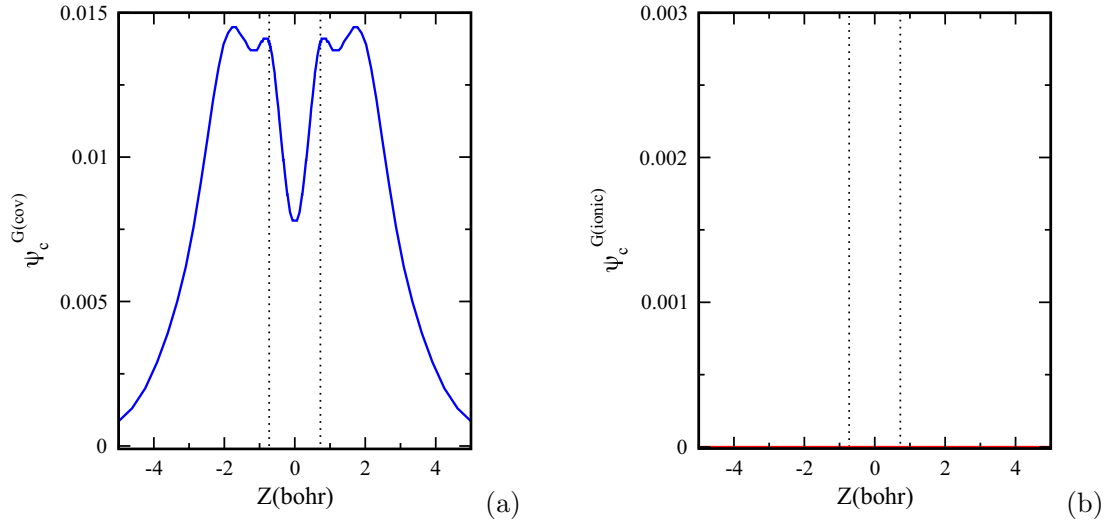
FIG. 3. (a) Covalent and (b) ionic correlons obtained with FCI wave function for H_2 molecule in the ground state. Dotted lines indicate positions of nuclei. Molecule positioned along the Z axis.

(3) The regions with the relative on-top depletion (ODC) or accumulation (OAC) of the electron charge (compared to the uncorrelated reference), which are related to the covalent or ionic character of a given state, can be conveniently separated to the imaginary or real, respectively, parts of the correlon wave function (see below).

In the next section a detailed description of the proposed correlon quasiparticle approach to electron correlation will be given.

II. CORRELON QUASIPARTICLE DESCRIPTION OF ELECTRON CORRELATION

In this section we propose a kinematic quasiparticle local description of electron correlation of the opposite-spin electrons, which does not use any interaction operators. Instead, it is derived solely from the generic wave function Ψ_N^P of the considered molecular state. To this end, we introduce for

closed-shell systems the on-top reduction chain (ORC) of the correlation functions

$$\Pi_c^{P(\uparrow\downarrow)}(\boldsymbol{r}) \rightarrow \rho_{\text{cond}}^{c,P(\uparrow\downarrow)}(\boldsymbol{r}) \rightarrow g_c^{P(\uparrow\downarrow)}(\boldsymbol{r}) \rightarrow \psi_c^P(\boldsymbol{r}). \quad (5)$$

The ORC starts with the correlation on-top pair-density function $\Pi_c^{P(\uparrow\downarrow)}(\boldsymbol{r})$ of Eq. (4). Its second member is the correlation part $\rho_{\text{cond}}^{c,P(\uparrow\downarrow)}(\boldsymbol{r})$ of the on-top conditional density $\rho_{\text{cond}}^{P(\uparrow\downarrow)}(\boldsymbol{r},\boldsymbol{r})$ obtained with the division of $\Pi_c^{P(\uparrow\downarrow)}(\boldsymbol{r})$ by the electron density $\rho^P(\boldsymbol{r})$

$$\rho_{\text{cond}}^{c,P(\uparrow\downarrow)}(\boldsymbol{r}) = \frac{\Pi_c^{P(\uparrow\downarrow)}(\boldsymbol{r})}{\rho^P(\boldsymbol{r})} = \rho_{\text{cond}}^{P(\uparrow\downarrow)}(\boldsymbol{r},\boldsymbol{r}) - \frac{1}{2}\rho^P(\boldsymbol{r}). \quad (6)$$

The third member of the ORC is the opposite-spin on-top pair-correlation function $g_c^{P(\uparrow\downarrow)}(\boldsymbol{r})$ obtained, again, with the division of the preceding ORC member by the density $\rho^P(\boldsymbol{r})$

$$g_c^{P(\uparrow\downarrow)}(\boldsymbol{r}) = \frac{\rho_{\text{cond}}^{c,P(\uparrow\downarrow)}(\boldsymbol{r})}{\rho^P(\boldsymbol{r})}. \quad (7)$$
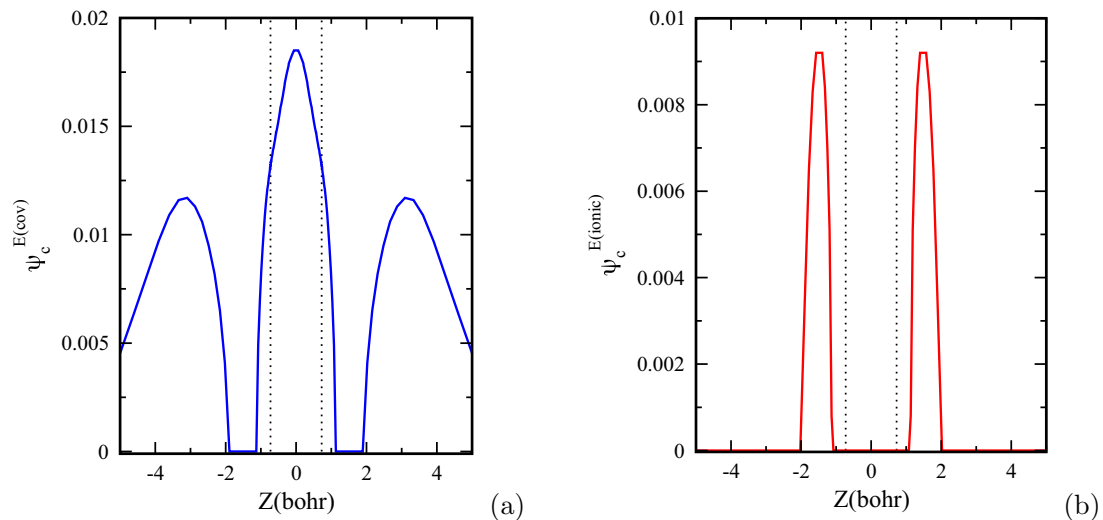

