

Group functions for the analysis of the electronic structures of polymers

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The *ab initio* calculations of the electronic structures incorporating periodic boundary conditions allow to bring the well-developed standard methods of molecular quantum chemistry into the realm of solid-state physics and chemistry, especially important if the correlated treatment of the electronic structure is necessary. In this paper, we consider the general electron-group functions formalism for the electronic structure calculations as applied to one-dimensional periodic systems. The method for polymers is implemented in a close analogy with the recently proposed method for molecules. It allows us to calculate one-dimensional systems with different distributions of orbitals and electrons among groups which are subject to the strong orthogonality condition. The wave function is optimized both with respect to one- and two-electron density matrices for electron groups as well as the structure of molecular orbitals forming their carrier spaces. The method is applied to model systems: chains of hydrogen atoms, a linear hydrogen fluoride chain, and a lithium hydride chain. The convergence of the energy with respect to the explicitly covered range of interactions and the long-ranged Coulomb interactions is studied. It is shown that the local properties of one-electron states are very important for the whole performance of the method. The flexibility of the wave function based on the choice of electron groups is thoroughly analyzed.

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I. INTRODUCTION

The theoretical prediction of the electronic structure of solids is a direct way to understand their physical properties and their behavior in chemical processes. It is well known that the proper description of many characteristics of molecular systems (including solids) requires taking into account significant amount of electron correlations.¹ The density-functional methods have nowadays become the most popular tool to find the electronic structure of solids. Although these methods have shown a great potential in systematic studies of weakly correlated solids, they have significant drawbacks inherent to one-electron approaches, especially in the situations where a detailed account of electron correlation is necessary (for example, they typically underestimate band gaps in nonconducting solids). In addition, a systematic improvement of density-functional approaches is extremely difficult. The wave function-based methods are also well known but they typically use model Hamiltonians which make the results parameterization-dependent and can lead to the necessity of reparameterization for each new wave function.

The methods based on the *ab initio* consideration of the electronic structure using wave functions and “true” many-body Hamiltonians seem to be more promising and also challenging since the account of electron correlation can and must be performed in a controlled way.² The methods of quantum chemistry as applied to molecules provide high-quality estimates for the electronic structure and physical and chemical properties.³ It is desirable to bridge the gap between molecular and solid-state electronic structure calculations and bring the most successful methods of quantum chemistry into the realm of the solid state.

The simplest way to do it is to approximate the solid by a cluster of sufficient size. There are many problems on this way. The first one is that the edge effects are typically not

small and the convergence of the estimated physical characteristics with the size of the cluster is rather slow. Although adsorption processes on many solids with well-localizable electronic states (for example, zeolites) can be successfully described by small (even minimal) clusters, the vast majority of problems require very large clusters. The effective way to decrease the necessary cluster size is to treat the infinite environment of the cluster by adding some effective potential taking into account the long-range effects (embedding cluster schemes; see, for example, Ref. 4, and references therein). The development of effective methods with linear scaling of computational costs on the system size^{5,6} can further diminish the importance of this problem.

Another problem is how to define the boundary of the cluster when the solid is covalently bound. A number of approaches were proposed for this purpose. We mention here only three simple recipes: saturation of the cluster by hydrogen atoms,⁷ assumption of half an electron pair bond,⁸ and partitioning based on the Adams-Gilbert theorem leading to a localized set of equations.⁹ Although these methods can be quite effective in some particular situations, quite generally, the artificial boundary of the cluster introduces additional errors into the calculations. The problems of choosing a cluster, a proper definition of the boundary, and taking into account the environment eventually coincide with the problems arising in hybrid quantum-mechanical/molecular-mechanical schemes,¹⁰ where small part of a molecule is treated by a rigorous quantum chemical method and the rest is described in a more simple way (usually, by classical force fields).

In contrast, the methods imposing periodic boundary conditions on the electronic wave function are more promising since they allow to avoid significant errors arising from edge effects in the cluster. At the same time these methods require significant modification of standard quantum-chemical techniques and, as a consequence, special implementations. Most methods are based on the Bloch orbitals.¹¹ A fast multipole

method for long-range interactions and transformation of basis Gaussian orbitals into crystalline ones is very promising for bridging the gap between calculations of molecular and infinite periodic systems.¹² The methods based on the local (Wannier) orbitals spreading only over several lattice sites deserve special attention because the correlation hole is local in real space, and the local orbitals provide a natural basis for treating electron correlation in solids.¹³ Wannier orbitals can be obtained *a posteriori* by preliminary solution of the k -dependent SCF equations and Fourier transformation of the Bloch orbitals. At the same time, there are innovative procedures which allow to achieve the local orbitals directly in real space.^{14,15} It is done by formulating the SCF equations in real space in the assumption of the locality and fast (exponential) decay of one-electron states. The orthogonality of orbitals belonging to neighboring unit cells is ensured by adding a special orthogonalization potential to the one-electron effective Hamiltonian.

The local character of electron correlations provides numerous possibilities for going beyond the one-electron approximation. A series of different approximations is known in the literature.¹⁶ Characteristic examples include the second-order perturbation theory,¹⁷ the coupled-cluster expansions,¹⁸ Green function formalism,¹⁹ and local increments based on the approximate transferability of local effective Hamiltonians.²⁰ It is essential that most methods are nonvariational and based on the one-determinant approximation to the reference electronic state. The methods based on multiconfiguration reference electron states can be necessary if static electron correlations are strong. In this context, the MCSCF (multiconfiguration SCF) group function approach for periodic systems²¹ provides a good example of incorporating electron correlation into the calculations of solids although it uses a finite cluster based simulation of extended periodic structure.

