Different Orbitals for Different Spins in an Infinite Chain of Hydrogen Atoms

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The total energy of an infinite, linear chain of hydrogen atoms is computed by means of a "different orbitals for different spins" method, in which the correlation parameter is allowed to depend on the crystal momentum **k**. The resulting antiferromagnetic configuration is found to be stable over the range of interatomic distances studied $(1.0, \infty)$. The equilibrium lattice parameter is found to be slightly less than 2.0 a.u., and the cohesive energy ~ 0.05 a.u. An instability found earlier by Calais is removed.

I. INTRODUCTION

THE calculation of the total energy of a paramagnetic crystal by means of ordinary band theory is affected by a correlation error, which is dramatically illustrated by the incorrect asymptotic behavior of the total energy of the separated atoms. This is because the lack of correlation between electrons of different spins forces ionic states of high energy to appear among the dissociation products. To remedy this particular deficiency of the ordinary band model it has been proposed that electrons of different spins occupy different orbitals, leading to a spatial separation of the spin-up and spin-down charge densities on to two equivalent sublattices A and B.[1] This way of treating the correlation problem is generally called "the split-band" or "different orbitals for different spins (DODS)" model. Splitting the orbitals not only leads to the correct asymptotic behavior of the total energy, but also effects the magnetic and conductivity properties of the crystal. Specifically the split-band model results in an antiferromagnetic state, with an energy gap appearing at the top of the Fermi level. In the present work, however, we concentrate on the model as a means of obtaining more accurate values for the total energy. For heuristic purposes we will consider an infinite linear chain consisting of equidistant hydrogen atoms, a case which is of sufficient complexity to give hints about the treatment of real crystals. The infinite chain of hydrogen atoms has earlier been investigated by Tredgold[2] and Calais,[3] who both assumed that the "degree of splitting" is the same for all the Bloch states $|\mathbf{k}\rangle$. We will here refine this picture by letting the degree of splitting be dependent on the crystal momentum **k**. In the present case this extra flexibility of the wave function will lead to quantitative improvements over the earlier treat-

ments. Our main concern, however, will be to stress the qualitative differences which arise.

In Sec. II the split-band model is described briefly in terms of pairing. A "gap equation" of rather general nature results and the solutions to this equation determine the degree of splitting versus momentum **k**. In Sec. III the numerical results are presented and compared with earlier calculations. Section IV contains a short discussion. Throughout the paper atomic units are used.

II. MODEL

Let us assume that the Bloch functions of the paramagnetic state are given by

$$\varphi_{\mathbf{k},\sigma}(\mathbf{r}) = \frac{1}{\sqrt{\mathfrak{N}_{\mathbf{k}}}} \sum_g e^{i\mathbf{k}\cdot\mathbf{R}_g} \chi_{g,\sigma}(\mathbf{r}). \tag{1}$$

$\mathfrak{N}_{\mathbf{k}}$ is a normalization constant, $\mathbf{R}_g$ determines the lattice points, and $\chi_{g,\sigma}$ is a $1s$ function of spin σ centered at lattice point g. Each atom contributes one electron, i.e., the band of the paramagnetic state is half-filled, and the Fermi wave number k_F equals $\pi/2a$, where a is the lattice constant. In order to achieve the spatial separation of the spin-up and spin-down electron densities, $\rho_\uparrow(\mathbf{r})$ and $\rho_\downarrow(\mathbf{r})$, the unoccupied Bloch functions can be used as indicated schematically in Fig. 1: Construct new one-particle orbitals by the pairing of an occupied state $\varphi_{\mathbf{k},\sigma}$ with an unoccupied state $\varphi_{\mathbf{k}+\mathbf{Q},\sigma}$. The vector **Q** is chosen as $\mathbf{Q} = -2k_F\mathbf{k}/|\mathbf{k}|$, which means
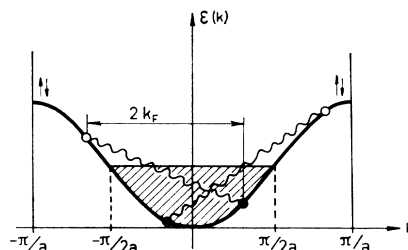

FIG. 1. Schematic picture of the pairing of occupied states (filled circles) with unoccupied states (open circles).

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[1] J. C. Slater, Phys. Rev. **82**, 538 (1951); P.-O. Löwdin, *ibid.* **97**, 1509 (1955); J. Appl. Phys. **33**, 251 (1962). See also C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1966), Vol. IV, p. 309, for further references.

[2] R. H. Tredgold, Proc. Phys. Soc. (London) **67A**, 1018 (1954).