FIG. 4. (a) Covalent and (b) ionic correlons obtained with FCI wave function for the H_2 molecule in the excited state. Dotted lines indicate positions of nuclei. Molecule positioned along the Z axis.

TABLE I. Interatomic distances in bohr for equidistance (R) and alternate (R_1 and R_2) linear hydrogen chains H_n. Geometries optimized with MOLPRO program package [20] for CAS(n, n) wave functions.

n	R	R_1	R_2
4	1.735	1.456	6.389
6	1.807	1.456	6.848
12	1.866	1.456	7.556

To convert the on-top description of electron correlation to the quasiparticle picture, we introduce the correlation amplitude $c^P(\mathbf{r})$, the square root of the function (7)

$$c^P(\mathbf{r}) = \sqrt{g_c^{P(\uparrow\downarrow)}(\mathbf{r})}. \tag{8}$$

The function $c^P(\mathbf{r})$ naturally separates the ODC and OAC regions with the depletion [$g_c^{P(\uparrow\downarrow)}(\mathbf{r}) < 0$] or accumulation [$g_c^{P(\uparrow\downarrow)}(\mathbf{r}) > 0$] of the charge of other electrons of opposite spin on top of the reference electron of a particular spin at $\mathbf{r}$.

Indeed, the first regions are represented with the nonvanishing imaginary part of the correlation amplitude $\text{Im}[c^P(\mathbf{r})]$ In their turn, the charge accumulation regions are represented with its non-vanishing real part $\text{Re}[c^P(\mathbf{r})]$.

By its definition, the correlation amplitude $c^P(\mathbf{r})$ does not vanish in the energetically unimportant regions of low electron density $\rho^P(\mathbf{r})$. Because of this, it is not normalizable by itself, so it cannot be directly employed as a quasiparticle wave function. Then, to turn it into a normalizable function, which would describe electron correlation in the important spatial regions, we apply the density cutoff to the on-top pair-correlation function (7)

$$\tilde{g}_c^{P(\uparrow\downarrow)}(\mathbf{r}) = g_c^{P(\uparrow\downarrow)}(\mathbf{r})\frac{\rho^P(\mathbf{r})}{a + \rho^P(\mathbf{r})}. \tag{9}$$

With a sufficiently small parameter a of the cutoff Padé approximant in Eq. (9), the function $\tilde{g}_c^{P(\uparrow\downarrow)}(\mathbf{r})$ is approximately equal to the original function $g_c^{P(\uparrow\downarrow)}(\mathbf{r})$, $\tilde{g}_c^{P(\uparrow\downarrow)}(\mathbf{r}) \approx g_c^{P(\uparrow\downarrow)}(\mathbf{r})$ in the energetically important regions of typical atomic and molecular energy densities. On the other hand, $\tilde{g}_c^{P(\uparrow\downarrow)}(\mathbf{r})$ decays exponentially with $\rho^P(\mathbf{r})$ in the regions of low density.
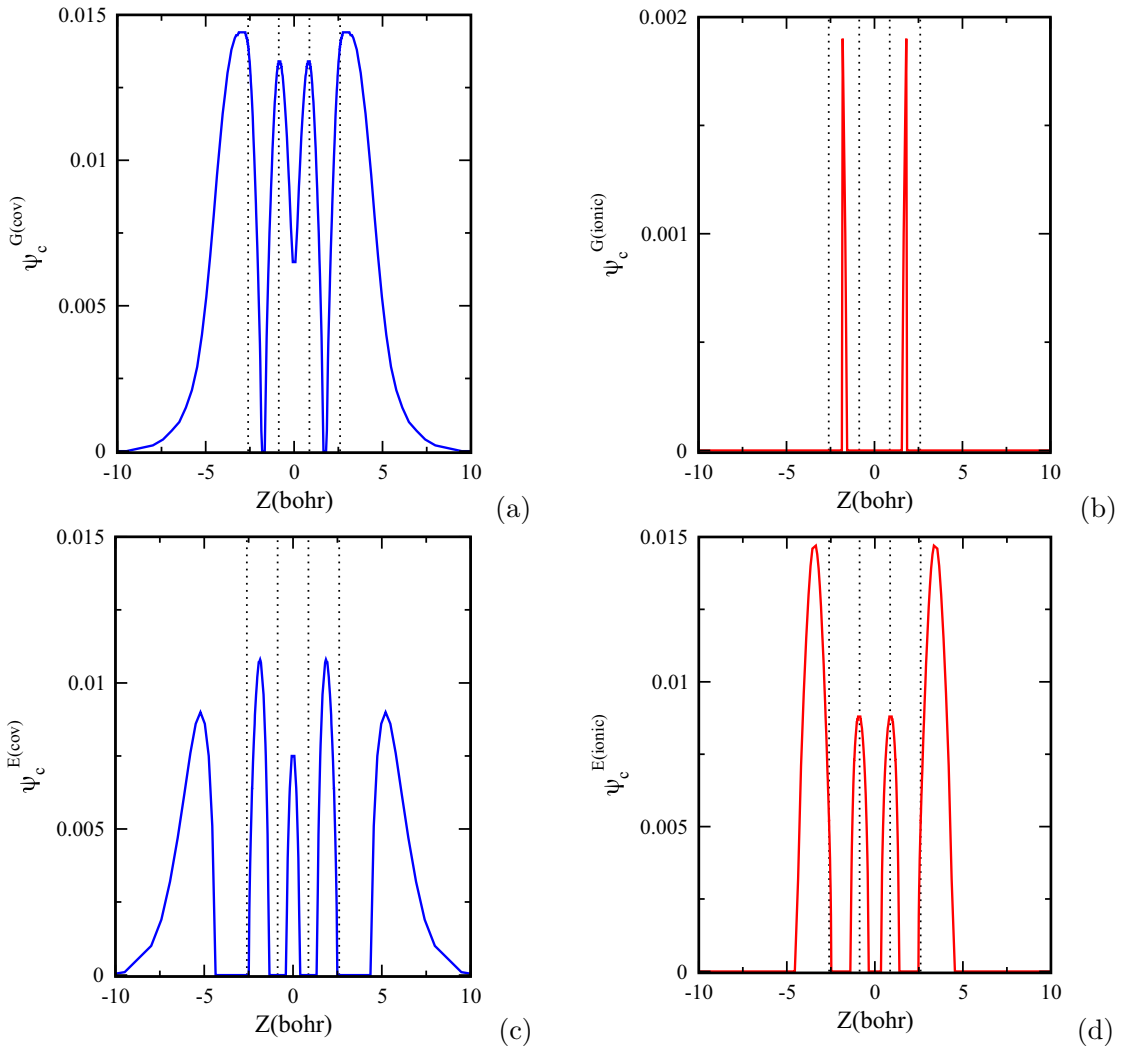