The group functions technique²² can serve in many ways as a useful tool for treating the electronic structures of solids because the wave function of a periodic system can be represented as an antisymmetrized product of identical wave functions for unit cells which is naturally described by the electron groups. The most well-known applications include the analysis of the response of the rest of the crystal to the defect region²³ and the *ab initio* model potential method for treating defects in solids.^{24,25} The group functions technique in its particular geminal (two-electron) form was effectively used to treat low-dimensional solids.^{26,27} More general electron groups were used to treat metallocene-based stacks.²⁸ An essential result was obtained in Refs. 29 and 30, where the application of delocalized and localized geminals to extended systems was studied. It was shown that the localized geminals are superior than the delocalized ones, confirming the preference of treating electron correlations in real space.

Systems with reduced dimensionality often serve as a good example for the application of different approaches to the electronic structure of infinite systems. It is mostly due to a significant reduction of computational costs and the possibility to treat a large part of interactions in a rigorous way. There are many studies on infinite polymers within the Hartree–Fock approach.^{31–33} Correlation treatments of polymers have become very popular nowadays and many ap-

proaches were used to study ionic and covalent systems.^{17,34–36} Most characteristics of electronic structure calculation methods for polymers are inherent from the analogous methods for three-dimensional systems.

In the present work, we pursue the goal of developing a multiconfiguration variational *ab initio* approach for the analysis of electronic structure and properties of one-dimensional systems. We base our construction on the general group functions technique because, if the wave function of a polymer is given by an antisymmetrized product of group functions representing the unit cells, the most natural way to obtain consistent (independent on the choice of unit cells) solution to the electronic structure problem is to treat the unit cells in the same fashion as a polymer. Moreover, group functions have a great potential in analysis and physically clear representation of the electronic structure of molecular systems because electron groups typically represent well-defined structural blocks like chemical bonds, lone electron pairs and cores. Our present development is essentially based on the previous study,³⁷ where general group functions were applied to the electronic structure of molecules; here, however, we impose the periodic boundary conditions on the wave function which makes the formalism more complicated.

The paper is organized as follows. In the next section we consider the general implementation of the group functions technique for systems with one-dimensional periodicity. Then we apply this technique to a series of model-like polymeric chains: metallic and semiconducting hydrogen chains as well as charged linear hydrogen fluoride and lithium hydride chains. These examples illustrate the general characteristics of the method: convergence of the results, localization properties of variationally optimized one-electron states and dependence of results on the choice of electron groups. Finally, we draw several conclusions about the general performance of the method and future perspectives of its development.

II. METHOD

A. General outline

In this section we consider the necessary working formulas as well as our particular implementation of the wave function which is based on the electron group functions with periodic boundary condition for infinite polymers. The whole construction of the method has a lot in common with that proposed for the analysis of the electronic structure of molecules³⁷ although the translational symmetry leads to significant modifications of the formalism. The trial wave function of a molecule can be written as an antisymmetrized product of wave functions for the unit cells:

$$|\Psi\rangle = \prod_{M=-\infty}^{+\infty} G_M^+ |0\rangle, \quad (1)$$

where G_M^+ is a composite operator of creation of the wave function for the M th unit cell. Due to the translational symmetry all these operators produce group functions with the same quantum numbers but shifted in real space according to

the translation vector. The unit cell wave functions also have the structure of a product of group functions:

$$G_M^+ = \prod_m g_{Mm}^+, \quad (2)$$

where the specification of the electron groups $g_{Mm}^+|0\rangle$ determines the overall quality of the wave function. Until the structure of these groups is not defined, the wave function expression Eq. (2) is quite general. To make the formalism feasible, we impose several important conditions on the structure of the constituent groups.

The strong orthogonality condition³⁸ (which is equivalent to expanding the electron groups in the mutually orthogonal subspaces³⁹ and physically corresponds to a hypothesis about the importance of only one-electron exchange between electron groups⁴⁰) is very important since it allows to avoid complications due to nonorthogonality of one-electron states (methods based on nonorthogonal group functions, however, can be also proposed^{41,42}). This condition imposes serious restrictions on the form of the wave function. In some cases it leads to an insufficient flexibility of the wave function and, therefore, to a relatively small coverage of correlation energy and, also, inconsistencies in the description of chemical bonding.^{43,44} At the same time in many situations the strong orthogonality condition is not very restrictive and the correct choice of electron groups in combination with variational determination of their carrier spaces provides a high quality description of electronic structure of molecules.³⁷

The second condition is that all the electron groups are assumed to be singlets. By this we avoid the explicit consideration of coupling schemes between different multiplets since the presence of one nonsinglet electron group leads to an infinite number of them because of the translational symmetry. The third condition specifies the structure of electron groups. They are calculated on the full CI level. These conditions are also applicable to calculations of molecules. By this, the parameters defining electron groups g_m^+ are (besides the usual choice of basis set) only number of electrons and number of orbitals for each electron group. Despite having only a small number of parameters, the wave functions for the unit cell cover a large range since virtual (without electrons) electron groups are also allowed. We mention here only a few examples of wave functions covered: the spin-restricted Hartree-Fock (RHF), generalized valence bond (GVB), complete active space self-consistent field (CASSCF), and full CI wave functions.

