

Thermodynamic properties of the Hubbard model for a diatomic molecule AB

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The Hubbard model has been subject of strong interest in the condensed matter community. It is the simplest model for strongly correlated electron systems. The text books of physics are based on applications, under the form of problems, which have exact analytical solutions. Itinerant magnetic system models, for that reason, are rarely considered in text books of statistical mechanics. The students interested in the study of strongly correlated electron systems, normally, feel in the beginning of their studies a great difficulty in understanding the complex correlations of these systems. In this work, we have studied, with a pedagogical approach, the thermodynamic properties of the Hubbard model for a diatomic molecule AB , that is, we consider a case translationally non-invariant. We apply the grand canonical ensemble method for allowing the analysis of a general situation of any average electron number per site. In the applications we consider, in particular, the case in which the average electron number per site is one. The analysis of the thermodynamic properties makes possible to conclude that the diatomic molecule AB of Hubbard exhibits ferrimagnetic behavior. Moreover, the studied system presents a conceptual and mathematical structure accessible to undergraduate students of physics in their last year, and the results show a rich variety of physics phenomena with details that make feasible a deeper comprehension of the quantum mechanisms involved in the thermodynamics properties and of the methods employed to obtain such properties.

Keywords: Hubbard model, diatomic molecule, exact diagonalization, thermodynamic properties.

O modelo de Hubbard tem sido um assunto de grande interesse para os pesquisadores da área de física da matéria condensada. Ele é o modelo mais simples para sistemas de elétrons fortemente correlacionados. Os livros didáticos de física são baseados em aplicações, sob a forma de problemas, que possuem soluções analíticas exatas. Modelos de sistemas magnéticos de elétrons itinerantes, por essa razão, raramente são considerados nos livros didáticos de mecânica estatística. Os estudantes interessados no estudo de sistemas de elétrons fortemente correlacionados, normalmente, sentem no começo de seus estudos uma grande dificuldade em compreender as complexas correlações desses sistemas. Neste trabalho, nós estudamos, de forma didática, as propriedades termodinâmicas do modelo de Hubbard para uma molécula diatômica AB , isto é, nós consideramos um caso translacionalmente invariante. Nós aplicamos o método do ensemble grande canônico para permitir a análise de uma situação geral de qualquer número médio de elétrons por sítio. Nas aplicações nós consideramos, em particular, o caso em que o número médio de elétrons por sítio é um. A análise das propriedades termodinâmicas faz possível concluir que a molécula diatômica AB de Hubbard exibe comportamento ferrimagnético. Além disso, o sistema estudado apresenta uma estrutura matemática e conceitual acessível a estudantes do último ano de graduação em física, e os resultados mostram uma rica variedade de fenômenos físicos com detalhes que fazem possível uma compreensão profunda dos mecanismos quânticos envolvidos nas propriedades termodinâmicas e dos métodos empregados para obter tais propriedades.

Palavras-chave: modelo de Hubbard, molécula diatômica, diagonalização exata, propriedades termodinâmicas.

1. INTRODUÇÃO

The Hubbard model [1] has been subject of strong interest in the Condensed Matter community [2]. It is the simplest model for strongly correlated electron systems [3]. Originally, it was created to describe the effect of correlations for d-electrons in transition metals, leading to collective effects as itinerant magnetism and metal-insulator transition, and has been often used to describe real materials exhibiting these phenomena [4,5]. After some time, beyond the

original applications, it also began to be used to study new phenomena such as heavy fermions and high-Tc superconductivity, among others [4].

The text books of physics, in general, and of statistical mechanics, in particular, are based on applications, under the form of problems, which have exact analytical solutions. Itinerant magnetic system models, for that reason, on the contrary of the localized magnetic system models, are rarely considered in the text books of statistical mechanics. A previous paper [6], of which this may be regarded as a continuation, has presented results of pedagogical exact calculations on thermodynamic properties of the two-atom Hubbard model. There the canonical ensemble method of statistical mechanics was applied. Here, we apply the grand canonical ensemble method for studying a pedagogical general situation of any average electron number per site. In the applications we consider, in particular, the case in which the average electron number per site is one.