FIG. 5. H_4 equidistant chain. Covalent [panels (a) and (c) for ground and excited states, respectively] and ionic [panels (b) and (d) for ground and excited states, respectively] correlons. Dotted lines indicate positions of nuclei. Molecule positioned along the Z axis.
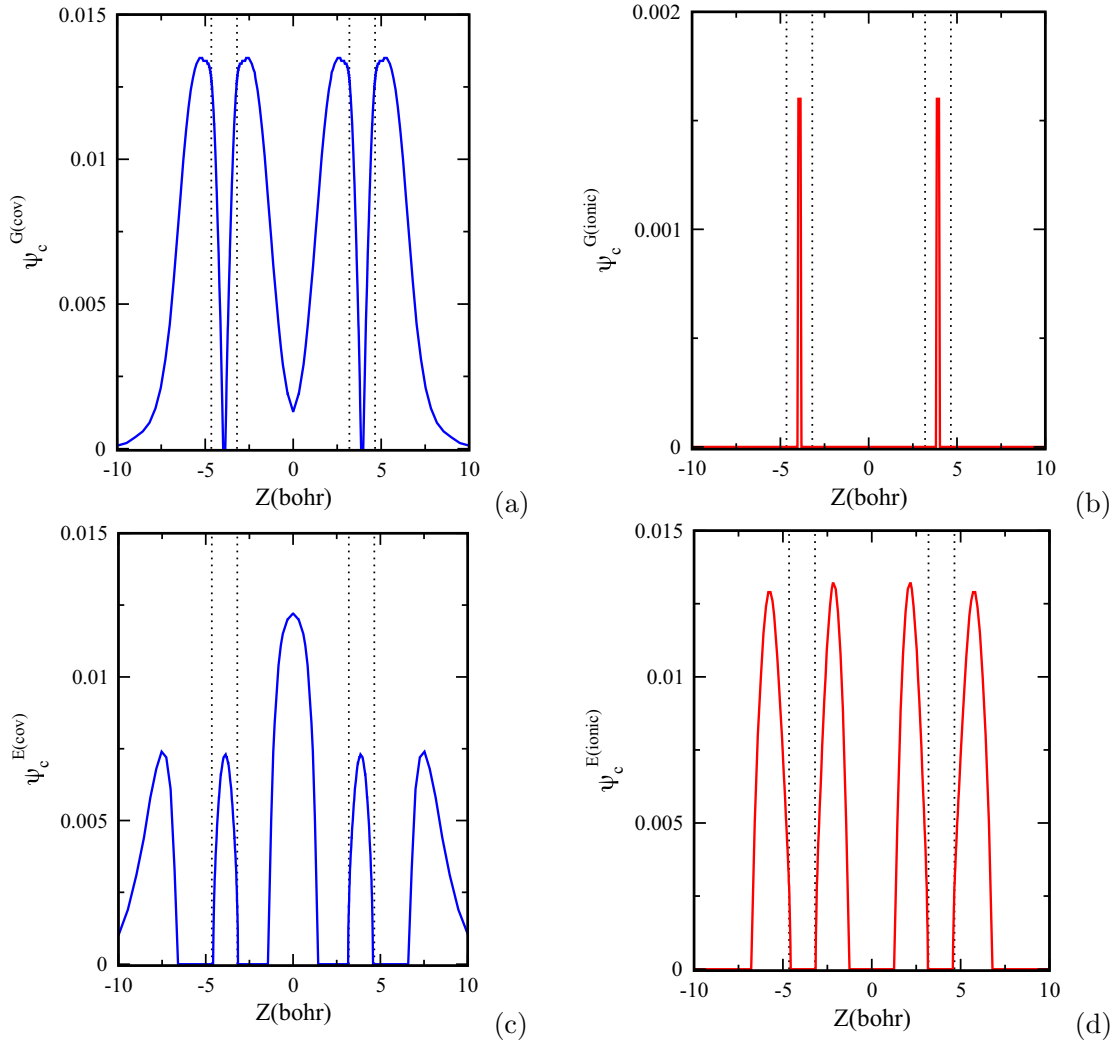
FIG. 6. H_4 alternate bond chain. Covalent [panels (a) and (c) for ground and excited states, respectively] and ionic [panels (b) and (d) for ground and excited states, respectively] correlons. Dotted lines indicate positions of nuclei. Molecule positioned along the Z axis.