The periodic boundary conditions lead to other limitations on the structure of wave function. Since we work in real space, the basis one-electron states forming carrier spaces for electron groups should have good (preferably exponential) decay properties. This leads to restrictions on the choice of systems which can be considered. Moreover, the basis set should be carefully chosen since the presence of very diffuse functions will lead to instabilities in the scheme.⁴⁵ For example, if we have an infinite chain of atoms with translation vector of length a , each of them has a Gaussian basis function of the form

$$\phi(r) = \left(\frac{2\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2}, \quad (3)$$

the overlap matrix between basis orbitals is a function of one parameter $\beta = \alpha a^2$. If β is larger than 1, the application of the symmetrical orthogonalization procedure to (localized) atomic orbitals leads to well-localized orthogonal orbitals with meaningful amplitudes only at several sites. If β has the order of magnitude about 0.1, the orthogonalized states spread over hundreds of sites that makes the whole procedure of orthogonalization unsuitable. This behavior of the procedure is a consequence of the quasilinear dependence of the basis orbitals.

It is obvious that some cut-off parameters are necessary to make the calculations possible. We introduce the parameter Q (delocalization length) characterizing the locality (decay properties) of carrier spaces for electron groups. By this each one-electron state is assumed to be spread over $2Q+1$ unit cells (from $-Q$ to Q if 0 specifies the unit cell to which the electron group is assigned). Another important parameter, R , characterizes the range of interactions explicitly covered. By this all molecular integrals within a cluster of length $R+1$ unit cells are calculated and fully used in the calculations while all other interactions are either totally neglected or covered approximately by summation of Coulomb interactions between atomic charges.

In the following, we denote atomic orbitals as $\mathbf{i}, \mathbf{j}, \mathbf{k}$, and \mathbf{l} , and molecular orbitals as $\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{d}$, and \mathbf{e} . The complex index for the arbitrary atomic orbital \mathbf{i} is given by two numbers: the number of the unit cell (I) and the number of the orbital (i) within the set of orbitals assigned to this unit cell. Analogously, for molecular orbitals \mathbf{a} is equivalent to Aa . Matrix C then determines the transformation from the atomic orbitals to the molecular ones:

$$a_\sigma = \sum_{I=-Q}^Q \sum_i C_{Ia} \mathbf{i}_\sigma, \quad (4)$$

where a stands for $\mathbf{a}=0a$. The set of all MOs is assumed to be orthonormalized (it is possible since we use full CI wave functions for all electron groups). The *ab initio* Hamiltonian in the basis of atomic orbitals can be written as

$$\hat{H} = \sum_{\mathbf{i}, \mathbf{j}} h_{\mathbf{i}\mathbf{j}} \hat{E}_{\mathbf{i}\mathbf{j}} + \frac{1}{2} \sum_{\mathbf{i}, \mathbf{j}, \mathbf{k}, \mathbf{l}} (\mathbf{i}\mathbf{j}|\mathbf{k}\mathbf{l}) [\hat{E}_{\mathbf{i}\mathbf{j}} \hat{E}_{\mathbf{k}\mathbf{l}} - S_{\mathbf{j}\mathbf{k}}^{-1} \hat{E}_{\mathbf{i}\mathbf{l}}], \quad (5)$$

where $\hat{E}_{\mathbf{i}\mathbf{j}} = \sum_\sigma \mathbf{i}_\sigma^\dagger \mathbf{j}_\sigma$ is the elementary generator, and the standard convention for molecular integrals is used. Although Eq. (5) is quite general, the practical calculations of the integrals in the basis of MOs imply restrictions on the summations defined by the parameters Q and R . For example, the one-electron integrals are given by formula

$$h_{0a\mathbf{b}} = \sum_{I, J=-Q}^{+Q} \sum_{i, j} C_{Ia} C_{Jb} h_{0i(B+J-I)j}. \quad (6)$$

The summation is over all unit cell indices I and J which satisfy the criteria $|B+J-I| \leq R$. The two-electron integrals are calculated analogously. Significant simplifications in the calculations are due to the symmetry of the molecular inte-

grals with respect to an interchange of indices. As in the case of molecular calculations,³⁷ only a small part of two-electron integrals in the basis of MOs is actually necessary due to the specific choice of the wave function.

The group functions structure of the wave function Eqs. (1) and (2) leads to a simple expression for the electronic energy which is a sum of intragroup contributions and Coulomb and exchange interactions between groups.²² In the case of imposed periodic boundary conditions, the electronic energy per unit cell can be written as

$$E^{\text{el}} = \sum_m \left[\sum_{a,b \in m} h_{0a0b} P_{ab} + \frac{1}{2} \sum_{a,b,c,d \in m} (0a0b|0c0d) \Gamma_{abcd} \right] + \sum_{M \geq 0} \sum_{m,n} \sum_{a,b \in m} [(MaMb|0c0d) - \frac{1}{2} (Ma0d|0cMb)] P_{ab} P_{cd}, \quad (7)$$

where P_{ab} and Γ_{abcd} denote intragroup elements of one- and two-electron density matrices. The electronic energy Eq. (7) is a function of two sets of parameters. The first one contains elements of density matrices (or amplitudes of different configurations in the full CI expansions of electron group wave functions), while the second reflects the structure of molecular orbitals given by the matrix C . We determine the parameters by a two-step iteration procedure.

