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Two-Electron Homopolar Molecule: A Test for Spin-Density Waves and Charge-Density Waves

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The eigenstates of the one-band Hamiltonian for a two-electron homopolar molecule can be exactly determined. The exact solution for the ground state and all its properties can thus be used as a standard to assess the accuracy and validity of several commonly used approximations: the normal molecular-orbital ground state, the Heitler-London states, the spin-density waves and the charge-density waves. The most general unrestricted self-consistent field approximations are studied in both the Hartree and Hartree-Fock approximations and are compared with one another as well as with the exact results. New and simple correlated states are also proposed and tested: a symmetrized spin-density wave and a symmetrized charge-density wave. These new states are easily obtained from the corresponding Hartree-Fock states, and whenever they exist, they are extremely good approximations to the exact ground state. General consequences and extensions to more complicated systems can be inferred from this study.

I. INTRODUCTION

In the course of studying the ground-state configuration of $C_{4N+2}H_{4N+2}$ cyclic polyenes,^{1,2} and in discussing the accuracy and validity of various approximations, we found an exactly soluble problem that could be fruitfully used as a standard and a guide.

This problem, i.e., the ground-state configuration of the π electrons in ethylene, is identical to the well-known and profusely studied system of the two-electron homopolar molecule,³ of which H_2 is the classic textbook example. We are not aware, however, of any place where the unrestricted self-consistent field solutions, namely the spin-density wave (SDW)⁴ and the charge-density wave (CDW),⁵ are treated on the same footing

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¹ R. A. Harris and L. M. Falicov, *J. Chem. Phys.* **50**, 4590 (1969).

² R. A. Harris and L. M. Falicov, "Self-Consistent Theory of Bond Alternation in Polyenes: Normal State, Charge-Density Waves, and Spin-Density Waves," *J. Chem. Phys.* (to be published).

³ See any standard textbook on molecular quantum physics, e.g., J. C. Slater, *Quantum Theory of Matter* (McGraw-Hill Book Co., New York, 1951), Chap. 8; L. Salem, *The Molecular Orbital Theory of Conjugated Systems*, (W. A. Benjamin, Inc., New York, 1966), pp. 420-424.

⁴ A. W. Overhauser, *Phys. Rev. Letters* **4**, 415, 462 (1960); *Phys. Rev.* **128**, 1437 (1962).

⁵ A. W. Overhauser, *Phys. Rev.* **167**, 691 (1968).

as (and compared with) either the more traditional normal molecular orbital (MO) and Heitler-London (HL) approximations, or with the exact one-band solution. Such a unified approach is presented here: The error in the ground-state energies and the various correlation functions of each approximate solution are displayed and compared with one another.

Since the SDW and CDW are states of broken symmetry, we propose here a simple improvement on these solutions which is immediately obvious: symmetrized versions of them which we call symmetrized spin-density wave (SSDW) and symmetrized charge-density wave (SCDW). These are correlated states, i.e., they go beyond the Hartree-Fock approximation, which are very easily obtained from their parent states. Whenever they exist, we show that they are excellent approximations to the true ground state.

Section II discusses the Hamiltonian used throughout the paper. Section III is concerned with the exact solution and its properties as well as with the most common approximations. Section IV is devoted to the generalized Hartree approximations. Section V discusses the various Hartree-Fock solutions. Section VI studies the new symmetrized states. Section VII contains the discussion and conclusions.

II. THE ONE-BAND HAMILTONIAN

We use second quantization operators and restrict ourselves to four Löwdin orbitals, one of each spin in

each of the two centers. The Hamiltonian can thus be written

$$\mathcal{H}_T = \mathcal{H}_\alpha + \mathcal{H}_\beta + \mathcal{H}_U + \mathcal{H}_K, \quad (2.1)$$

where

$$\mathcal{H}_\alpha = \alpha(n_{1\uparrow} + n_{1\downarrow} + n_{2\uparrow} + n_{2\downarrow}), \quad (2.2)$$

$$\mathcal{H}_\beta = -\beta(c_{1\uparrow}^\dagger c_{2\uparrow} + c_{1\downarrow}^\dagger c_{2\downarrow} + c_{2\uparrow}^\dagger c_{1\uparrow} + c_{2\downarrow}^\dagger c_{1\downarrow}), \quad (2.3)$$

$$\mathcal{H}_U = U(n_{1\uparrow}n_{1\downarrow} + n_{2\uparrow}n_{2\downarrow}), \quad (2.4)$$

$$\mathcal{H}_K = K(n_{1\uparrow}n_{2\uparrow} + n_{1\downarrow}n_{2\downarrow} + n_{1\downarrow}n_{2\uparrow} + n_{1\uparrow}n_{2\downarrow}). \quad (2.5)$$

