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Correlation effects in the magnetism of small aggregates and in polyenes

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First, we apply a Gutzwiller technique developed in other papers to the problem of the appearance of magnetism in small aggregates. We show that the intra-atomic correlation energy U_{crit}, for which magnetism appears, varies with the number of atoms N in the clusters considered ($N=55$ and 147) and with the band filling n ($n=\frac{1}{4}$, $\frac{5}{8}$, and $\frac{1}{2}$). This behavior can be understood by the first-order (in U) Stoner criterion. However, our results are more precise and include higher orders of U; i.e., they include the rearrangements of electrons due to correlations. Second, we apply the technique to the study of the triplet-singlet separation in various six-atom polyenes. Our model reproduces the results of a precise calculation for almost all the shapes considered, except for the shapes where $m_\uparrow \neq m_\downarrow$. We also apply the model to the study of the ionization energy of relatively large polyenes (up to $N=34$ carbon atoms). Many features of the experimental results are reproduced.

I. INTRODUCTION. THE GUTZWILLER METHOD FOR AGGREGATES

We have developed in other works[1-3] a method which allows one to take into account dielectronic correlations in the study of the electronic structure of small aggregates. This technique is an extension of the Gutzwiller variational method originally proposed for the bulk.[4-6] It is based on the Hubbard Hamiltonian H and, therefore, depends on two parameters: the intra-atomic correlation energy U and the hopping term β. Other variational models based on similar principles have also been published recently.[7-9]

The validity of our method has been tested in the previous papers. One knows that it is possible to obtain for small molecules with five or six atoms the "exact" eigenvalues and eigenfunctions by diagonalizing the Hubbard matrix, whose elements are $\langle \Phi_i | H | \Phi_j \rangle$, where Φ_i are the atomic Slater determinants. Our values obtained for the ground-state energy agree well with the "exact" results, with a precision better than 5% for a large range of $U/|\beta|$ values ($0<U/|\beta|<5$).[2] Moreover, for the molecule H_2 the Gutzwiller result is identical to the "exact" result.[10] Thus one sees that the Gutzwiller method gives the correct dissociation ($H+H$) of H_2 for large $U/|\beta|$ values; it is therefore directly comparable to theories which include interaction of configurations.

Let us recall the main features of the method. We consider a molecule with N atoms; on each atom i is centered a nondegenerate atomic function Φ_i. The overlap integral between neighboring sites has been neglected:

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} .$$

The first step of the method is the calculation of the ground-state linear combination of atomic orbitals (LCAO) determinantal wave function Ψ_0 obtained without correlations. Then a modified function Ψ is written where the new weight on a given Slater atomic determinant Φ_i is

$$\langle \Psi | \Phi_i \rangle = A(\eta) \langle \Psi_0 | \Phi_i \rangle \eta^{\nu_i} ,$$

where η is a variational parameter, ν_i the number of doubly occupied sites in function Φ_i, and $A(\eta)$ a normalization coefficient.

Gutzwiller has shown[4] that for a simple cubic lattice in the bulk, the energy can be written

$$E(\eta) = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = Q(\eta) E^H + \chi(\eta) U , \tag{1}$$

where $Q(\eta)$ and $\chi(\eta)$ are η functions given in Ref. 10 for the general case of N sites and N_e electrons ($N_\uparrow$ with spin up, $N_\downarrow$ with spin down) and E^H is the Hückel energy corresponding to Ψ_0.

We have verified in the aforementioned works that when the sites are no longer equivalent one can also use expression (1) where E^H is the Hückel energy corresponding to the considered shape. This point will be reexamined later in this paper.

When the number of atoms (or of electrons) becomes large the expressions $Q(\eta)$ and $\chi(\eta)$, which are complex series of factorial terms, can be reduced to the largest term of the series. This approximation has also been tested[2] and can be used for $N \gtrsim 10$. We have again verified this point in this work (Sec. III).

When this approximation is made a new variational parameter ν appears and the energy can be written

$$E(\nu) = Q(\nu) E^H + \nu U ,$$

with

$$Q(\nu) = \frac{(N_\uparrow - \nu)}{N_\uparrow (N - N_\downarrow)} \left[(N - N_\uparrow - N_\downarrow + \nu)^{1/2} + \nu^{1/2} \left[\frac{N_\downarrow - \nu}{N_\uparrow - \nu} \right]^{1/2} \right]^2 . \tag{2}$$

It is worth noticing that ν has a physical meaning and represents the total number of doubly occupied sites.

