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Different orbitals for different spins for solids: Fully variational *ab initio* studies on hydrogen and carbon atomic chains, polyene, and poly(sulphur nitride)

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The spin unrestricted-Hartree-Fock (UHF) method (the fully variational version of the different-orbitals-for-different-spins crystal-orbital method) is applied to four infinite one-dimensional model-system linear chains of hydrogen and carbon atoms, polyene [i.e., $(CH)_x$] and poly(sulphurnitride). The calculations were performed by using the linear-combination-of-atomic-orbitals (LCAO) approximation evaluating exactly all the integrals over atomic orbitals within a given interaction radius. The part of the correlation energy which is taken into account by the method as well as the width of the forbidden energy gap are studied as function of the geometry parameters of H and C chains. It is concluded that the electrons lying around the Fermi level are strongly correlated by this method, while the other electrons are practically not correlated at all. No metal-insulator transition can be described by the method for the H and C chains. The very large gap obtained with the equidistant model of polyene chains supports the assumption that the model with alternating bond lengths should be preferred. In contrast to what is a common assumption, the UHF stabilization energy per unit cell is much smaller than the forbidden bandwidth owing to self-consistent rearrangement of electrons.

I. INTRODUCTION

The various kinds of different-orbitals-for-different-spins (DODS) many-electron wave functions of the form[1] ($\mathfrak{A}$ is the antisymmetrizer)

$$\phi_{\text{DODS}} = \mathfrak{A}(\{\varphi_1^\alpha(1)\alpha(1)\varphi_1^\beta(2)\beta(2)\varphi_2^\alpha(3)\alpha(3)\cdots\}) \qquad (1)$$

are able to account for a part of the electronic correlation energy without losing the simplicity of the one-electron picture. Since this wave function is not a pure spin state, Löwdin suggested[2,3] the so called "alternant molecular orbital" (AMO) version of the method where the one-determinantal DODS wave function is subjected to spin projection,[2]

$$\phi_{\text{AMO}} = \mathcal{O}^S \phi_{\text{DODS}}, \qquad (2)$$

and special assumptions for the one-electron orbitals φ_i^α and φ_i^β are used, e.g., on the basis of the alternancy of the considered molecule.

The DODS method as applied to the study of the electronic structure of solids[4-12] exhibits an interesting property[10]: The total energies per elementary cells of the spin-projected and unprojected wave functions tend to each other in the solid-state limit (N, the number of elementary cells, increases to infinity). Furthermore, the one-particle energies obtainable with the projected and unprojected methods are usually supposed to agree to order $1/N$.[10] We shall, therefore, discuss merely unprojected methods for solids, in this paper.

There is an important feature of all DODS methods most clearly apparent for one-dimensional (1-D) solids: Eq. (1) describes an antiferromagnetic-type long-range order if $\varphi_i^\alpha \neq \varphi_i^\beta$, as shown by Misurkin and Ovchinnikov.[9] Furthermore, with the restriction

$$\varphi_i^\alpha = \varphi_i^\beta, \qquad (3)$$

ϕ_{DODS} goes over to a doubly occupied determinant ϕ_R (restricted). Therefore, it may be of interest to study under which circumstances the restricted ϕ_R is unstable with respect to the relinquishment of the double-occupancy requirement (3).[13]

This problem has been studied recently in connection with the jellium model using the cubic Fermi surface[8] and a single (wave-vector-independent) variational parameter, and also with regard to Li metal[6] using an *ab initio* approach. Both studies indicated that albeit the DODS wave function is appropriate for the description of the electron gas in the low-density limit, near the equilibrium densities of real materials the extra variational freedom introduced does not lead to improvement of the total energy, i.e., no correlation energy is obtained because the orbitals are spontaneously doubly occupied.

Nevertheless the DODS method and its different variants seem to be particularly interesting as applied to a certain class of solids, the quasi-one-dimensional materials.[11] As mentioned above, it is particularly well suited for the description of their antiferromagnetic state. It was also suggested[12] that if the lattice parameter is changed the DODS methods may be able to describe a transition from a metallic state to an insulating one.