In these equations $c_{i\sigma}^\dagger$, $c_{i\sigma}$, and $n_{i\sigma} \equiv c_{i\sigma}^\dagger c_{i\sigma}$ are, respectively, the usual creation, destruction, and number operators for the Löwdin orbital of spin σ centered about i ; they satisfy the usual Fermi-Dirac anti-commutation rules. \mathcal{H}_α and \mathcal{H}_β are the single-particle diagonal and off-diagonal terms, respectively, \mathcal{H}_U is the intraatomic Coulomb repulsion, and \mathcal{H}_K is the corresponding interatomic term. The parameters β , U , and K are positive definite quantities and such that $U > K$. However, for the sake of completeness in our discussion of the possible ground states, we take β to be always positive, but let U and K take arbitrary values, both positive and negative.

Since we restrict ourselves only to two-electron states the following considerations can be applied:

(A) The electron-number operator

$$N = \sum_{i\sigma} n_{i\sigma} \quad (2.6)$$

is completely diagonal and can everywhere be replaced by the number 2, e.g.,

$$\mathcal{H}_\alpha = 2\alpha. \quad (2.7)$$

(B) The operator

$$N^2 = \sum_{ij\sigma\sigma'} n_{i\sigma} n_{j\sigma'} \quad (2.8)$$

is also completely diagonal and can be replaced by the number 4.

(C) If we also recall that

$$n_{i\sigma} n_{i\sigma} \equiv n_{i\sigma} \quad (2.9)$$

for any i and σ , properties (A) and (B) allow us to write the following identity:

$$4 = 2 + 2(n_{1\uparrow}n_{1\downarrow} + n_{2\uparrow}n_{2\downarrow}) + 2(n_{1\uparrow}n_{2\uparrow} + n_{1\downarrow}n_{2\downarrow} + n_{1\downarrow}n_{2\uparrow} + n_{1\uparrow}n_{2\downarrow}). \quad (2.10)$$

(D) The Hamiltonian can now be rewritten

$$\mathcal{H}_T = 2\alpha + K + \mathcal{H}, \quad (2.11)$$

$$\mathcal{H} = \mathcal{H}_\beta + \mathcal{H}_U + (\mathcal{H}_K - K), \quad (2.12)$$

and the last term can be expressed as

$$\mathcal{H}_K - K = -K(n_{1\uparrow}n_{1\downarrow} + n_{2\uparrow}n_{2\downarrow}) = -(K/U)\mathcal{H}_U. \quad (2.13)$$

From the above expressions (as well as from simple physical considerations) it can be easily seen that the

eigenvalues of \mathcal{H} can depend on U and K only through a $(U-K)$ type dependence. This allows us to write the ground-state energy E_T as

$$E_T = \langle \mathcal{H}_T \rangle = 2\alpha + K + E, \quad (2.14)$$

where

$$E = \langle \mathcal{H} \rangle = \beta \epsilon(x) \quad (2.15)$$

and ϵ is only a function of

$$x \equiv (U-K)/\beta \quad (2.16)$$

As we show later on, these properties are satisfied by the Hartree-Fock and improved solutions in addition to the exact one, but not by the unrestricted Hartree approximations.