With this cutoff, we propose a unified quasiparticle description of electron correlation in the ground and excited states. To this end, we introduce for each N-electron state $\Psi_N^P(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)$ the corresponding correlon quasiparticle representing, with the one-electron wave function $\psi_c^P(\boldsymbol{r})$, the last member of the ORC (5)

$$\psi_c^P(\boldsymbol{r}) = \frac{1}{\sqrt{N_c^P}}\sqrt{\tilde{g}_c^{P(\uparrow\downarrow)}(\boldsymbol{r})}, \tag{10}$$

where N_c^P is its normalization

$$N_c^P = \int \left|\tilde{g}_c^{P(\uparrow\downarrow)}(\boldsymbol{r})\right| d\boldsymbol{r}. \tag{11}$$

Turning into the correlation amplitude $c^P(\boldsymbol{r})$ of Eq. (8) in the regions of the nondecaying electron density, the correlon wave function $\psi_c^P(\boldsymbol{r})$ of Eq. (10) acquires a natural separation of the ODC and OAC regions of the former function. Specifically, the imaginary part of the correlon wave function $\mathrm{Im}[\psi_c^P(\boldsymbol{r})]$ represents ODC due to correlation with the reference electron at $\boldsymbol{r}$, which characterizes the many-electron states of the covalent nature. Then, this part can be called a

"covalent" correlon

$$\mathrm{Im}\!\left[\psi_c^P(\boldsymbol{r})\right] \equiv \psi_c^{P(\mathrm{cov})}(\boldsymbol{r}), \tag{12}$$

a kinematic local index describing the magnitude and location of the covalent correlation mode. In its turn, the real part $\mathrm{Re}[\psi_c^P(\boldsymbol{r})]$ represents OAC due to the "ionic squeezing" of electrons. So this part can be called an "ionic" correlon

$$\mathrm{Re}\!\left[\psi_c^P(\boldsymbol{r})\right] \equiv \psi_c^{P(\mathrm{ionic})}(\boldsymbol{r}). \tag{13}$$

In the next section the introduced covalent and ionic correlons will be constructed for the ground and first excited states of the paradigmatic H_2 molecule.

III. COVALENT AND IONIC CORRELONS FOR THE HYDROGEN MOLECULE

In the case of the H_2 molecule, the sharpest separation of the ODC and OAC effects is given with the simplest two-configuration approximations Ψ_2^G and Ψ_2^E to the ground (G) covalent $1\,^1\Sigma_g^+$ and excited (E) ionic $1\,^1\Sigma_u^+$ states, respectively, mentioned in the Introduction. Specifically, the
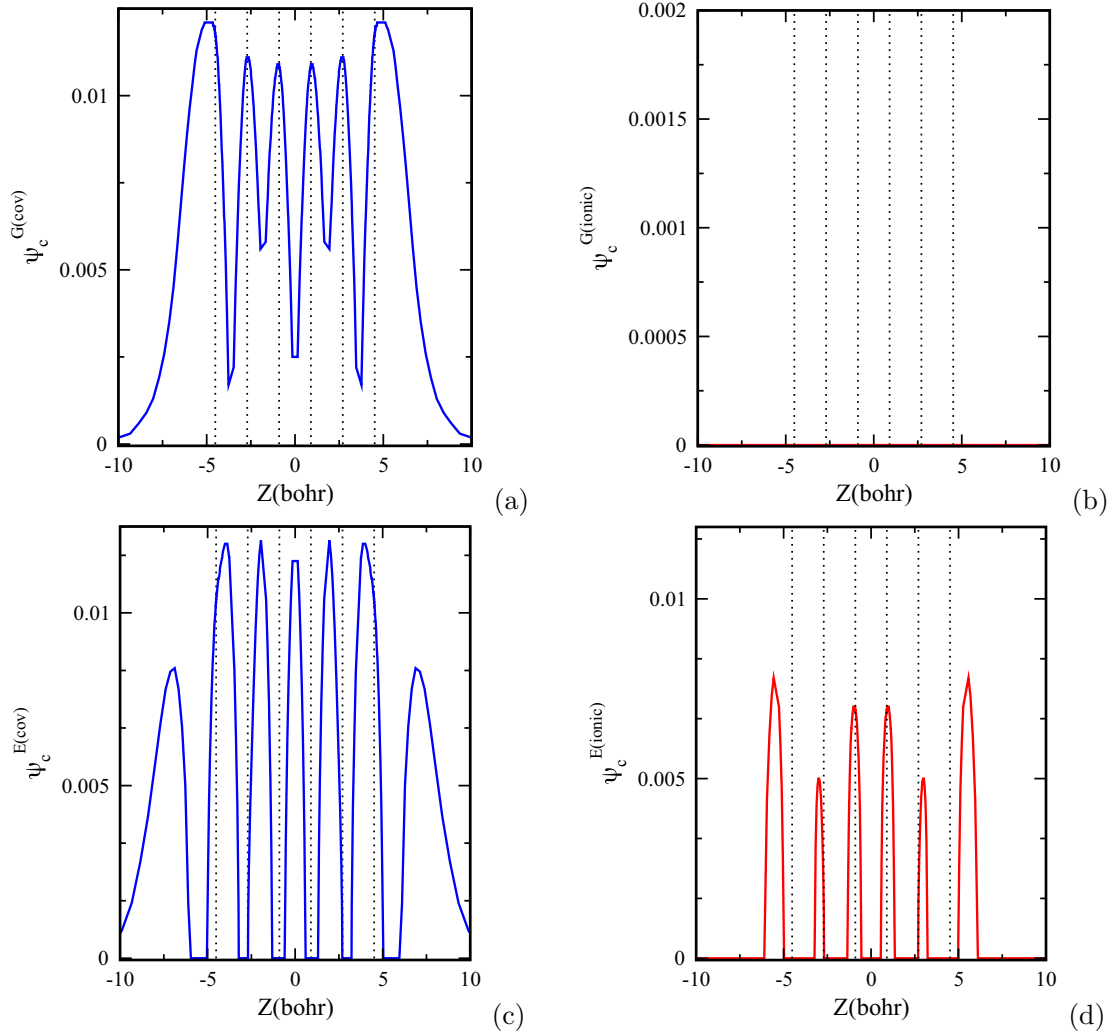
FIG. 7. H_6 equidistant chain. Covalent [panels (a) and (c) for ground and excited states, respectively] and ionic [panels (b) and (d) for ground and excited states, respectively] correlons. Dotted lines indicate positions of nuclei. Molecule positioned along the Z axis.