The aim of the present paper is to study numerically the merits of a specific form of the DODS method, namely, the fully variational unrestricted-Hartree-Fock method, as applied to realistic 1-D polymers and solid-state models. Restricted-Hartree-Fock studies (i.e., those with variational doubly occupied determinantal wave functions) carried out simultaneously enabled us to consider the correlation energy obtained by the DODS method. Comparing the energy gaps of the two methods in question we comment also on the question of to which extent the gap in these models should be attributed to the correlation of electrons or to the alternation of the bond lengths. Finally, by changing the geometry parameters the adequacy of the DODS method as applied to the problem of metal-insulator transitions can also be commented on.

II. METHOD AND SYSTEMS STUDIED

The form of our crystal orbitals was chosen to be a linear combination of atomic orbitals (LCAO),

$$\varphi^{\eta}_{n,\vec{k}}(\vec{r})=\frac{1}{\sqrt{N}}\sum_{\vec{R}}\sum_{\mu}e^{i\vec{k}\cdot\vec{R}}C^{\eta}_{n,\vec{k},\mu}\chi_{\mu}(\vec{r}-\vec{R}),$$

where $\eta=\alpha$ or β (spins), $\vec{R}$ is a lattice vector (periodic boundary conditions are used), $\chi_\mu(\vec{r})$ is the set of basis atomic orbitals (AO's) in the reference cell ($\mu=1,2,\ldots,m$), $\vec{k}$ is a reciprocal-space wave vector, and n is the energy-band index. If this form is substituted into (1) a fully variational procedure by means of the free coefficients $C^{\eta}_{n,\vec{k},\mu}$ leads to the crystal-orbital form of the Pople-Nesbet-Berthier unrestricted-Hartree-Fock formalism.[14] The corresponding equations are given, e.g., in Ref. 15 and we are not going to rewrite them here. The atomic-orbital basis of Pople *et al*[16] has been used. Except where mentioned explicitly, we used the STO-3G (minimal basis set of Slater-type orbitals, each expanded in terms of 3 Gaussian functions according to Ref. 16) AO basis set. Our computer program was described in Ref. 15, where our choice of starting density matrices was discussed, besides other computational aspects. In a previous paper reporting our first calculations of this kind[17] we have already emphasized that the main advantage of this specific form of the DODS method has been its computational simplicity. It may be noted that this formalism can be easily extended to systems with more than one electron and AO in the elementary cell.

In order to find the UHF solutions, the unit cell has to be formally doubled. This choice allows the two energy bands for different spins to become identical, while the translational symmetry of the wave function is reduced by the splitting of the orbitals with different spins.[1] Owing to the specific form of this spin arrangement, the correlation taken into account in this way is mainly a correlation of electrons on neighboring sites (neighboring chemical units).

For the characterization of the degree of splitting of the wave functions of the α and β electrons the diagonal elements of the density matrices are subtracted and this difference is referred to in the text as "splitting parameter" or "density splitting."

The model systems studied were the following.

H *atomic chain*. Linear chains with equidistantly arranged H atoms have been studied previously by the present authors[17] with the aid of the *ab initio* UHF crystal-orbital method. Here we consider models with alternating shorter and longer bonds, keeping their average at 1.95 bohrs, the energetically most stable bond length of the equidistant model.[17] (The basis set here was the STO-4G.)

C atomic chain. Linear chains have been studied previously with equidistant and alternating models by the *ab initio* restricted-Hartree-Fock (RHF) crystal-orbital method.[18] Accordingly, the most stable geometry is expected for an alternating model with parameters around r (average bond length) $=1.27$ Å and Δr (difference of short and long bond lengths) $=0.27$ Å. The models studied by the UHF method in this paper were centered around the model with $r=1.26$ Å.

Polyene, $(\mathrm{CH})_x$. The nonalternating zig-zag geometry, used in our previous RHF study,[19] was applied.

Polysulphur nitride, $(\mathrm{SN})_x$. An experimental zig-zag geometry[20] was used. (This calculation has been fully reported in Ref. 21 and the results are given here merely for comparison purposes.)

It is to be noted that the elementary cells of these two latter models have odd numbers of electrons leading to a metallictype spectrum in the RHF scheme, similar to the equidistant arrangements of the first two systems.

III. RESULTS

Selected results are summarized in Tables I–IV. It is to be emphasized that a number of attempts to obtain UHF solutions for nonequidistant models quite apart from the equidistant model failed and the RHF solution was reobtained. It is enlightening from this point of view to look at the sharp decrease in the difference of total energies per unit cell obtained by the two methods ($E^{\mathrm{RHF}}_{\mathrm{tot}}-E^{\mathrm{UHF}}_{\mathrm{tot}}$) for the H chain, when departing from the equidistant model (Table I, last column).