Some applications of the method have already been published.[3] For instance, we have studied the magnetism of small clusters with $N=55$ and 147 atoms for a half-filled band. Section II is a continuation of this work in which we analyze other band fillings.

In Sec. III we examine the question of π electrons in polyenes. One knows that the experimental results are numerous for these molecules.[11] Our technique will be more precisely applied to the magnetism and the ionization energy of some of these molecules.

II. MAGNETISM OF CUBOCTAHEDRAL CLUSTERS WITH 55 AND 147 ATOMS

Since the number of atoms in the clusters is relatively large, we can use formula (2); we call E the energy obtained after minimization. For each band filling n, with

$$n=(N_\uparrow+N_\downarrow)/2N \ ,$$

we will consider two configurations: on the one hand, the less magnetic state ($N_\uparrow \sim N_\downarrow$) called "nonmagnetic," on the other hand, a magnetic state with a magnetization μ, given by

$$\mu=\frac{N_\uparrow-N_\downarrow}{N_\uparrow+N_\downarrow} \ .$$

μ has a value of about $\frac{1}{3}$.

When U increases the energies E are destabilized. To first order in U this increase is given by

$$U\frac{N_\uparrow N_\downarrow}{N} \ ,$$

which shows that the magnetic state is destabilized less rapidly than the nonmagnetic state. Generally, a crossing of the two curves occurs for a value of U called U_{crit}.

The values of U_{crit} and E are given in Table I for $n=\frac{1}{2}$, $\frac{5}{8}$, and $\frac{1}{4}$. In the framework of this model, the study of cases with $n>\frac{1}{2}$ is not physically meaningful because when U increases the electronic energies become rapidly positive. For instance, the lower limit of E for the two states is

$$E^H+(N_\uparrow+N_\downarrow-N)U \ . \tag{3}$$

We see that for a 55-atom cuboctahedral cluster with $n=\frac{5}{8}$, (3) is positive for U larger than $\sim -6\beta$. Moreover, for $U>-6\beta$ the two positive energies do not cross each other.

Let us come back to the results of Table I. An explanation of the behavior of U_{crit} when N varies can be found by looking at Fig. 1 where we have drawn smoothed densities of states for the two molecules (each molecular level is broadened by a Gaussian function). When the highest occupied level ϵ_F of the "nonmagnetic" state falls in a part of the density of states $\rho(\epsilon)$ larger for $N=55$ than for $N=147$, according to the Stoner criterion

$$U_{\text{crit}}\rho(\epsilon_F)=1 \ , \tag{4}$$

one can expect that the value of U_{crit} is smaller for $N=55$. This situation appears for $n=\frac{1}{2}$ and $n=\frac{1}{4}$; U_{crit} (Table I) is smaller, as expected, for $N=55$. The reverse situation appears for $n=\frac{3}{8}$ (Fig. 1).

TABLE I. Values of U_{crit} and E (energy where the magnetic and nonmagnetic states cross each other) in units of β.

Band filling	n	$\frac{1}{2}$	$\frac{3}{8}$	$\frac{1}{4}$
$N=55$	U_{crit}	-8.39	-9.23	-11.61
	E	28.58	74.80	88.82
$N=147$	U_{crit}	-17.75	-7.71	-14.15
	E	4.58	222.34	246.41

So our results reproduce the conclusion of the Stoner criterion which is deduced from a first-order (in U) model. However, larger orders in U are important. This is shown by the study of the susceptibility made, for the bulk, by Brinkman *et al.*[12] who use the Gutzwiller method (half-filled band and ρ constant) and obtain instead of (4)

$$U_{\text{crit}}\rho\frac{1+U_{\text{crit}}/16E_B}{(1+U_{\text{crit}}/8E_B)^2}=1$$

(E_B is the Hückel energy per atom in the bulk) which displaces U_{crit} toward high energy. Our results include, as formula (5), the effect of the correlations at all U orders.