B. Optimization of group wave functions

The first step in the two-step iteration procedure is the determination of the density matrices by solving full CI problems for electron groups in the effective field of other groups. We assume that the current set of MOs as well as intragroup elements of the one-electron density matrix in the basis of MOs are known. The direct use of Eq. (7) for an optimization of the density matrices is computationally demanding because it involves the calculation of the Coulomb and exchange integrals in the basis of MOs for pairs of electron groups. A more effective way is to explore the basis of atomic orbitals as much as possible.⁴⁶ For this purpose, we perform a transformation of the one-electron density matrix from the basis of molecular orbitals to the basis of atomic orbitals

$$P_{0ij} = \sum_{\substack{|M| \leq Q \\ |J-M| \leq Q}} \sum_m \sum_{a,b \in m} C_{-Ma} C_{(J-M)jb} P_{ab}. \quad (8)$$

The Fock matrix (including interactions between electrons within the same group) in the basis of atomic orbitals is constructed as

$$F_{0ij} = h_{0ij} + \sum_{\mathbf{k}, \mathbf{l}} [(0i\mathbf{j}|\mathbf{k}\mathbf{l}) - \frac{1}{2} (0i\mathbf{l}|\mathbf{k}\mathbf{j})] P_{0\mathbf{k}(L-K)\mathbf{l}}, \quad (9)$$

where the indices J , K , and L are restricted by a range given by the R parameter ($J \geq 0$; $J, K, L \leq R$; $K, L \geq J - R$). The matrix elements with negative values of J can be easily obtained due to symmetry of the Fock matrix with respect to an interchange of its indices. The transformation of the Fock matrix

to the basis of MOs is performed by the C matrix,

$$F_{0\mathbf{a}\mathbf{b}} = \sum_{I,J=-Q}^{+Q} \sum_{i,j} C_{i\mathbf{a}} C_{j\mathbf{b}} F_{0i(B+J-I)j}. \quad (10)$$

The construction of effective Hamiltonians for groups requires only intragroup matrix elements of the Fock matrix. The one-electron matrix elements of effective Hamiltonian for orbitals a and b assigned with group m (irrespective to the unit cell) are obtained by removing the intragroup Coulomb interaction

$$h_{ab}^{\text{eff}} = F_{0a0b} - \sum_{c,d \in m} [(0a0b|0c0d) - \frac{1}{2} (0a0d|0c0b)] P_{cd}. \quad (11)$$

The effective electronic Hamiltonian for the m th group can be written as

$$\hat{H}_m^{\text{eff}} = \sum_{a,b \in m} h_{ab}^{\text{eff}} \hat{E}_{0a0b} + \frac{1}{2} \sum_{a,b,c,d \in m} (0a0b|0c0d) \times [\hat{E}_{0a0b} \hat{E}_{0c0d} - \delta_{bc} \hat{E}_{0a0d}]. \quad (12)$$

The full CI solutions for all electron groups are found by using the Unitary Group Approach for the many-electron correlation problem.⁴⁷

The intragroup elements of the one- and two-electron density matrices are calculated with these wave functions as the corresponding averages

$$P_{ab} = \langle \Phi_m | \hat{E}_{0a0b} | \Phi_m \rangle,$$

$$\Gamma_{abcd} = \langle \Phi_m | \hat{E}_{0a0b} \hat{E}_{0c0d} - \delta_{bc} \hat{E}_{0a0d} | \Phi_m \rangle. \quad (13)$$

The electronic energy can be calculated as a sum over groups since the interactions between them are included into effective one-electron matrix elements,

$$E^{\text{el}} = \frac{1}{2} \sum_m \sum_{a,b \in m} \left[(h_{ab}^{\text{eff}} + h_{0a0b}) P_{ab} + \sum_{c,d \in m} (0a0b|0c0d) \Gamma_{abcd} \right]. \quad (14)$$

C. Optimization of molecular orbitals

The second step in the iteration procedure is the optimization of carrier spaces for electron groups which corresponds to the mixing of orbitals assigned to different groups (the mixing of orbitals within the same group does not change the energy). An arbitrary rotation that mixes two orbitals Aa and $0b$ from groups m and n can be written as a function of one parameter ϵ ,

$$\begin{cases} \mathbf{a}' = \sqrt{1 - \epsilon^2} \mathbf{a} + \epsilon \mathbf{b} \\ \mathbf{b}' = -\epsilon \mathbf{a} + \sqrt{1 - \epsilon^2} \mathbf{b}, \end{cases} \quad (15)$$

if the orthonormality of the set of MOs is preserved.