III. THE EXACT GROUND STATE, THE MOST COMMON APPROXIMATIONS, AND THEIR PROPERTIES

Any eigenstate of (2.12) with two electrons should be a linear combination of the six states

$$|1\uparrow 2\uparrow\rangle, |1\downarrow 2\downarrow\rangle, |1\uparrow 1\downarrow\rangle, \\ |2\uparrow 2\downarrow\rangle, |1\uparrow 2\downarrow\rangle, \text{ and } |2\uparrow 1\downarrow\rangle,$$

where

$$|i\sigma j\sigma'\rangle = c_{i\sigma}^\dagger c_{j\sigma'}^\dagger |0\rangle, \quad (3.1)$$

and $|0\rangle$ is the vacuum state. The matrix elements of \mathcal{H} in this manifold are given in Table I. An exact diagonalization of the \mathcal{H} matrix yields for the ground state $|G\rangle$

$$|G\rangle = 2[16 + x^2 + x(x^2 + 16)^{1/2}]^{-1/2} (|1\uparrow 1\downarrow\rangle + |2\uparrow 2\downarrow\rangle) \\ + 0.5[x + (x^2 + 16)^{1/2}][16 + x^2 + x(x^2 + 16)^{1/2}]^{-1/2} \\ \times (|1\uparrow 2\downarrow\rangle + |2\uparrow 1\downarrow\rangle) \quad (3.2)$$

while the energy, expressed in the form (2.14)–(2.16) is given by

$$\epsilon_G = 0.5[x - (x^2 + 16)^{1/2}]. \quad (3.3)$$

In order to study the structural properties of the states we define three correlation functions:

$$\rho_S \equiv 1 - 2\langle n_{1\uparrow}n_{1\downarrow} \rangle - 2\langle n_{2\uparrow}n_{2\downarrow} \rangle, \quad (3.4)$$

$$\rho_{AS} \equiv |\langle n_{1\uparrow}n_{2\downarrow} \rangle - \langle n_{2\uparrow}n_{1\downarrow} \rangle|^2, \quad (3.5)$$

$$\rho_{AC} \equiv |\langle n_{1\uparrow}n_{1\downarrow} \rangle - \langle n_{2\uparrow}n_{2\downarrow} \rangle|^2. \quad (3.6)$$

Of these, ρ_S has the full symmetry of the Hamiltonian, and consequently, its value in the ground state is not required by symmetry to take any specific value. The other two, ρ_{AS} and ρ_{AC} , are antisymmetric with respect to spin and charge inversion respectively, and should be identically zero in the true ground state. Therefore ρ_S gives a good measure of true correlation properties,⁶ while ρ_{AS} and ρ_{AC} are indicators of how badly the symmetry requirements have been broken.

⁶ ρ_S is chosen such that it is zero in the normal molecular-orbital approximation, the uncorrelated state.

TABLE I. Matrix elements of \mathcal{H} .

	$ 1\uparrow 2\uparrow\rangle$	$ 1\downarrow 2\downarrow\rangle$	$ 1\uparrow 1\downarrow\rangle$	$ 2\uparrow 2\downarrow\rangle$	$ 1\uparrow 2\downarrow\rangle$	$ 2\uparrow 1\downarrow\rangle$
$\langle 1\uparrow 2\uparrow $	0	0	0	0	0	0
$\langle 1\downarrow 2\downarrow $	0	0	0	0	0	0
$\langle 1\uparrow 1\downarrow $	0	0	$U-K$	0	$-\beta$	$-\beta$
$\langle 2\uparrow 2\downarrow $	0	0	0	$U-K$	$-\beta$	$-\beta$
$\langle 1\uparrow 2\downarrow $	0	0	$-\beta$	$-\beta$	0	0
$\langle 2\uparrow 1\downarrow $	0	0	$-\beta$	$-\beta$	0	0

In the true ground state we find

$$\rho_S(G) = x(x^2 + 16)^{-1/2}, \quad (3.7)$$

and, as expected,

$$\rho_{AS}(G) = \rho_{AC}(G) = 0. \quad (3.8)$$

The most commonly used approximations to the ground state are the normal molecular orbital (MO) and the Heitler-London (HL) wave vectors; in the last case both the neutral solution (HLN) and the polar one (HLP) have to be considered for arbitrary interactions.