As a general conclusion on the dependence of U_{crit} with size one can expect that for band fillings such as $n=\frac{1}{2}$, $\frac{3}{8}$, or $\frac{1}{4}$, for which E_F falls in a region close to the nonbonding energy, U_{crit} will increase with N. This is due to the fact that the number of bonds per atom increases leading to a decrease in ρ ($\epsilon\sim 0$). One can notice that this behavior has not been obtained here for $n=\frac{3}{8}$ due to a fortuitous fluctuation in the distribution of energy levels. However, for larger-N values this general behavior should appear.

III. STUDY OF SOME POLYENES

Polyenes are planar organic molecules where carbons are nonsaturated. In these molecules carbon $2s$ and $2p$ orbitals combine with each other and form hybrid orbitals which are very close to (and sometimes exactly) sp^2 hybrids. The remaining orbital is of $2p_z$ type.

The hybrids form a band of bonding levels occupied by three electrons per carbon. The hybrids also form an empty antibonding band. Between these two bands there is a π band formed by $2p_z$ levels occupied by one electron per atom. One sees that this π band can be described by the model presented in Sec. I.

As the highest occupied levels are of π type, the π electrons strongly influence electronic properties. Let us men-

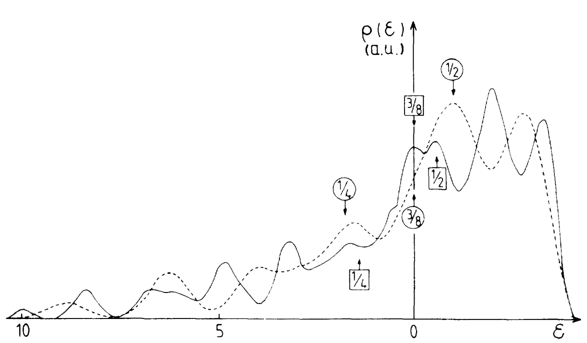

FIG. 1. Smoothed density of states (each molecular level has been broadened with a Gaussian function) of the two considered cuboctahedral molecules (dotted line $N=55$, solid line $N=147$). The energies ϵ are given in β units. The arrows give the energy of the highest spin-up level for the nonmagnetic (band filling written in a square) or magnetic (band filling written in a circle) state.

tion, among others, the following: the ionization potential, the absorption properties (which depend on the separation between the ground and the excited states) and the diamagnetism for cyclic polyenes.

π electrons also play an important role in the binding energy. The first model which has been applied to the study of polyenes was a one-electron Hückel model. It explained the fact that molecules or ions with closed-shell electronic structures (such as $C_5H_5^-$) were particularly stable.[11] However, one knows that the intra-atomic correlations have a strong influence on the stability. For instance, a Gutzwiller calculation has shown that when $U/|\beta|$ is larger than a critical limit (of about 4), the closed-shell effect disappears.[3] As a consequence, the polyenes [for which $U/|\beta| \sim 2.34$ (Ref. 13)] are systems where the conclusions of a Hückel model can only be qualitative.

For this reason we have used the Gutzwiller method for studying two properties of polyenes: the singlet-triplet separation and the ionization potential, problems where the stabilities of the molecule and of various excited states are required. Let us first consider the singlet-triplet separation. In Sec. II we studied the variation with $U/|\beta|$ of the energy of various magnetic configurations of two clusters; here, the value of U/β is fixed (we consider two cases: $\beta=-2.35$ eV, $U=5.5$ eV, values used in Refs. 13 and 14, and $\beta=-2.6$ eV, $U=5.5$ eV) and we study the most stable nonmagnetic and magnetic configurations for various six-atom and eight-atom molecules. For these molecules there exist very precise calculations by Döhnert *et al.*[15] (full interactions of configurations) that we will take as reference values. Our results and the values of Ref. 15 are given in Table II.

We see that for the six-atom molecules [Figs. 2(a)–2(k)] the values of the singlet-triplet separations are ordered in the same way as in the paper of Döhnert *et al.*: the largest separation is for shape (k) (benzene), followed by shape (h), shapes (i), (a), and (c) (with nearly the same value), then shape (b), followed by shapes (e), (f), (d), and (j). The main difference between the two sets of results is that, for these four last shapes, the Gutzwiller method gives the triplet state more stable than the singlet, whereas Döhnert *et al.* obtain this result only for shapes (d) and (j).