[3] J.-L. Calais, Arkiv Fysik **28**, 511 (1965).

it equals the first reciprocal lattice vectors of the sublattice A (or B). Therefore the density ρ_σ associated with the new, paired orbitals has the translational symmetry of the sublattice. In terms of a canonical transformation, the pairing of the Bloch states reads

$$A_{k,\uparrow}{}^\dagger = u(k)a_{k,\uparrow}{}^\dagger + v(k)a_{k+Q,\uparrow}{}^\dagger,$$
$$B_{k,\uparrow}{}^\dagger = -v(k)a_{k,\uparrow}{}^\dagger + u(k)a_{k+Q,\uparrow}{}^\dagger, \tag{2a}$$
$$(|k| \leq k_F)$$
$$A_{k,\downarrow}{}^\dagger = v(k)a_{k,\downarrow}{}^\dagger + u(k)a_{k+Q,\downarrow}{}^\dagger,$$
$$B_{k,\downarrow}{}^\dagger = -u(k)a_{k,\downarrow}{}^\dagger + v(k)a_{k+Q,\downarrow}{}^\dagger. \tag{2b}$$

The operator $a_{k,\sigma}{}^\dagger$ creates a particle in the Bloch state $\varphi_{k,\sigma}(r)$, the operator $A_{k,\sigma}{}^\dagger$ is a particle in an orbital mainly localized on the sublattice A, let us say, and the operator $B_{k,\sigma}{}^\dagger$ is a particle in an orbital on the complementary sublattice B. For the ground state of the system, we now have in mind the Hartree-Fock type of approximation

$$|\Phi\rangle = \prod_{|k| \leq k_F} A_{k\uparrow}{}^\dagger B_{k\downarrow}{}^\dagger |0\rangle \tag{3}$$

($|0\rangle$= the vacuum state). The difference in signs in the definition of $A_{k,\uparrow}{}^\dagger$ and $B_{k,\downarrow}{}^\dagger$ in Eq. (2) ensures that the densities $\rho_\uparrow$ and $\rho_\downarrow$ associated with Eq. (3) are located mainly on different sublattices, i.e., electrons of opposite spins are given the possibility of avoiding each other in accordance with their repulsive interaction and in the limit of separated atoms, ionic states do not have to appear. The operators $A_{k,\downarrow}{}^\dagger$ and $B_{k,\uparrow}{}^\dagger$ not present in the state (3) represent virtual excitations from the ground state.

The "mixing parameters" $u(k)$ and $v(k)$ in Eq. (2), which satisfy the normalization condition $u^2(k) + v^2(k) = 1$, determine the degree of splitting of the one-particle orbitals. Tredgold's[2] and Calais's[3] approximation mentioned in the Introduction implies the choice $u(k) = \lambda$ and $v(k) = (1-\lambda^2)^{1/2}$, where the parameter λ is to be determined from the minimization of the total energy. Because we allow u to depend upon k, for our purposes it seems profitable to use a formulation by means of Green's functions,[4] which we will outline briefly below (see, e.g., Ref. 5 for details). To get a hint about the type of Green's functions to be used, it is instructive take a look at the expression for the densities $\rho_\uparrow$ and $\rho_\downarrow$ corresponding to the Hartree-Fock state (3):

$$\rho_\uparrow = \sum_{|k| \leq k_F} [u^2(k)\varphi_k\varphi_k^* + v^2(k)\varphi_{k+Q}\varphi_{k+Q}^*$$
$$+ u(k)v(k)(\varphi_k\varphi_{k+Q}^* + \text{c.c.})],$$
$$\rho_\downarrow = \sum_{|k| \leq k_F} [u^2(k)\varphi_k\varphi_k^* + v^2(k)\varphi_{k+Q}\varphi_{k+Q}^* \tag{4}$$
$$- u(k)v(k)(\varphi_k\varphi_{k+Q}^* + \text{c.c.})].$$

If the Green's function is $G_\sigma(xx')$ [$x = (r,t)$ stands for space r and time t], its relation to ρ_σ is[4]

$$\rho_\sigma(r) = -i \lim_{\substack{r' \to r \\ t' \to t+0}} G_\sigma(xx') = -iG_\sigma(x\,x+0). \tag{5}$$

From Eqs. (4) and (5) we thus conceive that the expansion of G_σ in the basis $\{\varphi_k\}$ should have the form

$$G_\sigma(xx') = \sum_{|k| \leq k_F} [G_{f,\sigma}(k; tt')\varphi_k(r)\varphi_k^*(r')$$
$$+ G_{e,\sigma}(k; tt')\varphi_{k+Q}(r)\varphi_{k+Q}^*(r')$$
$$+ F_\sigma^+(k; tt')\varphi_k(r)\varphi_{k+Q}^*(r')$$
$$+ F_\sigma(k; tt')\varphi_{k+Q}(r)\varphi_k^*(r')]. \tag{6}$$