The determination of the set of the ϵ parameters is based on the minimum condition for the total electronic energy which can be written as a function of ϵ ,

$$\begin{aligned}
E^{\text{el}} = E_0^{\text{el}} + 2\epsilon \left\{ \sum_{c \in m} F_{0bAc} P_{ac} - \sum_{c \in n} F_{0cAa} P_{bc} \right. \\
- \sum_{c,d,e \in m} \left[(-Ab0c|0d0e) - \frac{1}{2}(-Ab0e|0d0c) \right] P_{ac} P_{de} \\
+ \sum_{c,d,e \in n} \left[(Aa0c|0d0e) - \frac{1}{2}(Aa0e|0d0c) \right] P_{bc} P_{de} \\
+ \frac{1}{2} \sum_{c,d,e \in m} (-Ab0c|0d0e) [\Gamma_{acde} + \Gamma_{cade}] \\
\left. - \frac{1}{2} \sum_{c,d,e \in n} (Aa0c|0d0e) [\Gamma_{bcde} + \Gamma_{cbde}] \right\} + O(\epsilon^2). \quad (16)
\end{aligned}$$

To calculate the gradient we only need a small part of the set of the two-electron integrals in the basis of MOs, namely, those of the form $(\mathbf{a}0c|0d0e)$. To construct an efficient procedure for finding optimal values of ϵ parameters, the second-order contribution to the energy with respect to ϵ 's should be used. At the same time its explicit calculation is very time demanding. Therefore we consider only the diagonal part of the Hessian matrix and make approximation to the second derivative with respect to ϵ ,³⁷

$$\frac{1}{2} \frac{\partial^2 E^{\text{el}}}{\partial \epsilon^2} = F_{0b0b} P_{aa} - \sum_{c \in m} F_{0a0c} P_{ac} + F_{0a0a} P_{bb} - \sum_{c \in n} F_{0b0c} P_{bc}. \quad (17)$$

When the first and approximate second derivatives are known, we obtain a vector of the ϵ parameters by applying the inverse Hessian matrix update procedure⁴⁸ based on the combination of variable-metric second order update schemes and direct inversion in the iterative subspace.⁴⁹ The matrix C is updated and the iteration procedure returns to the step of optimization of wave functions for electron groups with given molecular orbitals.

III. RESULTS AND DISCUSSION

In this section we consider a series of illustrative applications of the method described above. For this purpose we consider model systems and use minimal (STO-6G) basis set to reveal the basic properties of the procedure. The results for the real polymers and extended basis sets will be reported elsewhere. In the present consideration, special attention is paid to the convergence of the results, the choice of electron groups and the structure of one-electron states forming carrier spaces for electron groups.

A. Hydrogen chains

A chain of hydrogen atoms can serve as a good model system for the general analysis of characteristics of a new approach. Its electronic structure and properties as a function of structural characteristics have been studied in a series of works.⁵⁰⁻⁵³ The correlation effects are thought to be important in this system because in the case of an infinite metallic hydrogen chain the Hartree-Fock theory accounts for only about a half of the real cohesion.⁵⁰ The important question in application of the general group function formalism is how to choose electron groups. In Ref. 37 this problem was stud-

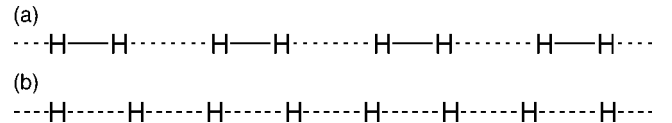


FIG. 1. Chains of hydrogen atoms: (a) set of H₂ molecules, (b) equidistant chain with the same density.

ied in detail on the example of electronic structure calculations of diatomics, and it was shown that the results strongly depend on this choice. When we have a chain of hydrogen atoms only two possibilities exist within a given formalism (and minimal basis set): the first one is to take one electron group per unit cell with 2 electrons and 2 orbitals (geminal approach) while the second one is to take two electron groups—1 doubly-filled orbital and 1 vacant orbital (SCF approach).

We consider two types of hydrogen chains depicted in Fig. 1: the first one (a) is a set of dihydrogen molecules with bond length 0.74 Å and translation vector of length 1.74 Å; the second chain (b) is an equidistant (metallic type) one with the same density as the chain (a). It is clear that these chains should differ significantly in the localization of one-electron states. The general instability of the metallic chain with respect to dissociation on the molecules reveals itself in the relative energies of these chains: the total energy of the system of type (a) is lower than that of the system of type (b) for both SCF and geminal approaches.

The construction of the computational procedure includes the cut-off parameters (Q and R). These parameters play quite different roles in the determination of the energy per unit cell. The parameter R defines the Hamiltonian (range of interactions calculated explicitly) and, therefore, the physical model. At the same time, the parameter Q controls the validity of the basic approximation—that of strong orthogonality between electron groups. It seems natural to study dependence of the results on the physical model (R) in the limit of large Q where the strong orthogonality approximation is valid, while the dependence of the results on the parameter Q does not provide physically meaningful information because in the case of small Q the model is broken. The hydrogen chains are not charged and, therefore, the long-range Coulomb interactions should not be significant. We studied the dependence of the calculated energy per unit cell on the R parameter for two hydrogen chains (a) and (b) (here and in the following studies we used $Q=15$, which is more than enough for validity of the strong orthogonality condition). The results for the geminal model are given by Fig. 2, where the relative energy (with zero level corresponding to the limit of infinite R) is plotted as a function of the range R of interactions covered. In the case of the localized chain (a) the energy increases when the R parameter grows. It corresponds to the generally repulsive character of interactions between unit cells and has a direct relation with the instability of the hydrogen chain with respect to a dissociation yielding dihydrogen molecules. The convergence is rather fast. For example, for $R=4$ the calculated energy differs from its limit only by 0.2 mH. The similar convergence properties can be obtained within the cluster model. At the same time the equivalent (according to the range of interactions covered)