We consider the Hubbard Hamiltonian in its simplest form [1],

$$H = -t \sum_{\langle ij \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + \sum_i U_i n_{i\uparrow} n_{i\downarrow} \quad (1)$$

where $c_{j\sigma}^\dagger$, $c_{j\sigma}$ and $n_{j\sigma}$ are the creation, annihilation and number operators for an electron with spin σ at the i th site, respectively. t is the nearest-neighbor hopping amplitude, and U_i is the on-site electron-electron repulsion. The symbol $\langle ij \rangle$ denotes the sum over nearest-neighbor sites. The on-site electron-electron repulsion U_i is usually assumed translationally invariant, namely $U_i = U$, but, in this work, we consider a translationally non-invariant case. Here, we examine a simple system of two different sites ($N_s = 2$) forming a diatomic molecule AB . In this case we denote the sites as $i = a, b$, and the Hamiltonian (1) can be rewritten as

$$H = -t \sum_{\sigma} (c_{a\sigma}^\dagger c_{b\sigma} + c_{b\sigma}^\dagger c_{a\sigma}) + U_a n_{a\uparrow} n_{a\downarrow} + U_b n_{b\uparrow} n_{b\downarrow} \quad (2)$$

As in reference [6], here we calculate exactly several thermodynamic properties of the Hamiltonian (2) using the method of exact analytical diagonalization calculations, but, in this case, with the application of the grand canonical ensemble.

We perform an study of the temperature dependence of the internal energy, specific heat, entropy, magnetic susceptibility, spin-spin correlation functions, besides others quantities, for a wide range of values of the relative magnitudes of the Coulombian repulsions to transfer integral (U_a/t ; U_b/t). We compare our results with those in references [6], [7], and [8], obtained for the translationally invariant two-sites Hubbard model, thus illustrating the effect of the translational non-invariance. It deserve to be detached that, we find that the translationally non-invariant two-sites Hubbard model, that is, our diatomic molecule AB , presents the magnetic moments of the sites with different magnitudes, and exhibits an antiferromagnetic correlation between them. The direct consequence this phenomenon is that the diatomic molecule AB of Hubbard presents a liquid magnetic moment, that is, it exhibits a ferrimagnetic behavior.

As was also detached in reference [6], here, in this case, also, the studied system presents a conceptual and mathematical structure accessible to undergraduate students of physics in their last year, and the results show a rich variety of physics phenomena with details that make feasible a deeper comprehension of the quantum mechanisms involved in the thermodynamics properties and of the methods employed to obtain such properties.

This paper is organized as follows. In Sec. 2 we obtain the energy eigenvalues of the system and we analyze it. In Sec. 3 the quantities that we calculate are defined, and the results are presented. We close with a conclusion in Sec. 4.

2. ENERGY EIGENVALUES

Since we are working in the grand canonical ensemble, all possible number N of electrons in the molecule (from 0 to 4) must be considered. There are four spin orbitals in the system, and each one can be either empty or occupied by an electron, thus, we have altogether $2^4 = 16$ possible eigenstates of the Hamiltonian (2) [9].

For obtaining the eigenstates of the system we use the sixteen basis vectors given in Table I, where S^z is the spin component on the z-direction, and $|0\rangle$ denotes the vacuum state of the molecule without electrons.

Table I. Configurations, basis vectors and spin components S^z of the molecule.

N	Configurations		Basis vectors	S^z
	A	B		
0			$ \phi_1\rangle = 0\rangle$	0
1	↑		$ \phi_2\rangle = c_{a\uparrow}^+ 0\rangle$	1/2
		↑	$ \phi_3\rangle = c_{b\uparrow}^+ 0\rangle$	
	↓		$ \phi_4\rangle = c_{a\downarrow}^+ 0\rangle$	-1/2
		↓	$ \phi_5\rangle = c_{b\downarrow}^+ 0\rangle$	
2	↑	↑	$ \phi_6\rangle = c_{a\uparrow}^+ c_{b\uparrow}^+ 0\rangle$	1
	↓	↓	$ \phi_7\rangle = c_{a\downarrow}^+ c_{b\downarrow}^+ 0\rangle$	
	↑	↓	$ \phi_8\rangle = c_{a\uparrow}^+ c_{b\downarrow}^+ 0\rangle$	0
	↓	↑	$ \phi_9\rangle = c_{a\downarrow}^+ c_{b\uparrow}^+ 0\rangle$	
	↑↓		$ \phi_{10}\rangle = c_{a\uparrow}^+ c_{a\downarrow}^+ 0\rangle$	
		↑↓	$ \phi_{11}\rangle = c_{b\uparrow}^+ c_{b\downarrow}^+ 0\rangle$	
3	↑↓	↑	$ \phi_{12}\rangle = c_{a\uparrow}^+ c_{a\downarrow}^+ c_{b\uparrow}^+ 0\rangle$	1/2
	↑	↑↓	$ \phi_{13}\rangle = c_{a\uparrow}^+ c_{b\uparrow}^+ c_{b\downarrow}^+ 0\rangle$	
	↑↓	↓	$ \phi_{14}\rangle = c_{a\uparrow}^+ c_{a\downarrow}^+ c_{b\downarrow}^+ 0\rangle$	-1/2
	↓	↑↓	$ \phi_{15}\rangle = c_{a\downarrow}^+ c_{b\uparrow}^+ c_{b\downarrow}^+ 0\rangle$	
4	↑↓	↑↓	$ \phi_{16}\rangle = c_{a\uparrow}^+ c_{a\downarrow}^+ c_{b\uparrow}^+ c_{b\downarrow}^+ 0\rangle$	0

