

MAGNETIC AND CORRELATION EFFECTS IN A NON-CLOSED-SHELL LINEAR CHAIN

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Résumé. — Les effets de magnétisme et de corrélation dans une chaîne linéaire consistant en $4n$ atomes d'hydrogène répartis suivant la forme d'un polygone régulier de $4n$ côtés sont étudiés par l'usage de différentes fonctions de Bloch pour différents spins dans le cadre de la méthode Hartree-Fock étendue. Les résultats numériques dans le cas où $n = 3$ sont présentés avec interactions entre tous les voisins évalués pour les distances interatomiques qui s'étendent de un à cinq rayons de Bohr.

Abstract. — Magnetic and correlation effects in a linear chain consisting of $4n$ hydrogen atoms arranged in the form of a regular polygon of $4n$ sides are studied within the framework of the extended Hartree-Fock method through the use of different Bloch functions for different spins. Numerical results for the $n = 3$ case are presented, with interactions between all neighbors evaluated for interatomic distances that range from one to five Bohr radii.

Introduction. — The antisymmetry of the total wave function in the energy band approximation, formulated in terms of the conventional Hartree-Fock method, leads to a form of correlation between electrons with the same spin which is absent between electrons of opposite spin. This unbalanced treatment of the spins may be remedied somewhat by allowing electrons with different spins to occupy spatially different one-electron wave functions [1]. In this paper, we use such an approach within the framework of the extended Hartree-Fock method [1, 2] to account for the Coulomb interaction e^2/r_{ij} between electrons in a non-closed-shell linear chain consisting of $4n$ hydrogen atoms arranged in the form of a regular polygon of $4n$ sides (Each atom is assumed to contribute a single 1s electron.) The influence of electron correlation upon the behavior of the low-lying singlet and triplet states of this system with both spin and orbital degeneracies as the interatomic separation R is varied is discussed in connection with numerical results obtained for the $n = 3$ case.

Method and Results. — With φ_μ representing the atomic orbital at the vertex with angular coordinate $\mu\pi/2n$, the Bloch functions ψ_m of the system are given by

$$\psi_m = \left\{ 4n \left[\sum_{\mu=0}^{4n-1} \exp\left(\frac{\mu m \pi i}{2n}\right) \langle \varphi_0 | \varphi_\mu \rangle \right] \right\}^{-1/2} \times \left[\sum_{\mu=0}^{4n-1} \exp\left(\frac{\mu m \pi i}{2n}\right) \varphi_\mu \right] \\ [m = 0, \pm 1, \dots, \pm n, \dots, \pm (2n-1), 2n]. \quad (1)$$

These functions may be paired by means of a parameter θ to give

$$\psi_{mI} = \cos \theta \psi_m + \sin \theta \psi_{-(2n-m)}, \quad (2a)$$

$$\psi_{mII} = \cos \theta \psi_m - \sin \theta \psi_{-(2n-m)}. \quad (2b)$$

The functions $\psi_{mI,II}$ are semilocalized so that electrons with opposite spin tend to avoid each other [1].

The total wave function may now be written in the form [2]

$$\Psi = {}^{(2S+1)}\mathcal{O}\mathcal{O}_R \Phi. \quad (3)$$

In eq. (3), ${}^{(2S+1)}\mathcal{O}$ is a spin projection operator [1] for selecting a pure spin state of multiplicity $(2S+1)$, \mathcal{O}_R is an operator (acting upon the spatial coordinates of the electrons [2]) leading to a wave function belonging to an irreducible representation of the group of the spin-free Hamiltonian

$$\mathcal{H} = \sum_{j=1}^{4n} \left(-\frac{\hbar^2}{2m} \nabla_j^2 - \sum_{g=1}^{4n} \frac{e^2}{r_{jg}} \right) + \sum_{j < k}^{4n} \frac{e^2}{r_{jk}} + \sum_{g < h}^{4n} \frac{e^2}{r_{gh}}, \quad (4)$$

and Φ represents a linear combination of antisymmetrized products of one-electron wave functions $\psi_{mI,II}$ [2] (In eq. (4), the indices j and k refer to the electrons while the indices g and h refer to the protons.)

The expectation value of the Hamiltonian is obtained by evaluating

$$E = \langle \Psi | \mathcal{H} | \Psi \rangle / \langle \Psi | \Psi \rangle. \quad (5)$$

In Table I, we present calculated values of E for the $n = 3$ case for the low-lying ${}^1\Gamma_4$ and ${}^3\Gamma_2$ states that asymptotically approach an energy of -12 Rydbergs

TABLE I

Total energy E as a function of interatomic separation R for the ${}^1\Gamma_4$ and ${}^3\Gamma_2$ states of the H_{12} linear chain.