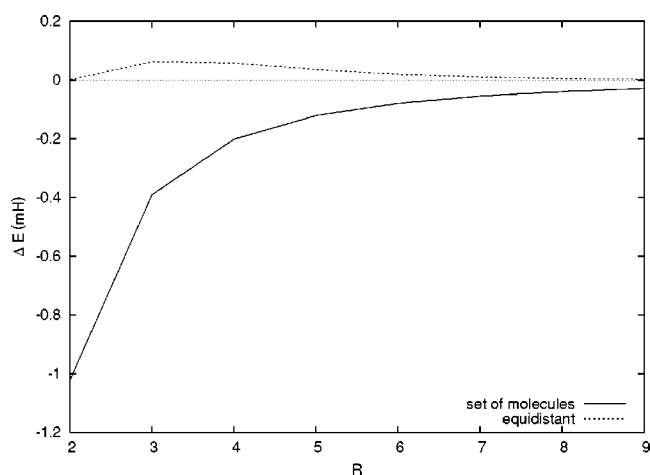


FIG. 2. Convergence of the energy per unit cell for hydrogen chains as a function of the interaction cut-off parameter.

cluster procedure for the unit cell energy uses difference of energies for H_{10} and H_8 molecules, i.e., needs two independent calculations. The computational costs in the case of the present method are significantly smaller than those in the case of cluster models because periodic boundary conditions significantly diminish the number of variables to be optimized. Moreover, calculations based on the periodic boundary conditions allow to obtain more reliable approximations to the structure of one-electron states than the equivalent cluster procedures.

The convergence properties for the metallic hydrogen system are more difficult. We can see a combination of two factors: by increasing R we include new interactions between further separated unit cells and this increases the energy just like in the case of the chain (a). At the same time, by increasing R we better treat the relatively large “tails” of the one-electron states. The combination of these two counteracting factors leads to a curve with a maximum at $R=3$. Moreover, for $R=2$ these factors are almost compensated and the energy is very close to its limit. Thus, surprisingly, the convergence of the energy in the case (b) is better than in case (a).

Here we address the problem of choice of electron groups for the case of periodic boundary conditions. The geminal and SCF approaches lead to quite different results. For example, the estimated equilibrium H-H distance in the equidistant chain is 0.970 and 0.942 Å for the geminal and the SCF approach, respectively. These values can be compared with previously reported value 0.974 Å, obtained in the framework of the RHF method with extended basis set.⁵⁴ Interesting examples of different choice of electron groups can be obtained if we double the unit cell, i.e., consider periodically repeated system of 4 hydrogen atoms. In this case we have three different possibilities: the first one is one 4-electron 4-orbital group (full CI approach for the unit cell), the second one is two 2-electron 2-orbital groups (geminal approach), and the third one is the SCF approach with 2 doubly-filled and 2 vacant orbitals. We can compare the energies per “ H_2 ” unit for different wave functions and different geometries. In the case of the system (a) the correlation energy covered is 13.58 and 15.93 mH for the geminal and the full CI approach, respectively. In the case of the system

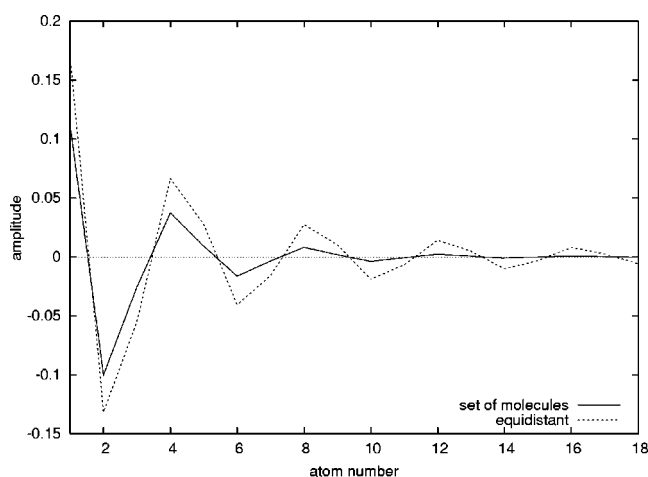


FIG. 3. Amplitudes of bonding orbital at atoms close to the central unit cell.

(b) these energies are 11.04 and 14.56 mH. The correlation energy covered for the chain (a) is larger than that for the chain (b) since the correlation is a local phenomenon and the electron states in the chain (b) are more delocalized than in the chain (a). The different degree of delocalization also explains why the transition from 2- to 4-electron group function is more important for the chain (b) than for the chain (a). Analogous conclusions can be drawn from consideration of two parallel hydrogen chains where the unit cell contains 4 hydrogen atoms.