The MO solution is of the form

$$\begin{aligned} |MO\rangle &= 0.5(c_{1\uparrow}^\dagger + c_{2\uparrow}^\dagger)(c_{1\downarrow}^\dagger + c_{2\downarrow}^\dagger) |0\rangle \\ &= 0.5(|1\uparrow 1\downarrow\rangle + |2\uparrow 2\downarrow\rangle + |1\uparrow 2\downarrow\rangle + |2\uparrow 1\downarrow\rangle). \end{aligned} \quad (3.9)$$

The energy [the expectation value of \mathcal{H}_T with (3.9)] expressed in the form (2.14)–(2.16) is

$$\epsilon_{MO} = 0.5x - 2, \quad (3.10)$$

while the correlation functions (3.4)–(3.6) yield

$$\rho_S(MO) = \rho_{AS}(MO) = \rho_{AC}(MO) = 0. \quad (3.11)$$

It is seen that the MO state does not break the symmetry requirements and gives a completely uncorrelated state. It is also seen that (3.9) and (3.10) reduce to (3.2) and (3.3) when $x=0$, i.e., the MO approximation reduces to the exact ground state when $U=K$.

The two neutral Heitler-London states are

$$|HLN1\rangle = |1\uparrow 2\downarrow\rangle, \quad |HLN2\rangle = |2\uparrow 1\downarrow\rangle. \quad (3.12)$$

They yield an energy

$$\epsilon_{HLN} = 0 \quad (3.13)$$

and correlation functions

$$\rho_S(HLN) = 1, \quad (3.14)$$

$$\rho_{AS}(HLN) = 1, \quad (3.15)$$

$$\rho_{AC}(HLN) = 0. \quad (3.16)$$

These solutions are overcorrelated and have completely

broken spin symmetry. In a similar way, the polar HL states are

$$|HLP1\rangle = |1\uparrow 1\downarrow\rangle, \quad |HLP2\rangle = |2\uparrow 2\downarrow\rangle, \quad (3.17)$$

with

$$\epsilon_{HLP} = x, \quad (3.18)$$

and

$$\rho_S(HLP) = -1, \quad (3.19)$$

$$\rho_{AS}(HLP) = 0, \quad (3.20)$$

$$\rho_{AC}(HLP) = 1. \quad (3.21)$$

In this last case there is also overcorrelation and completely broken charge symmetry.

Two remarks at this point are relevant: (i) the HLN and HLP solutions can be symmetrized

$$|SHLN\rangle = 2^{-1/2}(|HLN1\rangle + |HLN2\rangle), \quad (3.22)$$

$$|SHLP\rangle = 2^{-1/2}(|HLP1\rangle + |HLP2\rangle), \quad (3.23)$$

but although this restores the asymmetric correlation functions to their correct zero value, no change is induced in either the energy or in the symmetric correlation function; (ii) the symmetrized HL solutions approach asymptotically the exact solution in the limits $x \rightarrow \infty$ (HLN) or $x \rightarrow -\infty$ (HLP).

IV. THE GENERALIZED HARTREE SOLUTIONS

The Hartree approximation is obtained by expressing the energy of the system as

$$\begin{aligned} E_T(\text{Hartree}) &= \langle \mathcal{H}_\alpha \rangle + \langle \mathcal{H}_\beta \rangle + U(\langle n_{1\uparrow} \rangle \langle n_{1\downarrow} \rangle + \langle n_{2\uparrow} \rangle \langle n_{2\downarrow} \rangle) \\ &\quad + K(\langle n_{1\uparrow} \rangle \langle n_{2\uparrow} \rangle + \langle n_{1\uparrow} \rangle \langle n_{2\downarrow} \rangle + \langle n_{1\downarrow} \rangle \langle n_{2\uparrow} \rangle + \langle n_{1\downarrow} \rangle \langle n_{2\downarrow} \rangle) \end{aligned} \quad (4.1)$$

and determining the state vector so that it minimizes (4.1). It is worth remarking that the replacement of products of the type $n_{i\sigma} n_{j\sigma'}$ by the product of their expectation values introduces serious errors in the results. For instance, $[E_T(\text{Hartree}) - K]$ is no longer a function of $U - K$, but function of two variables, U and K , separately. The energy cannot in this case be expressed in the form (2.14)–(2.16). As it is apparent from what follows, the Hartree approximation is only