approximate ground state Ψ_2^G is a linear combination

$$\Psi_2^G = c_0 \Phi_0 + c_{gg}^{uu} \Phi_{gg}^{uu} = \left(c_0 - c_{gg}^{uu}\right)\Phi_0 + c_{gg}^{uu}\Psi_2^{HL} \qquad (14)$$

of the reference Slater determinant Φ_0 representing the $1\sigma_g^2$ configuration and its double excitation Φ_{gg}^{uu} to the configuration $1\sigma_u^2$, where $1\sigma_g$ and $1\sigma_u$ are the bonding occupied and antibonding virtual molecular orbitals (MOs) of H_2. Equivalently, Ψ_2^G is written in Eq. (14) as the linear combination of Φ_0 and the Heitler-London (HL)-type wave function Ψ_2^{HL} [19], which includes the $1\sigma_g^2$ and $1\sigma_u^2$ with the equal weights. It is Ψ_2^{HL}, which introduces strong electron correlation for the stretched H-H bond.

In this paper the multiconfiguration self-consistent-field (MCSCF) method is used, in which both expansion coefficients c_0, c_{gg}^{uu} and the orbitals $1\sigma_g$, $1\sigma_u$ of the wave function (14) are simultaneously optimized. The MCSCF calculations are performed with the MOLPRO program package [20]. The subsequent construction of the correlons is carried out with the home-brew codes, which accept the MOLPRO molecular integrals and pair densities. The basis set cc-pVDZ has been employed in all calculations presented in this work [21]. The

cutoff parameter in the on-top pair-correlation function (9) is set to $a = 0.01$.

Figure 1 displays the covalent $\psi_c^{G(cov)}$ and ionic $\psi_c^{G(ionic)}$ correlons obtained from the ground-state wave function (14) at the equilibrium H_2 geometry, with the H nuclei placed at 0.7 and -0.7 bohr. The covalent correlon spans prominently over the whole range of the electron coordinate r variation [see Fig. 1(a)]. Around the nuclei, $\psi_c^{G(cov)}$ reaches the maximum, while it rather sharply vanishes in the less important energetically bond midpoint region. At variance with this, the ionic correlon $\psi_c^{G(ionic)}$ reduces to only a very sharp residual peak around the bond midpoint [see Fig. 1(b)]. From this, one can conclude that, in agreement with the conventional assignment, the present correlon analysis attributes the covalent correlation character to the ground state of the H_2 molecule represented with Ψ_2^G.

We proceed with first excited state Ψ_2^E of H_2, which in the minimal MCSCF approach consists of just one spin-adapted singly excited $1\sigma_g 1\sigma_u$ configuration. It represents the above mentioned "ionic squeezing" of two opposite-spin electrons of H_2. Figure 2 depicts the corresponding covalent and ionic correlons. The magnitude and the location of the latter
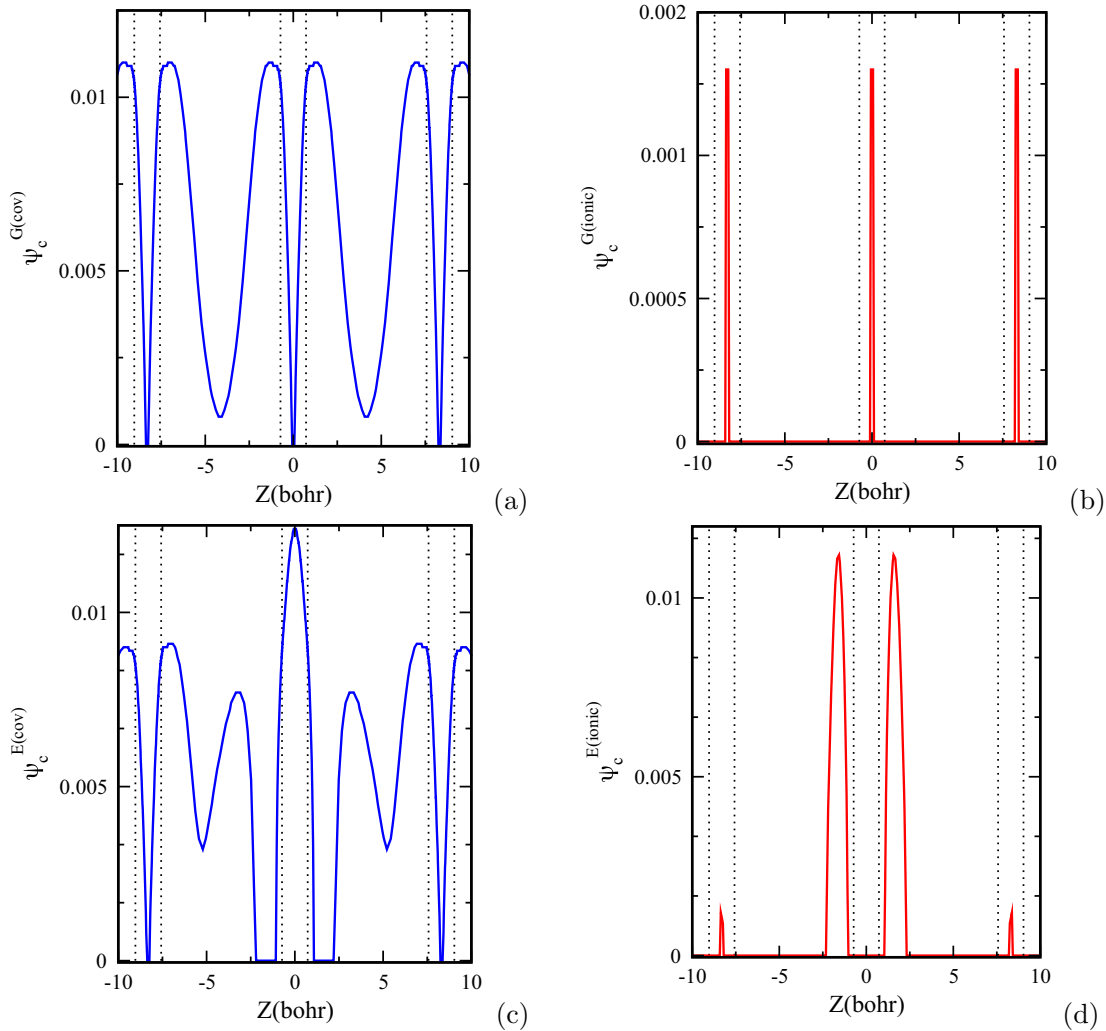
FIG. 8. H_6 alternate bond chain. Covalent [panels (a) and (c) for ground and excited states, respectively] and ionic [panels (b) and (d) for ground and excited states, respectively] correlons. Dotted lines indicate positions of nuclei. Molecule positioned along the Z axis.