$R^{(a)}$	$E^{(b)}$	$E^{(b)}$
	${}^1\Gamma_4$ state	${}^3\Gamma_2$ state
1.00	- 6.012 6	- 6.018 0
2.00	- 12.628 8	- 12.554 2
2.75	- 12.459 7	- 12.284 5
3.00	- 12.162 5	- 12.021 2
4.25	- 12.046 5	- 11.993 1
5.00	- 12.012 5	- 11.994 4

^(a) Units : a. u.

^(b) Units : Rydbergs.

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at large interatomic distances [2] (A description of the meaning of the state labels $^1\Gamma_4$ and $^3\Gamma_2$ may be found in ref. [2]). In carrying out this calculation, all integrals between hydrogen 1s atomic wave functions have been evaluated by direct quadrature with orbital exponents set equal to unity, and all relevant overlap integrals between the functions ψ_{mI} and ψ_{mII} have been taken into consideration [3]. The total energies at lattice spacings ranging from 1 to 5 a. u. (the unit of length in a. u. is taken to be the radius of the first Bohr orbit of the hydrogen atom) have been minimized with the mixing parameter $\lambda = \cos 2\theta$ varied in intervals of 0.0001. In figure 1, we show the dependence of λ values obtained by energy minimization upon interatomic separation R .

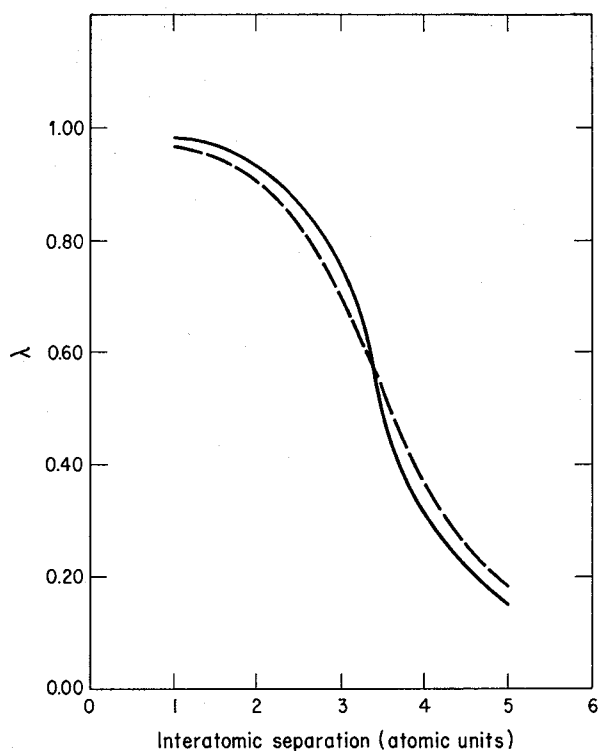


FIG. 1. — The mixing parameter λ for different values of the interatomic separation R . The solid curve is for the $^3\Gamma_2$ state. The dashed curve is for the $^1\Gamma_4$ state.

Discussion. — By letting θ vanish in eq. (2a, b), ψ_{mI} and ψ_{mII} reduce to the same Bloch function ψ_m , and the expectation values of the Hamiltonian exhibit the incorrect asymptotic behavior at large R characteristic of the conventional Hartree-Fock approximation [1]. Furthermore, the $^3\Gamma_2$ state becomes lower in energy than the $^1\Gamma_4$ state at all values of R ranging from 1 to 5 a. u. The inclusion of Coulomb correlation through the pairing of Bloch functions as in eq. (2a, b) reverses this ordering of energy levels for R slightly larger than 1 a. u. as indicated in Table I and figure 3 of ref. [2]. Figure 1 shows that the values of optimum λ for the $^1\Gamma_4$ and $^3\Gamma_2$ states are rather close to 1 for $R < 2$ a. u. Neither, however, is exactly unity at $R = 1$ a. u., implying that a certain amount of band splitting [1] is still present. In this sense, we can say that at $R = 1$ a. u., the system is not entirely « paramagnetic ». As R increases beyond 2 a. u., λ decreases quite rapidly and becomes less than 0.2 at $R = 5$ a. u. This is a reflection of the way in which ψ_{mI} and ψ_{mII} become increasingly semilocalized [1] in order to allow the nature of the total wave function to approach that of the Heitler-London or Heisenberg approximation at large R [1, 4]. By regarding the mixing parameter λ as being related in this way to the degree of itinerancy of the electrons, we find that although the electrons become less itinerant quite readily as R exceeds 2 a. u., a sharp transition does not seem to take place in this finite system [4, 5] for $R > 2$ a. u. However, as the ground state changes from the $^3\Gamma_2$ state to the $^1\Gamma_4$ state when R exceeds 1 a. u., a discontinuity in λ occurs resulting in a slight but abrupt lowering of the degree of itinerancy of the electrons. How this result would be modified if we were to adopt approximations different from the ones used in this paper is a question which remains to be explored.

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