[The notations in Eq. (6) are those of Ref. 5. The symbols F and F^+ are chosen in analogy with the Gorkov factorization[4] for superconductors. F and F^+ may therefore be referred to as "anomalous propagators," characteristic for the paired state.] By comparing Eq. (6) with Eq. (4) we further have that $F_\sigma^+ = -F_{-\sigma}^+$ for the present system. To determine the propagators $G_{f,\sigma}$, $G_{e,\sigma}$, F_σ, and F_σ^+, it is now convenient to use the equation of motion, which, in the Hartree-Fock approximation we are considering [cf. Eq. (3)], has the form[6]

$$\left[i\frac{\partial}{\partial t} - \hat{h}(r)\right]G_\sigma(xx') + i\sum_{\sigma''} \int dx'' \frac{1}{|r-r''|}$$
$$\times [G_{\sigma''}(x''x''+0)G_\sigma(xx')$$
$$- G_{\sigma''}(xx''+0)G_\sigma(x''x')\delta_{\sigma,\sigma''}] = \delta(x-x'). \tag{7}$$

In Eq. (7) $\hat{h}(r)$ is the one-particle Hamiltonian (the kinetic energy operator plus the field from the protons) and the symbol $(+0)$ denotes the time limits to be taken as indicated in Eq. (5) and in Ref. 6. By inserting the expansion (6) into the equation of motion (7) and taking the Fourier expansion with respect to time the following system of equations for the propagators is obtained:

$$[\omega - \epsilon(k+Q)]G_{e,\sigma}(k\omega) - \tfrac{1}{2}\Delta(k\sigma)F_\sigma(k\omega) = 1,$$
$$[\omega - \epsilon(k)]F_\sigma(k\omega) - \tfrac{1}{2}\Delta(k\sigma)G_{e,\sigma}(k\omega) = 0,$$
$$[\omega - \epsilon(k)]G_{f,\sigma}(k\omega) - \tfrac{1}{2}\Delta(k\sigma)F_\sigma^+(k\omega) = 1, \tag{8}$$
$$[\omega - \epsilon(k+Q)]F_\sigma^+(k\omega) - \tfrac{1}{2}\Delta(k\sigma)G_{f,\sigma}(k\omega) = 0.$$

In Eqs. (8) the "gap function" $\Delta(k\sigma)$ is defined as

$$\tfrac{1}{2}\Delta(k\sigma) = i\sum_{|k'| \leq k_F} \int \frac{d\epsilon}{2\pi}\langle k, k'+Q | k', k+Q\rangle$$
$$\times \{F_\sigma(k'\epsilon) + F_\sigma^+(k'\epsilon)\}e^{i\epsilon\tau}, \quad \tau \to +0, \tag{9}$$

[4] See, e.g., A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood-Cliffs, N. J., 1963). We are using the definition of the Green's function found in this book.

[5] K.-F. Berggren and B. Johansson, Intern. J. Quant. Chem. 2, 483 (1967).

[6] L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962).

where $\langle \mathbf{k}, \mathbf{k'}+\mathbf{Q} | \mathbf{k'}, \mathbf{k}+\mathbf{Q} \rangle$ are the exchange matrix elements of the interaction $1/r_{12}$ with respect to the basis (1). We notice that $\Delta(\mathbf{k}\sigma) = -\Delta(\mathbf{k}-\sigma)$ because $F_\sigma^{(+)}(\mathbf{k}\omega) = -F_{-\sigma}^{(+)}(\mathbf{k}\omega)$.

The quantities $\epsilon(\mathbf{k})$ and $\epsilon(\mathbf{k}+\mathbf{Q})$ in Eqs. (8) are taken as the orbital energies of the paramagnetic Hartree-Fock state.[7] The solution to the system of equations (8) is

$$G_{f,\sigma}(\mathbf{k},\omega) = v^2(\mathbf{k})g_+(\mathbf{k},\omega) + u^2(\mathbf{k})g_-(\mathbf{k},\omega),$$

$$G_{e,\sigma}(\mathbf{k},\omega) = u^2(\mathbf{k})g_+(\mathbf{k},\omega) + v^2(\mathbf{k})g_-(\mathbf{k},\omega),$$

$$F_\uparrow(\mathbf{k}\omega) = F_\uparrow^+(\mathbf{k},\omega) = u(\mathbf{k})v(\mathbf{k})\{g_+(\mathbf{k},\omega) - g_-(\mathbf{k},\omega)\},$$

$$F_\downarrow(\mathbf{k},\omega) = F_\downarrow^+(\mathbf{k},\omega) = -F_\uparrow(\mathbf{k},\omega)(|\mathbf{k}| \leq k_F).$$

(10)