displays the reversed pattern compared to that of the ground state. Indeed, the ionic correlon wave function $\psi_c^{E(\text{ionic})}$ consists of two prominent peaks in the atomic regions outside the bonding region [see Fig. 2(b)]. In its turn, the covalent correlon $\psi_c^{E(\text{cov})}$ is located in the less important bond midpoint region [see Fig. 2(a)]. From this marked qualitative difference with the ground-state correlon pattern mentioned above, one can conclude that, again in agreement with the conventional assignment, the correlon analysis attributes the ionic character to the first excited state of the H_2 molecule.

To analyze the additional effect of the short-range dynamic correlation on the shape and location of the correlons, Figures 3 and 4 display the covalent and ionic correlons obtained from the accurate ground $\Psi_2^{G(\text{FCI})}$ and excited $\Psi_2^{E(\text{FCI})}$ state wave functions of the full CI (FCI) in the chosen basis. Apparently, the additional dynamic correlation increases the ODC and decreases the OAC effects. Because of this, in the ground FCI state $\Psi_2^{G(\text{FCI})}$ only the covalent correlon $\psi_c^{G(\text{cov})}$ remains [see Fig. 3(a)], while the ionic correlon $\psi_c^{G(\text{ionic})}$ totally disappears [see Fig. 3(b)]. At variance with this, in the excited FCI state $\Psi_2^{E(\text{FCI})}$ the ionic correlon $\psi_c^{E(\text{ionic})}$ is present and it retains its location, though the amplitude and the width of

the ionic correlon peaks are considerably reduced compared to those obtained from the minimal MCSCF wave function [compare Figs. 2(b) and 4(b)]. Still, the observed qualitative difference in the correlon pictures allows to attribute the covalent character to the ground state and the ionic character to the first excited state also at the FCI level.

IV. COVALENT AND IONIC CORRELONS FOR HYDROGEN CHAINS

In this section, the extension of the simple two-configuration MCSCF approach of Sec. II is applied to the correlon construction for the ground Ψ_N^G and first excited Ψ_N^E of the even-member closed-shell linear hydrogen chains from H_4 to H_{12}. This extension employs all possible excitations of $n = N$ electrons in the "active" orbital space of $n/2$ frontier occupied and $n/2$ virtual orbitals of the reference determinant Φ_0. In quantum chemistry this MCSCF variant is called complete active space SCF, CASSCF(n, n) [22–24].

From the physical point of view it is essential that the adopted ground-state MCSCF wave function Ψ_N^G can be considered as a reliable carrier of nondynamic (strong) electron
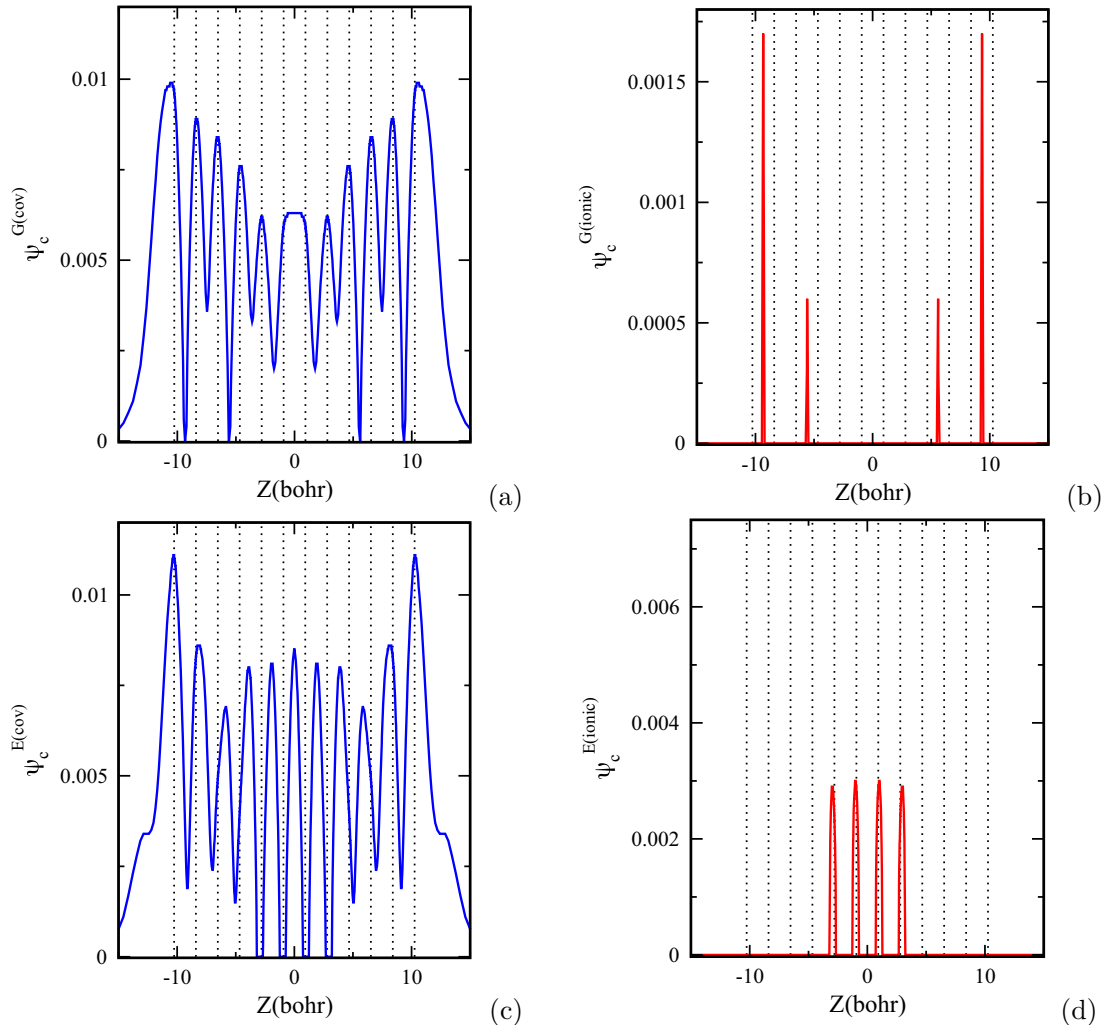
FIG. 9. H_{12} equidistant chain. Covalent [panels (a) and (c) for ground and excited states, respectively] and ionic [panels (b) and (d) for ground and excited states, respectively] correlons. Dotted lines indicate positions of nuclei. Molecule positioned along the Z axis.

