PHYSICAL REVIEW B VOLUME 26, NUMBER 11 1 DECEMBER 1982

Size effect on the stability and the magnetism of small aggregates when electronic correlations are taken into account

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(Received 13 January 1982; revised manuscript received 28 April 1982)

We present some results of the Gutzwiller method adapted to small aggregates. We mainly develop a version of the Gutzwiller method which can be applied to relatively large aggregates (s band; number of atoms N, ~ several hundred). The technique is first used for studying the disappearance of the alternation effect which is presented, for $U=0$, by the electronic energy E_N and the ionization energy I_N of a N-atom cluster, when N varies (when $U=0$ and for one electron per atom, $|\Delta_N|=|E_N-E_{N-1}|$ and I_N are larger for even N). It is shown that for $U \gtrsim 4|\beta|$ the alternation disappears for I_N. We also study the magnetism of small aggregates. One knows that for bulk metals magnetism appears when U is larger than a limit U_{crit}. For aggregates our results show that this limit is lowered.

I. INTRODUCTION

This paper is the third of a series of publications[1,2] which deal with the influence of dielectronic correlations on the electronic structure of small aggregates. Our method is an extension of the Gutzwiller variational treatment usually used for the bulk.[3–8] We will see that its interest is to lead calculation times shorter than those of molecular self-consistent models.[9] One of the consequences of this is that it becomes possible to study relatively large aggregates.

We have first applied it, in Sec. III, to the study of the ionization energies and of the stabilities of clusters with $N=4,5,6,7$ atoms which present, when the electronic correlations are negligible,[10,11] an alternating behavior according to the parity of N.

Then, we have used it, in Sec. IV for the study of magnetic properties of larger aggregates ($N=55$ and 147 atoms). A description of the model is given in Sec. II.

Let us notice that other variational treatments of the correlation effects have been proposed, for instance by Stollhof and Fulde, for the study of some molecules[12–14] and by Olés for bulk metal.[15]

II. DESCRIPTION OF THE MODEL

The study has been limited to identical atom clusters where the valency orbitals are of "s" type. We call $|i\rangle$ or ϕ_i the orbital centered on atom "i" (with spin index the notations become $|i\sigma\rangle$ or $\phi_i\sigma$). These functions are supposed to constitute an orthonormal basis:

$$\langle i\sigma | j\sigma'\rangle = \delta_{ij}\delta_{\sigma\sigma'} .$$

We use the Hubbard Hamiltonian which, with the usual notations, may be written

$$H=\beta\sum_{ij} c_{i\sigma}^{\dagger}c_{j\sigma}+U\sum_{i} n_{i\uparrow}n_{i\downarrow} . \tag{1}$$

β is the hopping integral ($\beta<0$) and U the intra-atomic correlation energy ($U>0$).

The method for calculating total electronic energies E has been described in the preceding papers.[2] For a molecular where the Hückel energy is E^H the result is

$$E(\eta)=Q(\eta)E^H+\chi(\eta)U , \tag{2}$$

where $Q(\eta)$ and $\chi(\eta)$ are two functions of the variational parameter η defined in Ref. 2 for a molecule with N sites, N_e electrons: $N\uparrow$ electrons with spin $\uparrow$, $N\downarrow$ with spin $\downarrow$.

Comparisons with "exact" results are given in Ref. 2 for a case where $N=5$, $N\uparrow=N\downarrow=2$. The agreement is better than 5% for a wide range of $U/|\beta|$ values: $0<U/|\beta|<5$. We have also compared our results with those of Shiba *et al.*[16,17] who made an exact calculation on the linear closed chain molecule with $N=N_e=6$ and various electronic configurations. As these authors, we find that, for any U value, the nonmagnetic configuration $N\uparrow=N\downarrow=3$ is the most stable.