TABLE I. Unrestricted-Hartree-Fock results for infinite hydrogen chains using the *ab initio* crystal-orbital method (energy in atomic units: 27.21 eV).[a,b]

Bond lengths (bohrs)	RHF E_{tot}	RHF E_{gap}	UHF E_{tot}	UHF E_{gap}	Density splitting	$E_{tot}^{RHF} - E_{tot}^{UHF}$
1.95 1.95	−6.352 65	0.0	−6.376 70	0.3904	0.426	0.024 05
1.94 1.96	−6.374 34	0.3451	−6.377 26	0.3897	0.408	0.002 92
1.925 1.975	−6.379 77	0.3677	−6.380 11	0.3948	0.359	0.000 34
1.90 2.00	−6.389 42	0.4130	−6.389 58	0.4130	0.128	0.000 16
1.80 2.10	−6.437 05	0.5431	−6.437 14	0.5431	0.020	0.000 09

[a] An STO-4 G atomic-orbital basis set was used (Refs. 16 and 17).

[b] E_{tot}^{RHF} and E_{tot}^{UHF} refer to total energy per unit cell obtained by the RHF and UHF crystal-orbital methods, respectively.

IV. DISCUSSION

A. Correlation energy included

For the H chain maximal correlation was included with equidistant geometry, particularly at large interatomic separations. This is due to the well-known failure of the RHF method, to be unable to describe dissociation into odd-electron subsystems. At the equilibrium geometry of the equidistant chain the modest value of 0.11 eV/electron was obtained.[17] For the carbon chain the largest correlation energy (1.3341 eV/atom) is also obtained with the nonalternating model. This value is significant if we take into account that within the minimal basis for this system all electrons except the core ones can be correlated, yielding an effective 0.3335 eV/(valence electron) correlation. However, by inspecting the wave functions (and density matrices) of the α and β spins, it is apparent that not all valence electrons are correlated; only those possessing a π-type symmetry are. The latter have alternatingly large and small amplitudes for the α and β spins. The large and small amplitudes alternate in an

TABLE II. Unrestricted-Hartree-Fock and restricted-Hartree-Fock results for infinite carbon chains using *ab initio* crystal-orbital methods.[a]

Bond lengths (Å)	RHF E_{tot}[b]	RHF E_{gap}	UHF E_{tot}[b]	UHF E_{gap}	Density splitting[c]
1.27 1.27			−149.457 39	0.053	0.043
1.26 1.26	−149.453 55	0	−149.502 58	0.330 46	0.425
1.24 1.28	−149.499 46	0.274 62	−149.507 00	0.335 95	0.373
1.22 1.30	−149.520 56	0.325 97	as in RHF	as in RHF	0
1.185 1.335	−149.545 89	0.509 50	as in RHF	as in RHF	0
1.135 1.385	−149.246 11	0.504 00	as in RHF	as in RHF	0

[a] Energy in atomic units (1 a.u. = 27.21 eV).

[b] As in Table I.

[c] Only π type; others are negligible.

TABLE III. Unrestricted-Hartree-Fock results for two "metallic-type" polymer models using the *ab initio* crystal-orbital method (energy in a.u.).

	$E_{\text{tot}}^{\text{RHF}} - E_{\text{tot}}^{\text{UHF}}$	$E_{\text{gap}}^{\text{UHF}}$	$E_{\text{gap}}^{\text{RHF}}$ [a]	"Density splitting"
Polyene	0.01518/CH	0.4974	0.1523 [b]	0.632 [c]
$(\text{SN})_x$	0.116/SN	0.535	0.120 [d]	0.91 [e]

[a] Gap corresponding to a charge-density-wave solution.

[b] Reference 19.

[c] Only π component is non-negligible.

[d] Reference 21.

[e] Cannot be characterized by a single number, as several valence orbitals split to a significant extent. The value refers to the largest "splitting," that of the $2p_z(\pi)$ electrons of the nitrogens.

electrostatically balanced way: large α density on π_z orbital, small β density on π_y orbital of the same atom and vice versa on neighboring atoms (the x axis is the chain axis). Taking this into account the correlation energy is effectively 0.667 eV/electron for the π electrons (which are most interesting from a physical point of view being close to the Fermi level) and zero for all others. For polyene also the electrons in the most highly occupied levels, i.e., the π electrons, are correlated to a non-negligible extent, as can be seen from the density matrices for the α and β spins. Therefore, the obtained correlation energy (0.4130 eV/CH unit) is to be attributed to one π electron of the cell leading to 0.413 eV/(electron) correlation energy for the π electrons (those closest to the Fermi level) and zero for all others.