The functions $g_+(k,\omega)$ and $g_-(k,\omega)$ are defined as

$$g_+(\mathbf{k},\omega) = [\omega - E_2(\mathbf{k}) + i\delta]^{-1},$$

$$g_-(\mathbf{k},\omega) = [\omega - E_1(\mathbf{k}) - i\delta]^{-1},$$

(11)

where $\delta \to +0$. The poles $E_{1,2}(\mathbf{k})$ of the propagators (10) determine the orbital energies (the band structure) associated with the split-band model. The explicit expression for $E_{1,2}(\mathbf{k})$ is, from Eqs. (8),

$$E_{1,2}(\mathbf{k}) = \tfrac{1}{2}[\epsilon(\mathbf{k}) + \epsilon(\mathbf{k}+\mathbf{Q})]$$
$$\mp \tfrac{1}{2}\{[\epsilon(\mathbf{k}) - \epsilon(\mathbf{k}+\mathbf{Q})]^2 + \Delta^2(\mathbf{k})\}^{1/2}$$
$$(|\mathbf{k}| \leq k_F),\quad (12)$$

where $\Delta(\mathbf{k}) = \Delta(\mathbf{k}\uparrow) = -\Delta(\mathbf{k}\downarrow)$. By inserting the propagators (10) into Eq. (5) and performing the integration over ω, one recovers the density ρ_σ of Eq. (4). We can therefore identify the $u(\mathbf{k})$'s and $v(\mathbf{k})$'s appearing in the explicit forms (10) for propagators with the mixing parameters in Eqs. (4) and (2). From the system of Eqs. (8) one has explicitly, for $u(\mathbf{k})$ and $v(\mathbf{k})$,

$$u^2(\mathbf{k}) = \frac{1}{2}\left(1 + \frac{\epsilon(\mathbf{k}+\mathbf{Q}) - \epsilon(\mathbf{k})}{\{[\epsilon(\mathbf{k}) - \epsilon(\mathbf{k}+\mathbf{Q})]^2 + \Delta^2(\mathbf{k})\}^{1/2}}\right),$$

$$v^2(\mathbf{k}) = \frac{1}{2}\left(1 - \frac{\epsilon(\mathbf{k}+\mathbf{Q}) - \epsilon(\mathbf{k})}{\{[\epsilon(\mathbf{k}) - \epsilon(\mathbf{k}+\mathbf{Q})]^2 + \Delta^2(\mathbf{k})\}^{1/2}}\right).$$

(13)

With $F_\sigma(\mathbf{k}\omega)$ and $F_\sigma^+(\mathbf{k}\omega)$ inserted into the definition (9) of $\Delta(\mathbf{k}\sigma)$, we finally obtain the equation for the gap $[\Delta(\mathbf{k}) = \Delta(\mathbf{k}\uparrow) = -\Delta(\mathbf{k}\downarrow)]$,

$$\Delta(\mathbf{k}) = 2 \sum_{|\mathbf{k'}| \leq k_F} \frac{\langle \mathbf{k}, \mathbf{k'}+\mathbf{Q} | \mathbf{k'}, \mathbf{k}+\mathbf{Q} \rangle}{\{[\epsilon(\mathbf{k'}) - \epsilon(\mathbf{k'}+\mathbf{Q})]^2 + \Delta^2(\mathbf{k'})\}^{1/2}} \Delta(\mathbf{k'}).$$

(14)

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[7] Strictly speaking, the $\epsilon(\mathbf{k})$ are the matrix elements $\langle \mathbf{k}|\hat{H}_0|\mathbf{k}\rangle$, where $\hat{H}_0$ is a Hartree-Fock Hamiltonian, in which the interaction term is

$$\sum_{\sigma''} \int dx'' \frac{1}{|\mathbf{r}-\mathbf{r}''|} \{G_{f,\sigma''}(x''x''+0) + G_{e,\sigma''}(x''x''+0)$$
$$- [G_{f,\sigma''}(xx''+0) + G_{e,\sigma''}(xx''+0)]\delta_{\sigma\sigma''}P\}.$$

P is a permutation operator with interchanges x with x'' and σ with σ''. Since we are interested in qualitative aspects rather that quantitative, it is sufficient to set the $\epsilon(\mathbf{k})$'s equal to the eigen-

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Equation (14) has always the trivial solution $\Delta(\mathbf{k}) = 0$ corresponding to the paramagnetic Hartree-Fock state. Nontrivial solutions signal that the split-band model is energetically favorable.