The structure of one-electron states is very important for the whole performance of the method. Their fast decay can significantly improve the convergence of the procedure with respect to the R parameter. The “tails” of one-electron state have two different origins. The first one is the orthogonality requirement and the second one is true delocalization. To make the correct comparison between the electronic structures of chains (a) and (b) we single out the delocalization “tails” of local orbitals. For this purpose, we express the molecular orbitals in the basis of symmetrically orthogonalized atomic orbitals. Thus defined amplitudes of molecular orbitals on the atoms not belonging to the central unit cell correspond to the orbital “tails” due to delocalization. Figures 3 and 4 represent the decay of the bonding and antibonding orbitals in the hydrogen chains treated within the geminal approach. The amplitudes corresponding to delocalization “tails” are plotted against number of hydrogen atom (number 1 corresponds to the atom closest to the central unit cell). These figures show the significant difference between two chains: the states in the chain (a) decay very fast (absolute values of the amplitudes become less than 0.01 starting from the fourth unit cell from the central one) while in the case of the chain (b) the decay is more smooth (absolute values of the amplitudes become less than 0.01 starting from the eighth unit cell from the central one). The same conclusion can be drawn from the total weights of tails for two chains: in the case of the chain (a) it is 0.050 while in the case of the chain (b) it is already 0.116.

B. Charged chains: Hydrogen fluoride and lithium hydride

Because the atoms in the hydrogen chains are uncharged, they are not suitable for studying the role of long-ranged

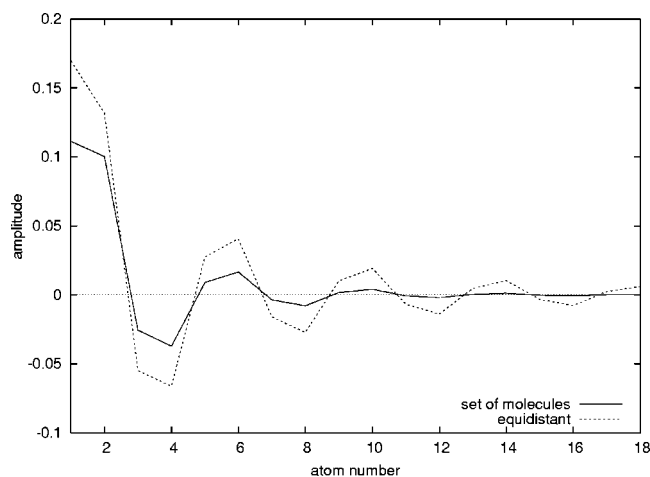


FIG. 4. Amplitudes of antibonding orbital at atoms close to the central unit cell.

Coulomb interactions. We extend our analysis of the properties of the procedure proposed to two characteristic asymmetric chains with non-zero total charges on the atoms: linear hydrogen fluoride and lithium hydride (Fig. 5).

The chain of hydrogen fluoride molecules is often used as a characteristic example for studying properties of computational procedures.^{55–57} It is important that the polar character of hydrogen fluoride molecules makes it necessary to take into account the long-ranged Coulomb interactions for obtaining high-precision results, and the hydrogen fluoride chain is an appropriate model for studying effects of these interactions.^{57,58} It is known that the correlation energy converges fast in this polymer (precision is about $1 \mu\text{H}$ per unit cell if the range of 15 \AA is taken into account).¹⁸ We consider here a model chain of hydrogen fluoride molecules with bond length 0.95 \AA and the translation vector of length 2.49 \AA . The electron groups are chosen in the following way: three doubly-filled orbitals describe the core electrons of the F atom and 2 lone pairs perpendicular to the chain direction while the rest is treated as one group with 4 electrons and 3 orbitals.

The estimated Mulliken charges in this chain are about ± 0.26 . Figure 6 illustrates the convergence of the energy in this system as a function of the R parameter for two cases: the first one corresponds to neglecting all interactions between unit cells with difference between their numbers more than R , while the second one approximates these (long-ranged) interactions by converged sum of Coulomb interaction between the Mulliken charges. The exchange interactions are assumed to be short-ranged since it is known that they decrease exponentially in the hydrogen fluoride chain.⁵⁸ The figure shows that a simple inclusion of the Coulomb

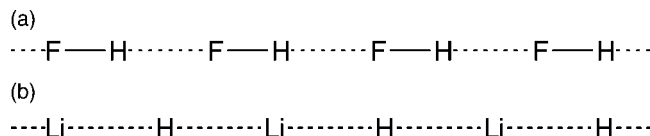


FIG. 5. Charged chains: (a) hydrogen fluoride, (b) lithium hydride.

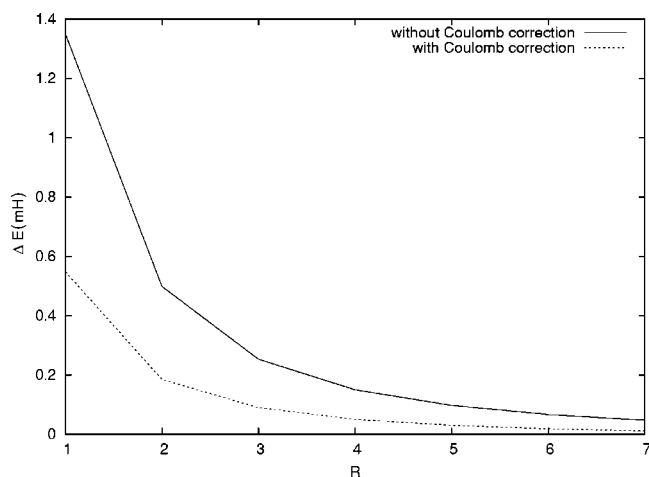


FIG. 6. Convergence of the energy per unit cell for linear hydrogen fluoride chain as a function of the interaction cut-off parameter.

interaction between charges significantly improves the convergence of the procedure. The difference between two procedures remains rather large even for $R=7$.