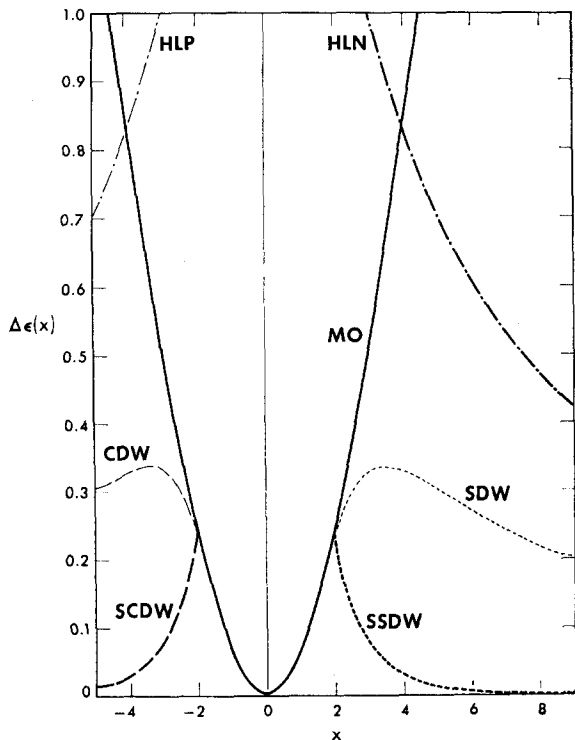


FIG. 1. The error in the energy of the system, as a function of the relative interaction strength $x \equiv (U-K)/\beta$, for the various models discussed in the paper.

good if

$$|K| \ll |U-K|, \tag{4.2}$$

and in the limit $K=0$, it is identical to the much better Hartree-Fock approximation. We therefore, for the sake of brevity and completeness, give here only a few relevant results.

Three solutions which minimize (4.1) exist:

- (1) the MO solution (3.9), valid for

$$U \leq 2\beta, \quad U - 2K \geq -2\beta, \tag{4.3}$$

and such that

$$E_T(\text{Hartree, MO}) = 2\alpha + K - 2\beta + 0.5U; \tag{4.4}$$

- (2) the SDW solution, similar to the one discussed in the next section for the Hartree-Fock approximation, and valid for

$$U \geq 2\beta, \tag{4.5}$$

for which

$$E_T(\text{Hartree, SDW}) = 2\alpha + K - 2\beta^2/U; \tag{4.6}$$

- (3) the CDW, valid for

$$U - 2K \leq -2\beta \tag{4.7}$$

whose Hartree energy is

$$E_T(\text{Hartree, CDW}) = 2\alpha + U - 2\beta^2/|U - 2K|. \tag{4.8}$$

Further discussion of these results are left for Sec. VII.

V. THE GENERALIZED HARTREE-FOCK SOLUTIONS

These approximations are obtained by minimizing the total energy (2.14), (2.15) with respect to the parameters $\theta_1, \theta_2, \chi_1, \chi_2$, such that

$$-\pi/2 < \theta_i \leq \pi/2, \tag{5.1}$$

$$0 \leq \chi_i < \pi \tag{5.2}$$

when the ground-state wave vector is written in the form

$$|\phi\rangle = (\cos\theta_1 c_{1\uparrow}^\dagger + e^{i\chi_1} \sin\theta_1 c_{2\uparrow}^\dagger) \times (\cos\theta_2 c_{1\downarrow}^\dagger + e^{i\chi_2} \sin\theta_2 c_{2\downarrow}^\dagger) |0\rangle. \tag{5.3}$$

After a straightforward but tedious calculation, we find that the states of minimum energy are:

- (1) If

$$-2 \leq x \leq 2, \tag{5.4}$$

the solution is the MO approximation (3.9) and the energy and correlation functions are given by (3.10) and (3.11), respectively.