A. Modification of the method: Change of the variational parameter

The calculation of E by using (2) becomes impossible for N and N_e larger than about 100 because $Q(\eta)$ and $\chi(\eta)$ are complex series of factorial terms. So, following Gutzwiller[4] we are led to make another approximation. The examination of the relative values of the terms in the series shows that they can be reduced to their largest term. After this operation, it appears a new variational parameter ν and the energy can be written

$$E(\nu) = Q(\nu)E^H + \nu U \tag{3}$$

with

$$Q(\nu) = \frac{(N\uparrow - \nu)}{N\uparrow(N - N\downarrow)}\left[(N - N\uparrow - N\downarrow + \nu)^{1/2} + \nu^{1/2}\left(\frac{N\downarrow - \nu}{N\uparrow - \nu}\right)^{1/2}\right]^2 . \tag{4}$$

The comparison of results obtained by formula (2) and by the approximate method [formula (3)] shows that the approximate method is better when N (and N_e) is large. For instance in the case of a molecule with $N = 55$ and $N_e \sim N$ the relative difference between the two results is smaller than 0.6% for $U < 10\beta$. However for $N < 10$ the use of formula (2) is preferable.

Let us make a general remark. For large N, in the particular case $N\uparrow = N\downarrow = N/2$ of a paramagnetic band with one electron per atom, by using (3), one obtains

$$\bar{E} = \bar{E}^H + \frac{U}{4} + \frac{U^2}{64\bar{E}^H} , \tag{5}$$

where a bar above a letter means that the quantity is given "per atom."

In the opposite case of $H_2(N = 2, N\uparrow = N\downarrow = 1)$, the development of the exact result for $\bar{E}$ in powers of (U/β) gives

$$\bar{E}(H_2) = \bar{E}^H + \frac{U}{4} + \frac{U^2}{32\bar{E}^H} ,$$

so the stabilizing third term is more important than in (5). This observation has already been made by Friedel[18] who has developed its consequence on the dimerization of solid H_2.

III. STUDY OF THE STABILITY AND OF THE IONIZATION ENERGY

Let us consider small aggregates with N atoms and $N_e = N$ electrons and let us recall a general result of the Hückel ($U = 0$) model, valid for $N \sim 10$: the increase (in absolute value) Δ of electronic energy E when passing from a $N - 1$ atom to a N-atom cluster ($\Delta_N = E_N - E_{N-1}$) is systematically larger when N is even.

The inverse effect arises for "ions" with N sites and $N_e = N - 1$ electrons: $\Delta_N^+ = E_N^+ - E_{N-1}^+$ is larger when N is odd.

Moreover the ionization energy I_N of a "neutral" system ($N_e = N$) is larger for N even. This alternating behavior has been observed experimentally for aggregates composed of elements where, as it is supposed in the Hückel scheme, intra-atomic electronic correlations are likely to be small. For instance the intensities of secondary emission of Cu_N^+, Ag_N^+, Li_N^+ (intensities which are related to the stabilities of the observed species: The larger the stability, the larger the intensity) are larger when N is odd.[10,11] Moreover, the direct measurement of I_N has been made for Na_N clusters and shows an alternating effect.[19]

The question is what occurs to these alternating effects when U increases. To answer this question we have performed calculations with our technique [formula (2)]. We have only considered linear open chains. This choice is justified by the fact that it has already been verified, for $U = 0$, that the study of Δ,

TABLE I. Values of $(\Delta_N - E_{\text{at}})$. $\Delta_N = E_N - E_{N-1}$, where E_N is the electronic energy of an open chain with N atoms and $N_e = N$ electrons. E_N is given by Eq. (2) plus a term $N_e E_{\text{at}}$.