Lithium hydride chain is also a very popular model one-dimensional system mostly due to its simplicity. It is well studied both on the Hartree-Fock level^{32,33} and with account of electron correlations.^{34,35} It is known^{59,60} that the equilibrium structure of this chain corresponds to the equidistant case with the hydrogen atom placed on the same distance from two neighboring atoms. This is because the large electronegativity difference between Li and H points towards ionic bonding which is bound to the condensed phase with equal Li-H and H-Li bond lengths. Therefore, the only geometric parameter is the lattice constant of the chain.

Three choices of group functions seem natural for this polymer. The first possibility is one 4-electron 6-orbital group (full CI approach), the second one is one doubly-filled orbital for the Li core and one 2-electron 5-orbital group (geminal approach), and the third one is the SCF approach with 2 doubly-filled and 4 vacant orbitals. This chain is ionic and, therefore, proper account of long-range Coulomb interactions is necessary. We performed calculations for all three choices of electron groups in the limit of large R and Q parameters with correction to the energy due to Coulomb interaction between atomic charges. The equilibrium geometry obtained in the framework of the full CI and geminal approach is almost the same (the optimized values of the lattice constant are 3.301 and 3.302 \AA , respectively). This is not surprising since the core-valence separation is physically well substantiated. In fact, the geminal approach covers more than 99.4% of the correlation energy (about 14.7 mH). In the case of a covalently bonded LiH molecule the analogous value is about 98.9%. The lattice constant obtained can be compared with those optimized within the Hartree-Fock approach (3.521 and 3.428 \AA for basis sets with 2 and 8 orbitals per unit cell³³).

In the case of the often studied asymmetric lithium hydride chain with alternating bond lengths of 4.0 and 6.0 a.u. ,^{32,35} we calculated the correlation energy per unit cell

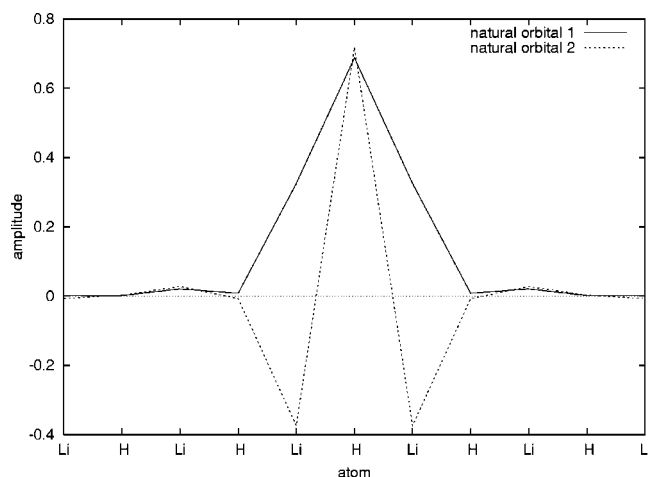


FIG. 7. Amplitudes of optimized natural orbitals for lithium hydride at the valence s -AOs for atoms close to the central unit cell.

using five different basis sets. We estimated it to be equal 26.5, 27.4, 15.6, 19.0, and 18.0 mH for STO-4G, STO-6G, Huzinaga's split valence, 4-31G, and 6-31G basis sets, respectively. These values are in a good correspondence with the coupled-cluster estimates³⁵ which, for different methods and different basis sets, cover the range from 19 to 27 mH. Finally, we present the structure of optimized one-electron states in the basis of symmetrically orthogonalized atomic orbitals. We consider the valence geminal obtained for symmetric LiH chain with the lattice constant 3.302 Å. Figure 7 shows the amplitudes of two mostly occupied natural orbitals (electron densities 1.976 and 0.023, respectively) on the valence s -orbitals ($2s$ for Li and $1s$ for H; of course, some density is also on the $2p_x$ -orbitals of Li). The figure shows that the decay of variationally optimized one-electron states in this system is exponential and it is faster than in the case of hydrogen chains which justifies the application of the method proposed.

IV. CONCLUSIONS

In the present work we considered the *ab initio* implementation of the general electron group functions approach

with periodic boundary conditions in the one-dimensional case. The trial wave function was chosen as an antisymmetrized product of identical electron groups representing unit cells which are constructed as antisymmetrized products of electron groups representing chemical bonds, lone pairs or more general molecular building blocks. The strong orthogonality condition imposed on the wave function allowed us to write down a simple expression for the energy. The method was constructed as a variational one, and the optimization of two classes of parameters (density matrices and carrier spaces for electron groups) was effectively implemented as a two-step iteration procedure. The calculations performed on the model systems have shown that the convergence of the procedure with respect to the range of interactions explicitly taken into account was quite fast. Taking into account the Coulomb interaction between charges behind this range can significantly improve the convergence. Our calculations have shown that for the systems considered, a geminal wave function covers significant part of the correlation energy and the transition to more general electron groups is less important than the transition from the one-electron approximation to the geminal one. In the case of different hydrogen chains it was shown that the decay properties of one-electron states strongly depend on the molecular geometry. The method can be applied to a wide range of one-dimensional systems. Further development may include taking into account perturbation corrections to the wave function, implementation of fast procedure for geminal wave function avoiding transformation of integrals from the basis of atomic orbitals to the basis of molecular orbitals, and bivariational construction allowing for weakly overlapping electron groups.

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