For the total energy of the crystal quite a convenient expression may be found.[5] The Galitskii-Migdal formula[8] gives the energy corresponding to the Hartree-Fock state (3) as

$$\mathcal{E} = \sum_{|\mathbf{k}| \leq k_F} [u^2(\mathbf{k})\langle \mathbf{k}|\hat{h}|\mathbf{k}\rangle$$
$$+ v^2(\mathbf{k})\langle \mathbf{k}+\mathbf{Q}|\hat{h}|\mathbf{k}+\mathbf{Q}\rangle + E_1(\mathbf{k})]; \quad (15)$$

$\hat{h}$ is the one-particle operator of Eq. (7). [In what follows we also assume that the proton-proton interaction term is included in the two first terms of Eq. (15).] Thus, once $u(\mathbf{k})$, $v(\mathbf{k})$, and $E_1(\mathbf{k})$ are computed, the total energy is easily obtained by means of expression (15). By letting $\Delta(\mathbf{k}) \to 0$ the Hartree-Fock energy of the paramagnetic state is recovered.

States involving pairing all tend to be mathematically similar. This means that the formalism outlined above has strong similarities with the description of superconductors[4] and the excitonic state of matter.[9] The general character of the solutions to the gap equation (14) may therefore be of a somewhat broader interest.

III. NUMERICAL COMPUTATIONS

The key quantities in the preceding section are the orbital energies $\epsilon(\mathbf{k})$ for $|\mathbf{k}| \leq 2k_F$ and the gap function $\Delta(\mathbf{k})$. Their calculation involves all the interaction matrix elements $\langle \mathbf{kk'}|\mathbf{kk'}\rangle$, $\langle \mathbf{kk'}|\mathbf{k'k}\rangle$, and $\langle \mathbf{k}, \mathbf{k'}+\mathbf{Q} | \mathbf{k}, \mathbf{k'}+\mathbf{Q}\rangle$, which usually represent a considerable computational obstacle. The $1s$ function overlaps appreciably at moderate internuclear separations, which means that neighbors up to high order must be included and that a great number of three- and four-center integrals must be evaluated. It is possible to progress with hydrogenic $1s$ functions, as was done by Calais,[3] but the computation of all the polycenter integrals becomes complex, relying on the expansion of an atomic function at a certain center around the other centers. We have therefore chosen another computational method. As shown by Reeves,[10] a hydrogenic $1s$ function can be expanded in a limited set of Gaussian functions $\exp(-\alpha_i r^2)$ to a good degree of accuracy. All the necessary integrals of Gaussian functions can be evaluated from closed formulas,[11] which are easy to program. For our computations, we have therefore used Reeves's

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values of the paramagnetic state. In the two limiting cases of narrow and broad bands this approximation can be shown to be completely warranted.

[8] See, e.g., D. A. Kirzhnits, *Field Theoretical Methods in Many-Body Systems* (Pergamon Press, Inc., New York, 1967), and Ref. 5.

[9] D. Jerome, T. M. Rice, and W. Kohn, Phys. Rev. **158**, 462 (1967), and references therein.

[10] C. M. Reeves, J. Chem. Phys. **39**, 1 (1963).

[11] See, e.g., I. Shavitt, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic Press Inc., New York, 1963), Vol. II, p. 1.
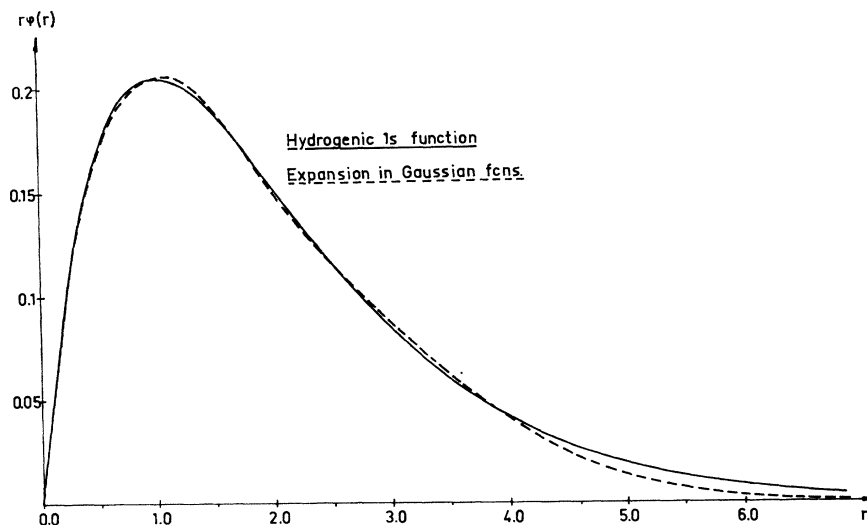
FIG. 2. Comparison of the hydrogenic 1s function (solid line) with its expansion in Gaussian functions [Eq. (16) in text].

expansion[10]

$$e^{-r}/\sqrt{\pi} \simeq 0.1084e^{-0.1483r^2} + 0.2164e^{-0.6577r^2}$$
$$+ 0.1575e^{-4.2392r^2}. \quad (16)$$

For the energy of an isolated hydrogen atom the expansion (16) gives the energy -0.497, i.e., 99.4% of the correct value, an accuracy which is definitely sufficient for our purposes. In Fig. 2 the expansion (16) is compared with the hydrogenic function. The over-all agreement is good, but for large values of r the expansion (16) falls off too fast. Because of the effect of the different basis on the many multicenter integrals in our calculation, however, we will consider only qualitative differences in comparing our numerical results with other calculations using a hydrogenic basis (Refs. 3, 12, and 13). In the calculations neighbors up to about twentieth order have been included.