correlation. Indeed, by its construction, it includes all the configurations required for the proper molecular dissociation, which represent strong correlation. It also includes a portion of short-range dynamic correlation, which increases with the chain length. In its turn, the excited MCSCF state Ψ_N^E incorporates the above mentioned OAC effect due to the "ionic squeezing" of electrons. The present MCSCF approach can be considered as a reasonable compromise between the accuracy and decent separation of the ODC and OAC effects, which allows to employ the resultant ionic correlon as a robust local descriptor of the ionic correlation character.

To relate the present study to the Peierls distortion in one-dimensional chains [25], two types of the geometry are considered. The first types are equidistant linear chains H_n with the optimized for the ground-state common H-H bond length R. The second types are the symmetrical chains with two alternate H-H bond lengths R_1 and R_2.

Table I presents the optimized H-H bond lengths. Optimizations were carried out for CAS(n, n) wave functions with the MOLPRO program package [20]. For the equidistant chains the common bond length R slightly increases with

the chain length from 1.735 bohr for H_4 to 1.866 bohr for H_{12}. The alternate chains are, essentially, the assemblies of weakly bound H_2 molecules. Indeed, the shorter optimized bond length R_1 is equal in all cases to 1.456 bohr, which is just slightly longer than the equilibrium bond length of the individual H_2 molecule. The other optimized bond length R_2 is much longer, increasing with the chain length from 6.389 bohr for H_4 to 7.556 bohr for H_{12} (see Table I).

Figures 5 to 10 display the covalent and ionic correlons for the hydrogen chains obtained from the MCSCF wave functions Ψ_N^G and Ψ_N^E. For the equidistant chains, the ground-state covalent correlons $\psi_c^{G(\text{cov})}(\mathbf{r})$ display the atomic peaks around the individual nuclei, which tend to merge for longer chains [compare Fig. 5(a) for H_4 with Fig. 9(a) for H_{12}]. Evidently, for the alternate chains the ground-state correlons represent in all cases the combinations of those for the individual H_2 fragments described in Sec. II. Then, a model Peierls distortion in the considered finite chains turns the correlon picture with the collective features (merging correlon peaks), which is natural for the equidistant chains with the half-filled valence band, to that for the alternate chains resembling the
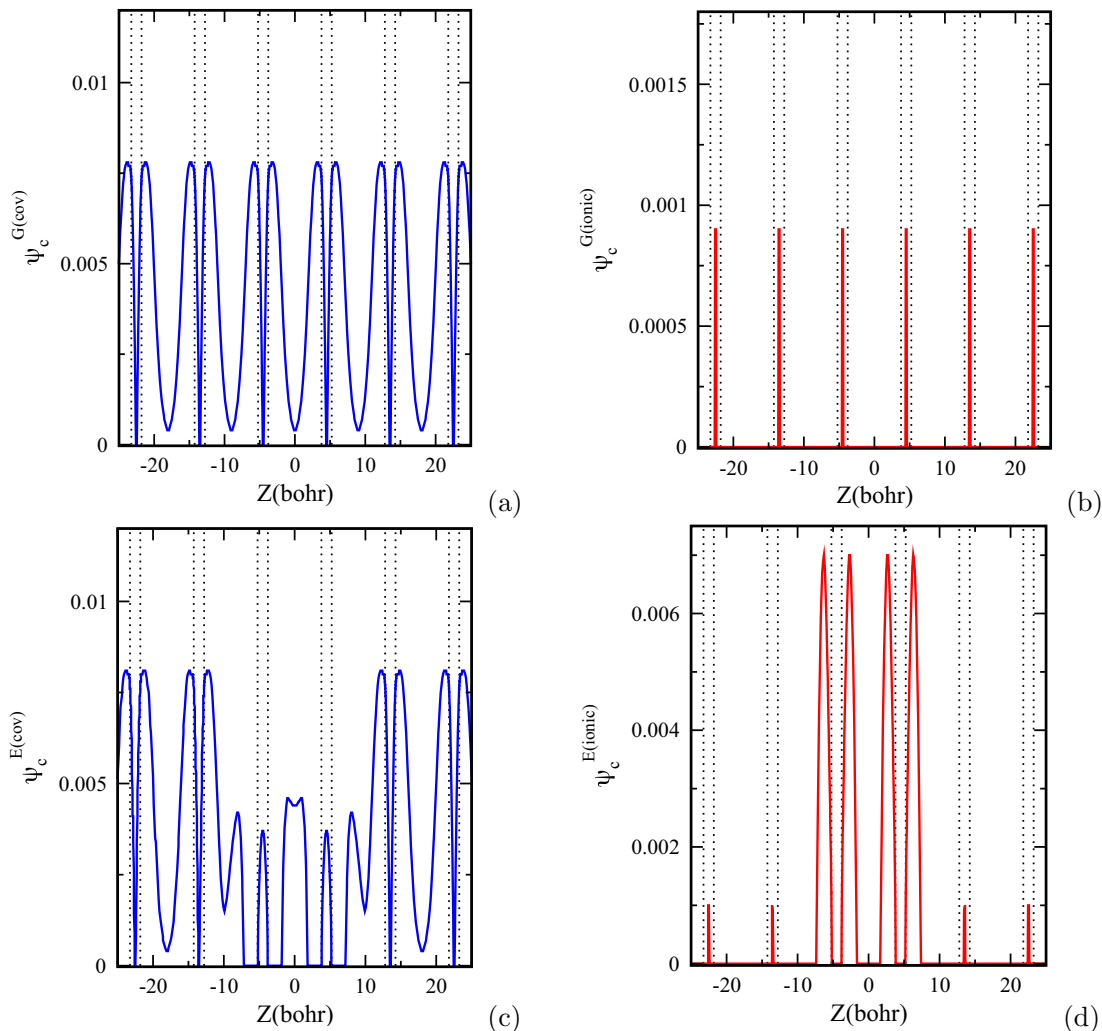
FIG. 10. H_{12} alternate bond chain. Covalent [panels (a) and (c) for ground and excited states, respectively] and ionic [panels (b) and (d) for ground and excited states, respectively] correlons. Dotted lines indicate positions of nuclei. Molecule positioned along the Z axis.