- (2) If

$$x \geq 2, \tag{5.5}$$

there are two SDW solutions,

$$|\text{SDW1}\rangle = \cos\theta \sin\theta (|1\uparrow 1\downarrow\rangle + |2\uparrow 2\downarrow\rangle + \cos^2\theta |1\uparrow 2\downarrow\rangle + \sin^2\theta |2\uparrow 1\downarrow\rangle), \tag{5.6}$$

and

$$|\text{SDW2}\rangle = \cos\theta \sin\theta (|1\uparrow 1\downarrow\rangle + |2\uparrow 2\downarrow\rangle + \sin^2\theta |1\uparrow 2\downarrow\rangle + \cos^2\theta |2\uparrow 1\downarrow\rangle), \tag{5.7}$$

where

$$0 \leq \theta \leq \pi/4, \tag{5.8}$$

and

$$\sin 2\theta = 2/x. \tag{5.9}$$

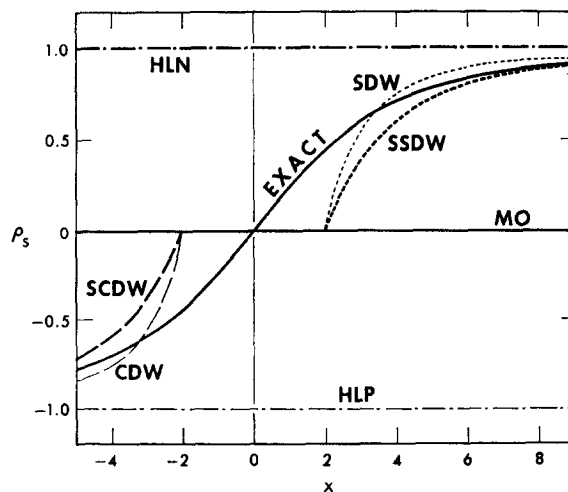


FIG. 2. The symmetric correlation function ρ_S as a function of x for the various models.

In this case the energy (2.14)–(2.16) is

$$\epsilon_{\text{SDW}} = -2/x, \quad (5.10)$$

and the correlation functions are

$$\rho_{\text{S}}(\text{SDW}) = (x^2 - 4)/x^2, \quad (5.11)$$

$$\rho_{\text{AS}}(\text{SDW}) = (x^2 - 4)/x^2, \quad (5.12)$$

$$\rho_{\text{AC}}(\text{SDW}) = 0. \quad (5.13)$$

It is worth noticing that

$$|\text{SDW1}\rangle = |\text{SDW2}\rangle = |\text{MO}\rangle, \quad x=2 \quad (5.14)$$

and

$$|\text{SDW1}\rangle \rightarrow |\text{HLN1}\rangle, \quad |\text{SDW2}\rangle \rightarrow |\text{HLN2}\rangle \quad \text{as } x \rightarrow \infty.$$

(3) If

$$x \leq -2 \quad (5.16)$$

there are two CDW solutions

$$|\text{CDW1}\rangle = \cos^2\theta |1\uparrow 1\downarrow\rangle + \sin^2\theta |2\uparrow 2\downarrow\rangle + \sin\theta \cos\theta (|1\uparrow 2\downarrow\rangle + |2\uparrow 1\downarrow\rangle), \quad (5.17)$$

$$|\text{CDW2}\rangle = \sin^2\theta |1\uparrow 1\downarrow\rangle + \cos^2\theta |2\uparrow 2\downarrow\rangle + \sin\theta \cos\theta (|1\uparrow 2\downarrow\rangle + |2\uparrow 1\downarrow\rangle), \quad (5.18)$$

where

$$0 \leq \theta \leq \pi/4 \quad (5.19)$$

and

$$\sin 2\theta = -2/x. \quad (5.20)$$

The energy is given by

$$\epsilon_{\text{CDW}} = x + 2/x \quad (5.21)$$

and the correlation functions are

$$\rho_{\text{S}}(\text{CDW}) = (4 - x^2)/x^2, \quad (5.22)$$

$$\rho_{\text{AS}}(\text{CDW}) = 0, \quad (5.23)$$

$$\rho_{\text{AC}}(\text{CDW}) = (x^2 - 4)/x^2. \quad (5.24)$$

Similarly to the SDW properties, we have

$$|\text{CDW1}\rangle = |\text{CDW2}\rangle = |\text{MO}\rangle, \quad x = -2, \quad (5.25)$$

$$|\text{CDW1}\rangle \rightarrow |\text{HLP1}\rangle, \quad |\text{CDW2}\rangle \rightarrow |\text{HLP2}\rangle \quad \text{as } x \rightarrow -\infty. \quad (5.26)$$

It is important to mention that these are the *best* Hartree–Fock-type solutions, i.e., no single Slater determinant can give a more accurate answer to the ground state of the system than those represented by (5.17)–(5.20) for $U - K \leq -2\beta$, (3.9) for $-2\beta \leq U - K \leq 2\beta$, and (5.6)–(5.9) for $2\beta \leq U - K$. Any improvement on these functions corresponds to using more than one Slater determinant in the expression for the ground-state wave vector.