$U(\lvert\beta\rvert$ units)	$\Delta_5(\beta$ units)	$\Delta_6(\beta$ units)	$\Delta_7(\beta$ units)
0	0.99	1.52	1.07
1	0.83	1.21	0.88
5	0.26	0.34	0.28
∞	0	0	0

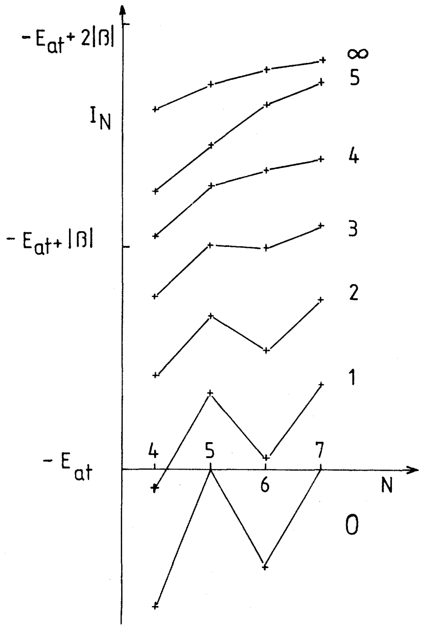

FIG. 1. Values of the ionization energies $I_N = -(E_N - E_N^+)$ of linear open chains. The energies E_N are calculated with formula (2) to which is added $N_e E_{\text{at}}$ (it is why the origin of I_N is $-E_{\text{at}}$). The values of U are given in $|\beta|$ units. The values of E_N for $U = \infty$ are calculated by the exact Nagaoka method (Ref. 22).

TABLE II. Values of the electronic energy E(β units) of a cuboctahedral cluster of $N=55$ atoms with $N_e=N$ for various magnetizations and various U values ($|\beta|$ units). The number of doubly occupied sites, ν_0, is also given.

$N\uparrow,N\downarrow$	U	0	1	4	7	10	13	16
28,27	E	114.87	101.53	66.46	38.80	18.53	5.67	0.20
	ν_0	13.74	12.99	10.52	8.04	5.57	3.09	0.68
29,26	E	114.87	101.57	66.57	38.92	18.65	5.75	0.22
	ν_0	13.71	12.96	10.49	8.09	5.62	3.15	0.68
38,17	E	105.10	93.64	62.86	37.87	19.02	6.53	0.55
	ν_0	11.74	11.22	9.40	7.40	5.29	3.17	0.94

Δ^+, and I for all possible shapes leads to the same results as for linear open chains (for $N\leqslant 5$).

In this study we have introduced in the Hamiltonian (1) a diagonal term:

$$E_{\text{at}}\sum_{i\sigma} c_{i\sigma}^{\dagger}c_{i\sigma} \quad (E_{\text{at}}<0)$$

which does not modify the preceding calculations. Its effect is only to add a term N_eE_{at} in the expression (2) of the energy.

Our results are given in Table I for (Δ_N-E_{at}) (study of the alternations of the stability of neutrals) and in Fig. 1 for I_N. Other results on the alternations of the stability of "ions" are given in Ref. 2.

Table I shows that, when U increases, the alternation of Δ_N disappears ($U=0$: $\Delta_6-\Delta_7\sim 0.5\beta$; $U=-5\beta$: $\Delta_6-\Delta_7\sim 0.05\beta$). Figure 1 shows that, simultaneously, the alternations of I_N disappear. This behavior is consistent with the $U=\infty$ limit calculated by the exact Nagaoka method.[20,21]

IV. SIZE EFFECT ON MAGNETIC PROPERTIES

As we already saw in Sec. II, when N is large enough ($N>10$) one can use formula (3) where the variational parameter is ν. We will limit ourselves to one electron per site ($N_e=N$). The magnetization is defined by $\bar{m}=N\uparrow/N$. In this case, it is possible to obtain E and ν_0, the value of ν for which expression (3) is minimum, as explicit analytic functions of the physical parameters E^H, U, and $\bar{m}$.

Our results for the variations of E with U and $\bar{m}$ are given in Tables II and III. It is interesting to discuss "the appearance of magnetism" by comparing the cases $N=55$ and 147. For instance, the crossing between the state ($N\uparrow=38,N\downarrow=17$, $\bar{m}=0,69$) and the least magnetic state occurs at $U_{\text{crit}}=9|\beta|$ for $N=55$, whereas the crossing between the state ($N\uparrow=102,N\downarrow=45$, which has nearly the same degree of magnetization: $\bar{m}=0,695$) and the least magnetic state occurs at $U_{\text{crit}}=13|\beta|$ for $N=147$.