The integral equation (14) for the gap function $\Delta(\mathbf{k})$ was solved by an iteration procedure. The integration was performed by Simpson's rule, and 17 points in the interval $(0.,k_F)$ were found sufficient. After about five cycles in the iteration procedure convergence was obtained. In Fig. 3 the solutions $\Delta(\mathbf{k})$ for different values of the lattice parameter a are displayed. For large internuclear separations $\Delta(\mathbf{k})$ approaches a finite constant value, which can be understood in the following way. As the lattice parameter a approaches ∞ the band width decreases, i.e., the quantity $[\epsilon(\mathbf{k}) - \epsilon(\mathbf{k}+\mathbf{Q})]^2$ in Eq. (14) can be omitted. In the same limit, $\langle \mathbf{k}, \mathbf{k}'+\mathbf{Q} | \mathbf{k}', \mathbf{k}+\mathbf{Q} \rangle \rightarrow \langle gg | gg \rangle/N$, where $| g \rangle$ stands for the atomic function (16) on center g, and N is the number of lattice sites. We therefore have for large values of a the relation

$$\Delta(\mathbf{k}) \simeq \langle 00 | 00 \rangle = 0.6252. \quad (17)$$

The hydrogenic function $e^{-r}/\sqrt{\pi}$ gives $\Delta(\mathbf{k}) = \frac{5}{8} = 0.625$.

[12] J. W. Moskowitz, J. Chem. Phys. **38**, 677 (1963).
[13] W. T. Kwo, Phys. Rev. **171**, 484 (1968).

Figure 3 shows that for $a = 10.0$ the asymptotic form (17) is practically fulfilled.

Because of the separation of $\rho_\sigma(\mathbf{r})$ onto the two sublattices A and B, the periodicity of the system is doubled. This means that the Brillouin zone associated with the split-band model extends out to $|\mathbf{k}| = k_F$. In Fig. 4 the effects of the pairing on the band structure is shown for two different situations. The dotted line is the paramagnetic dispersion $\epsilon(\mathbf{k})$, which for $|\mathbf{k}| > k_F$ has been flipped back onto the first Brillouin zone of the sublattices. As expected, the doubled periodicity of the
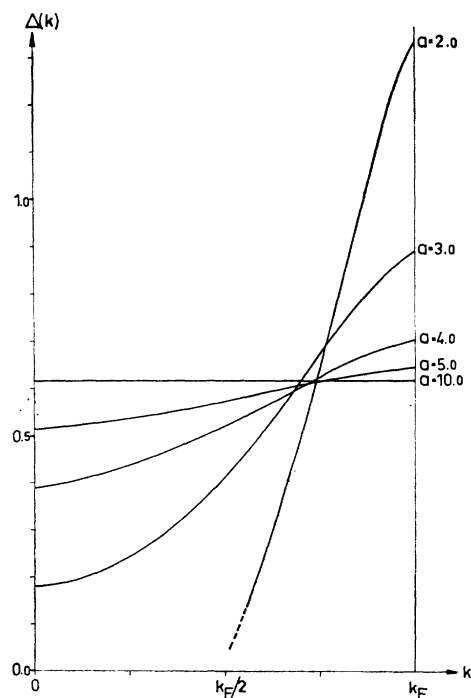

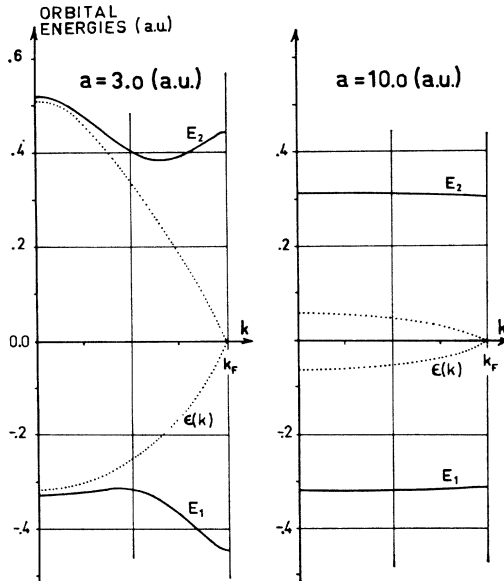FIG. 3. Gap function $\Delta(\mathbf{k})$ for different values of the lattice parameter a.