VI. NEW SYMMETRIZED APPROXIMATIONS

As is evident from (5.12) and (5.24), the best Hartree–Fock solutions in the range $|x| > 2$ correspond

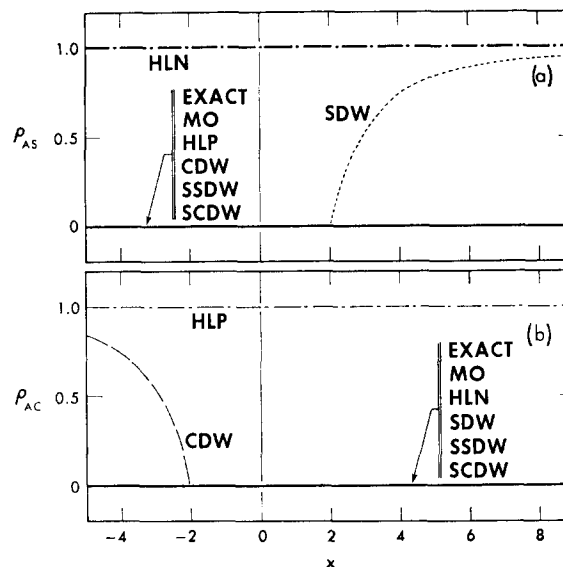


FIG. 3. The asymmetric correlation functions as functions of x : (a) spin asymmetry ρ_{AS} ; (b) charge asymmetry ρ_{AC} .

to states of broken symmetry. This fact suggest an obvious and easy way of improving the ground-state function without requiring complicated higher-order perturbation calculations: by projecting out of the best Hartree–Fock ground state those components which have the wrong symmetry, the approximate wave vectors can only be improved. This is easily accomplished by taking the symmetrized combinations of either (5.6) and (5.7), or of (5.17) and (5.18), remembering that in each case the members of the pair are not orthogonal to one another. In this way we obtain:

(i) The symmetrized spin-density wave, for $x > 2$

$$|\text{SSDW}\rangle = (2 + 2 \sin^2 2\theta)^{-1/2} [\sin 2\theta (|1\uparrow 1\downarrow\rangle + |2\uparrow 2\downarrow\rangle) + (|1\uparrow 2\downarrow\rangle + |2\uparrow 1\downarrow\rangle)], \quad (6.1)$$

where $\sin 2\theta$ is given by (5.9). The energy is now given by

$$\epsilon_{\text{SSDW}} = -4x/(x^2 + 4) \quad (6.2)$$

and the correlation functions are

$$\rho_{\text{S}}(\text{SSDW}) = (x^2 - 4)/(x^2 + 4), \quad (6.3)$$

$$\rho_{\text{AS}}(\text{SSDW}) = \rho_{\text{AC}}(\text{SSDW}) = 0. \quad (6.4)$$

(ii) The symmetrized charge-density wave, for $x < -2$,

$$|\text{SCDW}\rangle = (2 + 2 \sin^2 2\theta)^{-1/2} [(|1\uparrow 1\downarrow\rangle + |2\uparrow 2\downarrow\rangle) + \sin 2\theta (|1\uparrow 2\downarrow\rangle + |2\uparrow 1\downarrow\rangle)], \quad (6.5)$$

where (5.20) holds and

$$\epsilon_{\text{SCDW}} = x(x^2 + 8)/(x^2 + 4), \quad (6.6)$$

$$\rho_{\text{S}}(\text{SCDW}) = (4 - x^2)/(4 + x^2), \quad (6.7)$$

$$\rho_{\text{AS}}(\text{SCDW}) = \rho_{\text{AC}}(\text{SCDW}) = 0. \quad (6.8)$$