The case of $(\text{SN})_x$ is more complicated. Here several valence electrons take part in the spin polarization, although the π electrons play a predominant role with regard to the electronic properties of the system, because they are most close to the Fermi level. The following simple argument may be used: In the minimal basis set for nitrogen one valence orbital and for sulphur two valence orbitals are necessarily doubly occupied. This leads to $(5-2)+(6-4)=5$ valence electrons per SN unit which can be spin polarized, leading formally to the value of 0.631 eV/(electron correlation energy) for 5 valence electrons per SN unit, and zero for all others.

B. Stability of the restricted HF state as a function of geometry

It is apparent from the results for the H and C chain that all metallic-type (equidistant) Hartree-Fock wave functions are unstable with respect to release of the double-occupancy restriction (3) and therefore the opening of an energy gap leads to gain in total energy. This fact is connected with the degeneracy of the state. (One of the two energy levels with Fermi energy is occupied, the other is empty in the case of a 1-D material with metallic band

TABLE IV. Forbidden energy gaps obtained for some linear chains by different *ab initio* crystal-orbital methods (eV).

System	Geometry	RHF	UHF
H chain	Equidistant $R=1.95$ bohrs	6.23 [a]	10.62
	Alternating $R_1=1.94$ bohrs $R_2=1.96$ bohrs	9.39	10.60
Carbon chain	Equidistant $R=1.26$ Å	5.91 [a]	8.99
	Alternating $R_1=1.185$ $R_2=1.335$ Å	11.14	Same as RHF
Polyene	Equidistant	4.14 [a]	13.53
	Alternating	7.24	Same as RHF
$(\text{SN})_x$	Nonalternating Zig-zag chain [b]	3.27 [a]	14.56

[a] For equidistant or nonalternating models the gap obtained by the Hartree-Fock method (RHF) is zero (metallic band structure). However, in such cases, another solution of the RHF problem could be found using doubled *unit cells*. This solution exhibits a charge-density wave. This gap refers to such a solution.

[b] Reference 20.

structure.) Using the analytical expressions obtained by Paldus and Čižek[22] for cyclic polyenes and the very simple Hubbard Hamiltonian one can easily show that for an infinite chain with $N=4\nu$ electrons ($N\rightarrow\infty$) this instability is always present. With the much more involved *ab initio* Hamiltonian which we are using, such general analysis does not seem possible to us. Therefore, we merely draw attention to the fact that the two rather different chains of H and C atoms, in the investigated range of interatomic spacings, behaves in this respect as in the above-mentioned analytical model.

With models having alternating shorter and longer bonds (insulators) the situation is different: There appears to be a range of geometrical parameters where instability with respect to UHF is present and the UHF method describing a magnetic (antiferromagnetic) insulator is energetically slightly more stable than the RHF method describing a nonmagnetic insulator. From Tables I, II, and IV as well as from our unpublished calculations we estimate this range of parameters to be limited to the neighborhood of the equidistant (metallic) models where the alternation introduced is relatively small. This may explain our numerous unsuccessful attempts to find an UHF solution of the crystal-orbital form of the Hartree-Fock-Roothaan method for several linear chains with many different geometrical arrangements (as, e.g., for polydiacethylenes, hydrogen and carbon chains, hydrogen-fluoride chains, alternating polyenes, etc.). It is of interest to mention, however, that for alternating polyene at π-electron level using a PPP (Panjer-Parr-Pople) Hamiltonian we could find an UHF solution with significant stabilization energy (0.13 eV/electron[23]). The above stability relations do not imply, of course, that the antiferromagnetic insulator is automatically an appropriate description of the situation even if it has lower total energy, because other spin functions should be also considered.[2] For example, for the case of $(SN)_x$, this is obviously an inappropriate approximation.[21]