Fig. 4. Effect of pairing on the band structure for two different lattice constants a. The dashed curve is the paramagnetic dispersion $\epsilon(\mathbf{k})$, which for $|\mathbf{k}|>k_F$ has been flipped back onto the first Brillouin zone of the sublattices. The solid line is the dispersion $E_{1,2}(\mathbf{k})$ obtained by the split-band model. The Fermi energy ϵ_F is chosen as the reference energy.

system causes a gap in the single particle excitation spectrum at the zone boundaries. The magnitude of this gap is $\Delta(\mathbf{k}_F)$. By the pairing the system thus becomes insulating (as well as antiferromagnetic). Figure 4 shows further that for smaller internuclear separations the pairing has a small effect on the electron dispersion for values of $|\mathbf{k}|$ away from k_F. For $|\mathbf{k}|$ closer to k_F the pairing has a profound effect; the new dispersion deviates strongly from the paramagnetic dispersion, and the curvature is completely changed. For large values of a the whole part of the spectrum is changed in a significant way. The bands flatten out to almost discrete levels, and in the limit $a \to \infty$ we get [see Eq. (17)]

$$E_{1,2}(\mathbf{k}) = \mp \tfrac{1}{2}\langle 00|00\rangle = \mp 0.3126, \qquad (18)$$

where $\epsilon(k_F)$ is the reference energy. For $a = 10.0$ relation (18) is almost realized.

In Fig. 5 the total energy/atom of the split-band model and the ordinary band model are shown as a function of the lattice parameter a. Our energy curves are based on the results for $a = 1.0$–10.0 in steps of 1.0 a.u. In the same figure are also shown the results on H_∞ by Calais,[3] the H_6 ring by Moskowitz,[12] and the H_{12} ring by Kwo.[13] [It should be mentioned that our calculations for $a = 1.0$ involve certain simplifications. One notices during the calculations that the sum of the two first quantities in the energy expression (15) are almost identical for the paramagnetic and the antiferromagnetic states, and that for a approaching zero this sum becomes by far the dominant quantity. The last

term is small and negative, and decreases slowly with decreasing a. For $a = 1.0$ we therefore only evaluated the first part of Eq. (15) for the paramagnetic state in a rigorous way, and the last part giving only a minor contribution was taken from extrapolation. All the quantities involved behave smoothly with a, and we therefore feel that this procedure is safe.] For large values of a the energy corresponding to $\mathbf{k}$-dependent mixing approaches the correct asymptotic value, which in the case of the expansion (16) is -0.497. The energy of the paramagnetic state approaches in the same limit an energy/atom

$$\mathcal{E}/N = \langle 0|\hat{h}|0\rangle + \tfrac{1}{4}\langle 00|00\rangle = -0.3408. \qquad (19)$$

The matrix elements are over atomic functions. A hydrogenic $1s$ function gives $\mathcal{E}/N = -\tfrac{11}{32} = -0.34375$.[14] The minimum of our energy curve for the split-band
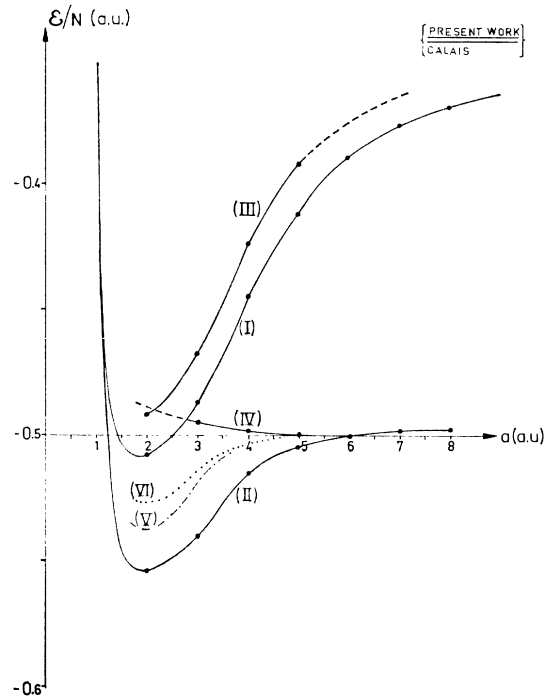

Fig. 5. Total energies/atom ($\mathcal{E}/N$) for: (I) The paramagnetic state of H_∞ (present calculation), (II) the antiferromagnetic state of H_∞ (present calculation), (III) the paramagnetic state of H_∞ (Calais, Ref. 3), (IV) the antiferromagnetic state of H_∞ (Calais, Ref. 3), (V) the H_6 ring (Moskowitz, Ref. 12), (VI) the H_{12} ring (Kwo, Ref. 13). The heavy dots are calculated points, and dashed lines are extrapolations. The energy of the paramagnetic state for $a = \infty$ is indicated in the upper right corner by two bars—the upper for the result of the present work, the lower for that of Ref. 3.