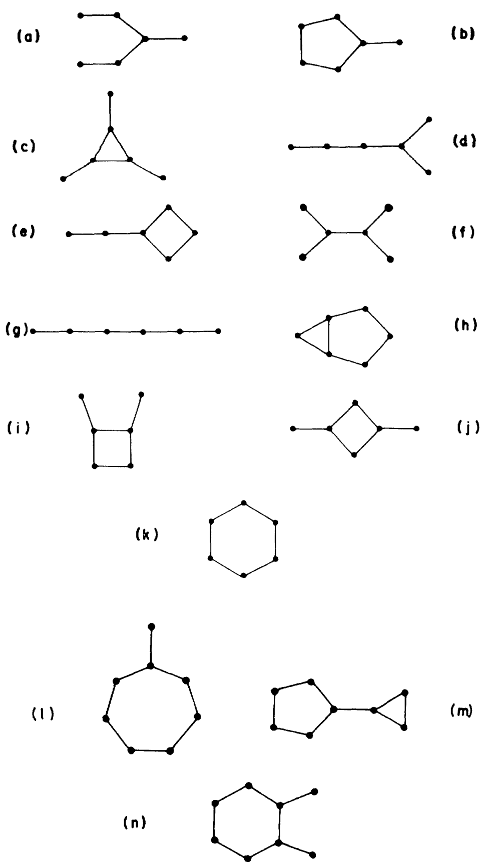

FIG. 2 (a)–(k), shapes of the various six-atom molecules; (l)–(n), shapes of the various eight-atom molecules.

For explaining this difference one must take into account a remark made by Ovchinnikov.[16] This author starts from the fact that, for large $U/|\beta|$ values, the Hubbard Hamiltonian tends towards a Heisenberg Hamiltonian (as shown in Ref. 17) with negative exchange integral. Then, the Φ_i wave functions to be considered are limited to the subensemble Φ_i^1 of functions with one electron per site. Let us suppose that, for a given shape, one writes an alternate graph (i.e., one arranges the spins so that they are different on nearest neighbors) where the total number $n_\uparrow$ of spin up is larger than the total number $n_\downarrow$ of spin down, say $n_\uparrow = n_\downarrow + 2$, for example. We can expect in this case that, as the wave function of the subensemble Φ_i^1 corresponding to this alternate graph is one

TABLE II. Difference (in eV) between the energy of the triplet and the energy of the singlet. The shapes are drawn in Fig. 2. For each shape we give in the first row the calculated values (with $\beta=-2.35$ eV and $U=5.5$ eV, first column; with $\beta=-2.6$ eV and $U=5.5$ eV, second column) and in the second row the value of Döhnert *et al.* (Ref. 15), except for shape which has not been calculated.

(a)	1.67	1.90	(f)	−0.58	−0.59	(k)	3.76	4.27
	2.02			0.09			3.92	
(b)	1.31	1.50	(g)	1.35	1.55	(l)	1.00	1.15
	1.50						1.16	
(c)	1.66	1.89	(h)	2.55	2.94	(m)	2.80	3.23
	2.22			3.04			2.15	
(d)	−0.58	−0.59	(i)	1.83	2.08	(n)	0.84	0.97
	−0.50			2.12			0.97	
(e)	−0.59	−0.59	(j)	−0.58	−0.59			
	0.25			−0.71				

TABLE III. Experimental and theoretical values of the ionization energy of some polyenes (given in eV). We have used $\beta=-2.35$ eV and $U=5.5$ eV for the first column and $\beta=-2.6$ eV and $U=5.5$ eV for the second. For the three first molecules the experimental values are taken from Ref. 20, the other molecules from Ref. 21. The experimental results are obtained by the photoelectron technique; in most cases, we give the interval in which they are obtained. The shapes of the molecules are drawn in Ref. 22.