Since the number N of electrons is conserved, and $0 \leq N \leq 4$, for a given N there are $[4!/N!(4-N)!]$ eigenstates. The spin degree of freedom is also conserved by Hamiltonian (2). Thus, these eigenstates can be classified according to their number of electrons and spin [9].

Table II. Energy eigenvalues of the molecule.

N	Eigenvalues	S^z
0	$E_1 = 0$	0
1	$E_{2,4} = t$	$\pm 1/2$
	$E_{3,5} = -t$	$\pm 1/2$
2	$E_{6,7} = 0$	± 1
	$E_8 = 0$	0
	E_9, E_{10}, E_{11} are the roots of $\begin{vmatrix} \kappa - E & 0 & \tau \\ 0 & -E & -2t \\ \tau & -2t & \kappa - E \end{vmatrix} = 0$	
3	$E_{12,14} = \sqrt{t^2 + \tau^2} + \kappa$	$\pm 1/2$
	$E_{13,15} = -\sqrt{t^2 + \tau^2} + \kappa$	$\pm 1/2$
4	$E_{16} = 2\kappa$	0

Separately, for each one of the groups of basis vectors identified by different pairs (N, S^z) , we use a linear combinations of the basis vectors, $|\psi_v\rangle = \sum_n a_n |\varphi_n\rangle$, and, following the same procedure used in reference [6], we get the 16 eigenvalues of the energy given in Table II, where $\kappa = (U_a + U_b)/2$ and $\tau = (U_a - U_b)/2$. The coefficients a_n of the expansion above can be evaluated from the normalization conditions [10].

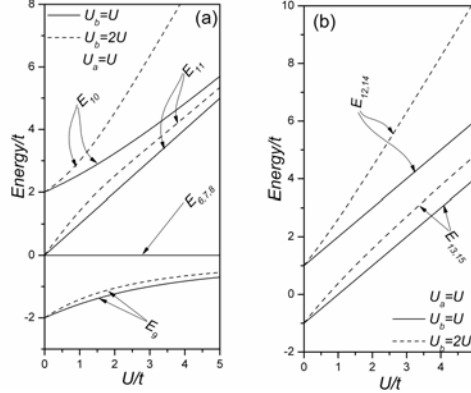


Figure 1. Eigenvalues of the energy versus U/t for (a) $N = 2$ and (b) $N = 3$.

The eigenvalues of the energy for $N = 0$ and 1 are independent of U_a and U_b , but some eigenvalues for $N = 2, 3$, and 4, that is, the energies $E_9, E_{10}, \dots, E_{16}$, are dependent of U_a and U_b . Figure 1 shows the interaction dependence of the eigenvalues of the energy for $N = 2$ and 3, in two cases: (i) $U_a = U_b = U$, and (ii) $U_a = U$ and $U_b = 2U$. In both cases the eigenvalues $E_9, E_{10}, \dots, E_{15}$ increase when U/t increases, but, when $U_a \neq U_b$ the increase of these eigenvalues with U/t is more rapid than in the case $U_a = U_b$. The ground states for $N = 1$ and 3 present $S^z = \pm 1/2$, while for $N = 0, 2$, and 4, present $S^z = 0$.

3. THERMODYNAMIC PROPERTIES

The partition function from which all thermodynamic functions are obtained is given by.

$$Z(\beta, \mu) = \sum_{v=1}^{16} \exp[-\beta(E_v - \mu N_v)], \quad (3)$$

where E_v denote the sixteen eigenvalues of Hamiltonian (2), N_v are the correspondent numbers of electrons in the eigenstates given in the Table II, $\beta = 1/k_B T$, and μ is the chemical potential.

AVERAGE NUMBER OF ELECTRONS

The average number of electrons per site $\langle n \rangle$ is determined by

$$\langle n \rangle = \frac{1}{Ns\beta} \frac{\partial}{\partial \mu} \ln Z(\beta, \mu) = \frac{1}{Ns} \sum_v \frac{N_v \exp[-\beta(E_v - \mu N_v)]}{Z(\beta, \mu)}, \quad (4)$$

For a half-filled band, that is, for $\langle n \rangle = 1$, and $U_a = U_b = U$, $\mu = U/2$ independent of temperature [8, 11, 12], but in the general case, $U_a \neq U_b$, μ must be determined by imposing $\langle n \rangle = 1$ in Eq. (4).