[14] We would like to attribute the over-all difference between Calais's (Ref. 3) and our energy curve for the paramagnetic state to the different basis functions used, and the different ways of computing the polycenter integrals. For these integrals Calais relies on the type of expansions mentioned in the Introduction. The fact that the Gaussian approximation (16) is somewhat more contracted than the hydrogenic function is probably in our favor. Moskowitz's calculations (see Ref. 12) on the H_6 ring show that a contraction (by scaling) occurs.
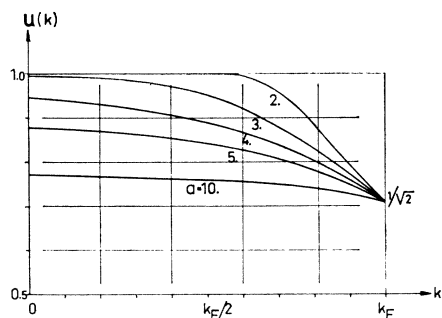
FIG. 6. Mixing parameter $u(\mathbf{k})$ for different values of the lattice parameter a.

model occurs at a value of a slightly less than $a=2.0$, i.e., about the same value as for H_6 [12] and H_{12}.[13] The cohesive energy is therefore $\sim 0.05_4$ per atom. It is interesting that this value of the cohesive energy is close to the value obtained for the three-dimensional hydrogen crystal by means of the Wigner-Seitz method.[15]

In Fig. 6 the mixing parameter $u(\mathbf{k})$ is displayed for different values of the lattice parameter. In the limit of large internuclear separation, i.e., narrow bands, $u(\mathbf{k}) \to 1/\sqrt{2}$, which means that the states mix with equal weights all over the zone. Figure 6 shows that for $a=10.0$ this situation is almost attained. For small values of a the mixing takes place practically only in a region close to $|\mathbf{k}|=k_F$. The band is now so broad that one-particle levels in the upper part of the band can contribute only very insignificantly to the ground-state energy.

IV. DISCUSSION

By the explicit calculations of the preceding section, we have shown that the formalism outlined in Sec. II leads to a computationally manageable scheme. The computer time needed for the calculations of the enormous amount of polycenter integrals and the quantities $\epsilon(\mathbf{k})$ is, however, considerable. This is the reason why we did not carry through a complete self-consistent procedure including also $\epsilon(\mathbf{k})$. We feel that the results of such an extended self-consistent calculation for the present unrealistic system would not stand in proper relation to the cost of the computations. As mentioned earlier, the neglect of self-consistency plays a minor role when the bands are very broad or narrow. Figure 6

shows that for broad bands the pairing is effective only close to the Fermi surface. To a good accuracy the mean field determining $\epsilon(\mathbf{k})$ depends therefore only on unpaired electrons and $\epsilon(\mathbf{k})$ can be chosen as the orbital energies of the paramagnetic state. For very narrow bands we have that the interaction matrix elements become independent of the crystal momenta. Together with the relation $u^2(\mathbf{k})+v^2(\mathbf{k})=1$ this gives a mean field independent of the pairing.

Our energy curve for the $\mathbf{k}$-dependent mixing should be compared with Calais's[3] results for constant mixing. Calais's calculations indicate a magnetic phase transition for a slightly larger than 2.0. This phase transition is removed (or at least moved to values of $a<1.0$) by our approach. We can understand the appearance of Calais's instability from Fig. 6. By using a constant mixing all the states in the zone mix with the same weight. For small values of a states in the upper part of the band are therefore forced into the ground-state wave function with much too large a weight and thereby causing the instability. The same behavior upon constant mixing has been found for an antiferromagnetic linear chain described by the Hubbard Hamiltonian.[16]

In Fig. 5 were also shown the energy curves for the H_6 ring[12] and the H_{12} ring,[13] both computed by means of different orbitals for different spins with constant mixing λ and unscaled hydrogenic $1s$ functions as basis. Taken together, Moskowitz's H_6, Kwo's H_{12}, and Calais's H_∞ demonstrate that the cohesive energy decreases as the number of atoms increases. One may speculate why our energy curve falls below the curves of these systems:

(a) The trend in H_6, and H_{12}, and Calais's H_∞ indicate that $\mathbf{k}$-dependent mixing becomes indispensable as the number of atoms goes to infinity.

(b) The basis functions are different.

(c) Self-consistency with respect to $\epsilon(\mathbf{k})$ should be included.

[15] E. Wigner and H. B. Huntington, J. Chem. Phys. **3**, 764 (1935). Wigner and Huntington obtain 0.025 for the cohesive energy. Corrections to Wigner and Huntington's calculations made by Lars Hedin (private communication) give a cohesive energy ~ 0.04–0.05.

[16] B. Johansson and K.-F. Berggren, Phys. Rev. **181**, 855 (1969).