	Molecule	Expt.	Theor. ($\beta=-2.35$ eV)	Theor. ($\beta=-2.6$ eV)
$N=6$	benzene	9.25	9.25	9.25
$N=10$	naphthalene	8.11–8.12	8.34	8.25
$N=14$	anthracene	7.47	7.87	7.73
	phenanthrene (benz[*a*]naphthalene)	7.87–7.92	8.30	8.21
$N=18$	naphthacene	6.97–7.04	7.59	7.42
	benz[*a*]anthracene	7.41–7.56	7.94	7.81
$N=22$	pentacene	6.61–6.74	7.42	7.23
	benz[*a*]naphthacene	7.14	7.71	7.55
	picene	7.52–7.54	8.05	7.93
$N=26$	Hexacene	6.36–6.44	7.30	7.09
	Hexaphene (naphthlen[*a*]naphthacene)	6.92–7.02	7.59	7.42
	benzo[*c*]picene	7.20	7.98	7.85
$N=30$	Heptaphene (anthracen[*a*]naphthacene)	6.89–6.98	7.44	7.25
	Trinaphthylene (dinaphthalen[*a*,*c*]anthracene)	7.35	8.07	7.96
$N=34$	tetrabenz[*a*,*c*,*j*,*l*]naphthacene	7.00	7.76	7.61

component of the triplet state ($S=1$, $S_z=1$), the triplet will be more stable than the singlet.

Then, if we examine the magnetic shapes obtained by Döhnert *et al.*, we see that they show two characteristics: In a Hückel scheme the highest occupied level is doubly degenerate and occupied by two electrons and the aforementioned alternate graph is such that $m_\uparrow = m_\downarrow + 2$. In our model only the first point is taken into account and all the shapes which present this feature are found to be magnetic. To simplify, one could say that, in our expression of the energy, a term depending on the difference $n_\uparrow - n_\downarrow$ is missing (we will not try to give here a precise form to this term).

In spite of this limit, the Gutzwiller model can be useful for studying a series of shapes with $n_\uparrow = n_\downarrow$. We have already noticed that for six-atom molecules the correct order was obtained; it is also the case for the four eight-atom molecules that we have studied [Table II; Figs. 2(l)–2(n)]. Moreover, the absolute values (in eV) are in a large majority of cases similar to the values of Döhnert *et al.*; for benzene our results agree with the experimental value [3.95 eV (Ref. 18)].

In the second study of the ionization energies we have compared our values to the experimental results for relatively large polyenes (up to $N=34$ carbon atoms). The ionization energy I is given by

$$I = -E_{\mathrm{at}} - E^0 + E^+ ,$$

where E_{at} is the atomic energy of a p electron and E^0 and E^+ are the energies of the ground states of the molecule and the positive ion. We have fixed E_{at} by fitting the ionization potential of benzene to the experimental result. We find, for $\beta=-2.35$ eV and $U=5.5$ eV, that $E_{\mathrm{at}}=9.65$eV and, for $\beta=-1.60$ eV and $U=5.5$ eV that $E_{\mathrm{at}}=9.40$ eV. These E_{at} values are similar to the values used by other authors in their calculations of the properties of polyenes [for instance, $E_{\mathrm{at}}=9.59$ eV (Ref. 19)].

For $N=6$, 10, and 14 we have used the two formulations [formulas (1) and (2)] of the method. When N increases, the relative differences between the two results decrease; as for $N=14$, it is 0.5%, we have only used formula (2) for $N>14$. The results are given in Table III.

We observe that two features of the experimental results are reproduced: First, we obtain the general decrease of the ionization potential when N increases (though the decrease of experimental values is faster), and second, for a given N, we obtain the same relative order for the various shapes studied.

IV. CONCLUSION

These applications of the Gutzwiller technique to various problems show its interest and its limits. As we have seen, in the $m_\uparrow = m_\downarrow$ cases, it can certainly be useful. Moreover, the method, which does not demand long computer times, allows the study of relatively large molecules in good conditions since the method includes intra-atomic correlations. In the study of the ionization potentials the method is easier to apply than Heisenberg-type models[13,14] because in this last case there are many wave functions in the Φ_i^1 basis which are different for the molecule and the ion.

The technique presents another interesting feature. It is possible to relate local charge or spin fluctuations to the number of doubly occupied sites v.[23] As in our calculation v (the variational parameter) is known, we get information on local charge and spin fluctuations. For instance, we know how they vary with U or with the shape; this is information important for polarizability or susceptibility problems.

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