molecular crystal. On the other hand, just as in the H_2 case, the ionic correlons for all hydrogen chain ground states are reduced to the very sharp residual peaks around the bond midpoints. This correlon picture indicates the covalent nature of all ground states of both equidistant and alternate hydrogen chains.

For the excited states of smaller equidistant hydrogen chains the correlon picture is reversed with respect to that for the ground states. In particular, for the H_6 chain rather sizable peaks of the ionic correlon $\psi_c^{E(\text{ionic})}(\boldsymbol{r})$ are located in the atomic regions near the nuclei [see Fig. 7(d)], while more narrow (than those in the ground state) peaks of the covalent correlon $\psi_c^{E(\text{cov})}(\boldsymbol{r})$ are located in the less important energetically bond midpoint regions [see Fig. 7(c)]. This correlon picture indicates the ionic nature of the Ψ_6^E state.

A remarkable feature of the excited states of the longer equidistant chain H_{12} is the localization of the ionic correlon $\psi_c^{E(\text{ionic})}(\boldsymbol{r})$ on the central H atoms of the chains [see Fig. 9(d)]. In its turn, the covalent correlon $\psi_c^{E(\text{cov})}(\boldsymbol{r})$ is more localized in this case on the side atoms [see Figs. 9(c)]. Further-

more, the localization of the ionic correlon on the central H_2 fragments becomes a common pattern of the excited states of the alternate hydrogen chains [see Fig. 10(d)].

The observed localization of the ionic correlon betrays the single-electron character of ionic excitation. Indeed, unlike collective electron excitations with their delocalization over the whole system, a single-electron excitation tends to the most energetically favorable region, which in the considered case is the central part of the H_n chains. Then, the coexistence of the central ionic correlon and the side covalent correlon signals the true mixed character of the states of the "ionic correlation nature." This, together with the fact, that the clear separation of the ODC and OAC effects requires the adopted MCSCF approach of the restricted accuracy, points to the limitations of the concept of "ionicity" of excited states.

At variance with this, the proposed in this paper correlon quasiparticle theory can be universally formulated for all states at any level of the accuracy of correlated wave functions. This allows one to employ the correlons obtained at the present MCSCF level as the robust descriptors of the

covalent or ionic correlation character of many-electron states. On the other hand, the correlons obtained at a higher correlated level offer an accurate local description of electron correlation.

V. CONCLUSION

In the paper a universal, reduced description of electron correlation in the ground and excited states is introduced via the chain (5) of the on-top correlation functions. Based on this description, a correlon quasiparticle is proposed to represent the local effect of electron correlation in a given state.

An individual correlon is characterized with a one-particle wave function. On one hand, the imaginary part of the wave function gives the amplitude of the depletion of the on-top conditional electron charge due to (strong) electron correlation. On the other hand, the real part corresponds to the amplitude of the accumulation of the on-top charge due to the ionic squeezing of electrons. This allows one to consider the imaginary and real parts of the correlon wave function as the local kinematic descriptors of covalent or ionic correlation character of a given state.

The proposed correlon quasiparticle theory is applied to analyze the local correlation effects in the ground and first excited states of the prototype hydrogen molecule as well as of the paradigmatic equidistant and alternate linear hydrogen chains from H_4 to H_{12}. The covalent and ionic correlons obtained at the restricted MCSCF level of correlated functions are demonstrated to be the robust descriptors of the covalency of the ground and the ionicity of the excited H_n states. They can be efficiently combined with correlons obtained at higher correlated levels to analyze the manifestation of the covalent or ionic features in the accurate distribution of the on-top conditional electron charge.

The considered H_n states are characterized with the typical patterns of the correlon amplitude. Specifically, in all ground states the ionic correlon is reduced to the residual peaks around the midpoints of the H-H bonds. At variance with this, in the excited states of the equidistant H_n chains ionic correlons display more prominent atomic peaks, while covalent correlons tend to localize in the bond midpoint regions. For the excited states of the alternate chains and longer equidistant chains the localization of ionic correlons in the central fragments and covalent correlons in the side fragments is observed. This betrays the single-electron nature of ionic excitations and indicates the true mixed character of "ionic" states in the general case.

Further development of the proposed correlon theory would include evaluation of the electron correlation energy of excited states with a correlon-electron effective interaction. It can serve as a basis of the corresponding one-electron approximations, alternative to those of DFT [4–7], the formulation of which for excited states suffers from the well-known complications. The above-mentioned development of the present correlon theory will be addressed in our further work.

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