In this case a significant improvement of the energy expressions, (6.2) and (6.6), over those for their parent states, (5.10) and (5.21) is found, and, whenever $|x| > 2$,

$$\epsilon_{\text{SDW}} > \epsilon_{\text{SSDW}} > \epsilon_{\text{G}}, \quad (6.9)$$

$$\epsilon_{\text{CDW}} > \epsilon_{\text{SCDW}} > \epsilon_{\text{G}}. \quad (6.10)$$

VII. DISCUSSION AND CONCLUSIONS

In order to assess the validity of each of the approximations here discussed, we have plotted in Fig. 1 the quantity

$$\Delta\epsilon(x) = \epsilon(x) - \epsilon_{\text{G}}(x) \quad (7.1)$$

as a function of x . In Fig. 2 the symmetric correlation function (3.4) is displayed. Figure 3 contains the spin asymmetry (3.5) and the charge asymmetry (3.6).

The following conclusions can now be obtained from an analysis of these figures and the formulas of the previous sections:

(A) Comparison of (4.4) with (3.10), (4.6) with (5.10), (4.8) with (5.21), and all these equations with (3.3) shows that the Hartree approximation is in general a very bad one in regards to treating the interatomic term (2.5) of the Hamiltonian.

(B) The Hartree and Hartree-Fock approximations are identical with respect to the intra-atomic term (2.4), i.e., in the limit $\bar{K} = 0$.

(C) We infer from this that, in more general cases, if the Hartree-Fock approximation becomes too cumbersome and difficult to manage, it is advisable to (1) neglect the interatomic terms, (2) replace in the intra-atomic terms

$$U \rightarrow U' \approx U - \bar{K}, \quad (7.2)$$

where U' is an effective intraatomic interaction and \bar{K} is an average interatomic interaction strength, and (3) then treat the Hamiltonian in the Hartree approximation (which has become now completely equivalent to the Hartree-Fock scheme).

(D) It is worth emphasizing that the Hartree approximation is particularly bad when interatomic interaction strengths (K) are of the same order of magnitude as the intra-atomic one U . Spurious solutions

(a CDW, for instance) could be found; these solutions are misleading and nonsensical.

(E) The best unrestricted Hartree-Fock solutions are, energy wise, fairly good approximations, and become exact in the limits $U - K = 0$; $|U - K|/\beta \rightarrow \infty$.

(F) The symmetrized Hartree-Fock solutions (MO, SSDW, and SCDW) are, energy-wise, extremely good over most of the range of the parameters; they are not quite so good when $|x| \sim 2$. The maximum error in the energy

$$\Delta E_{\text{max}} = 0.236\beta = 0.118(U - K) \quad (7.3)$$

appears at $|x| = 2$, and decreases rapidly as $|x|$ varies from 2.

(G) The symmetric correlation function ρ_{S} (Fig. 2), is a good indication of the accuracy of the approximations: the MO is always, by definition, uncorrelated; the HL states are always overcorrelated; the SDW and CDW are undercorrelated for $2 \leq |x| \leq 3.335$ and overcorrelated for $|x| \geq 3.335$; the SSDW and SCDW are always slightly undercorrelated.

(H) The symmetrization of the ground-state Hartree-Fock wave vectors yield a very good and simple way of improving only the ground-state energy and wave vector, but such a method, as is obvious from symmetry considerations, cannot be applied to the excited states, e.g., to the study of optical properties. It is perhaps possible to extend the method to encompass excited states by generalizing the symmetrization procedure to states of other symmetries and imposing in addition some orthogonality conditions. This possible generalization requires, however, more work and thought, and may not prove to be simple enough to have the appealing features described here for the ground state.

(I) In closing we would like to believe that the conclusions drawn here for this exactly soluble one-band model can be generalized to more complicated,^{1,2,7} many-electron chains, and that the symmetrized unrestricted Hartree-Fock states (the SSDW in particular), whenever they exist, constitute very good and simple approximations to the unknown exact ground state.

⁷ E. W. Fenton, Phys. Rev. Letters **21**, 1427 (1968).