C. Basis-set problems

The above considerations may imply that the UHF method yields results strongly dependent on the AO basis set. Unfortunately, we could not perform numerous calculations using larger basis sets even in the RHF case essentially because of computer limitations. (Inclusion of additional flat functions requires inclusion of many distant neighbors into the calculation, increasing the number of integrals enormously.) Nevertheless, as mentioned previously[17] for the H chain at equilibrium geometry (equidistant model), the STO-4-31G basis[16] yields essentially the same correlation energy by the UHF method: 0.12 eV/electron. (Compare with the 0.11 eV/electron value obtained in the STO-4G basis.) Furthermore, it is interesting to mention the experiments which have already accumulated[24] in connection with basis-set effects of the different DODS methods (projected and unprojected variational methods) for small molecules. It was concluded from these molecular studies that only part of the electrons split significantly and some basis-set dependence was found [e.g., in some cases only the core electrons split, as in LiH (Ref. 24)].

D. Energy gap

It is important to classify the gaps: Starting from a metallic model (zero gap) the introduction of electron correlation may open a gap in the one-particle excitation spectrum (see e.g., Refs. 7, 11) which may be called "correlation gap." On the other hand, the introduction of geometrical alternation leads to a gap due to the decrease of space-group symmetry (Peierls gap). The latter type of gap may appear if a charge-density wave (CDW) is allowed to form, within the Hartree-Fock scheme,[13] i.e., if in a metallic (nonalternating) model the variational freedom is increased by doubling the unit cell. The forbidden energy gaps (E_{gap}) obtained in the present UHF calculations are very large (9–15 eV). Since for all metallic-type models CDW solutions are also available using the same basis sets, mesh points in the Brillouin zone, etc., the gaps of these should be considered as Peierls gaps and the UHF gap is some resultant of such a gap and the correlation effect. As it is well known from the theory of insulators,[25] the gaps obtained by the RHF theory are systematically overestimated due to neglect of electron correlation. It appears to us, however, that the specific correlation inherent in the DODS wave function does not have this reducing effect on the gap. (The introduction of correlation significantly increases the gap instead of decreasing it.) Although for certain limiting cases (Hubbard model) the DODS method works reasonably well,[7] for more realistic Hamiltonians, like our *ab initio* one, the method does not adequately describe the gap.

Specifically for polyene, the origin of the gap was discussed repeatedly (see, e.g., Refs. 7, 19, and 26). At the semiempirical level it was concluded that the gap is at least partly of a correlational nature.[7,11] The extremely large UHF gap obtained in the present work indicates that a more appropriate model would be an alternating one for polyene. From the experimental point of view the situation is not fully resolved: A tentative assignment of the electronic and Raman spectra[27] of thin polyene films used, however, an alternating model.[27]

It is commonly believed that the gap opening connected with the occurrence of CDW or spin-density waves (SDW) opens a gap in the one-particle excitation spectrum leading to a significant stabilization energy. In connection with a CDW solution obtained for an equidistant polyene model, we have already pointed out that the self-consistent (Hartree-Fock) treatment of all electrons leads to a relatively small stabilization energy, while the gap is very large. In particular, two CDW's of opposite phase have been observed to be present in the Hartree-Fock wave function, one consisting of π electrons which leads to the gap and another consisting of σ electrons which tends to screen the first wave. This second wave is absent in the non-self-consistent one-particle treatments and thus the extra relaxation may lead to a smaller stabilization energy than in the non-self-consistent treatment. A similar effect may be present in the UHF calculations owing to a similar screening.

V. CONCLUSIONS

From the studies of the H and C chains it is apparent that a metal-insulator transition could not be described by the (variational form of the) DODS method. The absence of this transition was found previously for a one-dimensional Hubbard chain[6(b)] and for an electron gas with cubic Fermi surface.[6(a)] The correlation energies obtained here are considerable (~0.5 eV/electron) for the electrons around the Fermi sea and zero for all others. When alternation is introduced into the geometry, the included correlation drastically decreases, indicating that the electron correlation included for insulating-type models is very limited within the DODS method. Other, nonvariational forms of the method would of course give smaller correlation energies.

The very large (about 10-eV) energy gaps obtained with the present UHF calculations indicate that the metallic state described by the Hartree-Fock theory is unstable[13] for the systems considered and that the stabilization energy is perhaps not due to the advantages of the DODS scheme, but to the inadequacies of the restricted-Hartree-Fock method for the metallic state, as first suggested by Overhauser.[13]

Finally, a further argument is given, on the basis of the UHF calculation for an infinite polyene, that an alternating model with short and long bonds is most appropriate for this polymer.

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