TABLE III. Values of the electronic energy E(β units) of a cuboctahedral cluster of $N=147$ atoms with $N_e=N$ for various magnetizations and various U values ($|\beta|$ units). The number of doubly occupied sites, ν_0, is also given.

$N\uparrow,N\downarrow$	U	0	1	4	7	10	13	16	17
74,73	E	327.28	291.56	196.81	120.61	62.97	23.91	3.39	0.65
	ν_0	36.75	34.93	28.70	22.41	16.36	10.11	3.87	1.28
76,71	E	327.26	291.57	196.88	120.70	63.07	23.98	3.43	0.67
	ν_0	36.71	34.87	28.63	22.57	16.33	10.09	3.85	1.30
82,65	E	325.88	290.61	196.83	121.19	63.75	24.59	3.72	0.85
	ν_0	36.26	34.44	28.46	22.30	16.32	10.15	4.17	1.99

Let us remark that this decrease of U_{crit} when N decreases can be explained by a kind of Stoner criterion. It is simply due to the fact that the density of state at the center of the band is larger when N decreases because the number of bonds per atom is smaller.

V. CONCLUSION

We have presented in this paper some results obtained by using the Gutzwiller method adapted to small aggregates. First, we have studied the disappearance of the alternating behavior according to the parity of N of the binding energy and of the ionization energy of small molecules with one electron per atom. Our result is that the alternations obtained for $U=0$ are destroyed, but not reversed when U increases.

We also study the effect of size on the appearance of magnetism. Kanamori[22] has shown that, for the bulk, no ferromagnetic configuration can be the stablest for very low filling of the band, and this is so for any U value. The study of the dependence of this critical filling with size appears as an interesting question which can be studied with our model ($N_e \neq N$).

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[1] P. Joyes and S. Ortoli, J. Phys. Chem. Solids 41, 95 (1980).
[2] P. Joyes, Surf. Sci. 106, 272 (1981).
[3] M. C. Gutzwiller, Phys. Rev. 134, A993 (1964).
[4] M. C. Gutzwiller, Phys. Rev. 137, A1726 (1965).
[5] K. A. Chao, J. Phys. C 7, 127 (1974).
[6] J. Friedel and C. M. Sayers, J. Phys. (Paris) 38, 697 (1977).
[7] F. Kajzar and J. Friedel, J. Phys. (Paris) 39, 397 (1978).
[8] W. F. Brinkman and T. M. Rice, Phys. Rev. B 2, 4302 (1970).
[9] J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory* (McGraw-Hill, New York 1970).
[10] P. Joyes, J. Phys. Chem. Solids 32, 126 (1971).
[11] P. Joyes and M. Leleyter, C. R. Acad. Sci. 274B, 751 (1972).
[12] G. Stollhoff and P. Fulde, Z. Phys. B 26, 257 (1977).
[13] G. Stollhoff and P. Fulde, Z. Phys. B 29, 231 (1978).
[14] G. Stollhoff and P. Fulde, J. Chem. Phys. 73, 4548 (1980).
[15] A. M. Olés, Phys. Rev. B 23, 271 (1981).
[16] H. Shiba, Prog. Theor. Phys. 48, 2171 (1972).
[17] H. Shiba and P. A. Pincus, Phys. Rev. B 5, 1966 (1972).
[18] J. Friedel, Physica (Utrecht) (in press).
[19] A. Herrmann, E. Schumacher, and L. Wöste, J. Chem. Phys. 68, 2327 (1978).
[20] P. Joyes, M. Leleyter, P. Lederer, and M. Héritier J. Phys. (Paris) 36, 411 (1975).
[21] Y. Nagaoka, Phys. Rev. 147, 392 (1966).
[22] J. Kanamori, Prog. Theor. Phys. 30, 257 (1963).