For investigating the effect of the translational non-invariance in our molecule, a relevant quantity is the average number of electrons at each site, which we denote by $\langle n_a \rangle$ and $\langle n_b \rangle$.

The derivation of these physical quantities requires the use of auxiliary fields in the Hamiltonian. Thus, we rewrite the Hamiltonian of the system as

$$\bar{H} = H - \xi_a n_a - \xi_b n_b, \quad (5)$$

where H is the Hamiltonian (2), ξ_a and ξ_b are auxiliary fields, and the number operators n_a and n_b are defined by

$$n_i = n_{i\uparrow} + n_{i\downarrow}, \quad i = a, b. \quad (6)$$

Following, again, the standard procedure, we get the news 16 eigenvalues of the energy that are given in Table III, where $\kappa = (U_a + U_b)/2$, $\tau = (U_a - U_b)/2$, $\alpha = \xi_a + \xi_b$, and $\gamma = \xi_a - \xi_b$.

The inclusion of the auxiliary fields permits to determine $\langle n_a \rangle$ and $\langle n_b \rangle$ by

$$\langle n_i \rangle = \frac{1}{\beta} \frac{\partial}{\partial \xi_i} \ln Z(\beta, \mu, \xi_a, \xi_b) \Big|_{\xi_a, \xi_b=0}, \quad (7)$$

Table III. Eigenvalues of the Hamiltonian (5).

N	Eigenvalues	S^z
0	$E_1 = 0$	0
1	$E_{2,4} = \frac{1}{2}(\sqrt{\gamma^2 + 4t^2} - \alpha)$	$\pm 1/2$
	$E_{3,5} = -\frac{1}{2}(\sqrt{\gamma^2 + 4t^2} + \alpha)$	$\pm 1/2$
2	$E_{6,7} = -\alpha$	± 1
	$E_8 = -\alpha$	0
	E_9, E_{10}, E_{11} are the roots of $\begin{vmatrix} \kappa - \alpha - E & 0 & \tau - \gamma \\ 0 & -\alpha - E & -2t \\ \tau - \gamma & -2t & \kappa - \alpha - E \end{vmatrix} = 0$	
3	$E_{12,14} = (\kappa - 3\alpha/2) + \sqrt{t^2 + (\tau - \gamma/2)^2}$	$\pm 1/2$
	$E_{13,15} = (\kappa - 3\alpha/2) - \sqrt{t^2 + (\tau - \gamma/2)^2}$	$\pm 1/2$
4	$E_{16} = 2(\kappa - \alpha)$	0

There $Z(\beta, \mu, \xi_a, \xi_b)$ is the partition function obtained as in (3), but with the eigenvalues of the Hamiltonian (5). Naturally,

$$Z(\beta, \mu, 0, 0) = Z(\beta, \mu). \quad (8)$$

Figure 2 shows examples of the behavior of the average number of electrons at each site versus $k_B T/t$. The curves presented for three distinct pairs of values of the relative magnitudes of the Coulombian repulsions to transfer integral (U_a/t ; U_b/t). As in all presented cases $U_a > U_b$, the occurrence of double occupancy at site a is disfavored in comparison with the one of the site b . Thus, $\langle n_b \rangle > \langle n_a \rangle$ at all temperatures. Note that $n = (\langle n_a \rangle + \langle n_b \rangle)/2 = 1$.

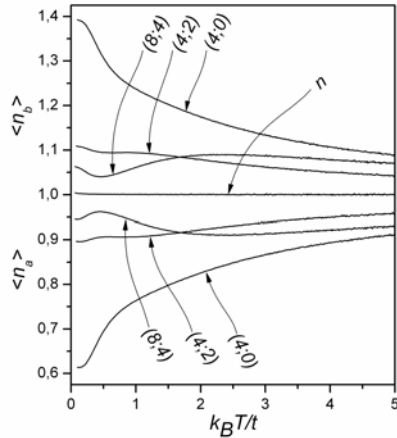


Figure 2. Average number of electrons at each site versus $k_B T/t$. The numbers labeling the curves refer to the values of $(U_a/t; U_b/t)$.

AVERAGE NUMBER OF DOUBLY OCCUPIED SITES

The average number of doubly occupied sites D is, also, an important quantity in the study of strongly correlated electron systems. It is defined by

$$D = \frac{1}{Ns} \sum_i \langle n_{i\uparrow} n_{i\downarrow} \rangle = \frac{1}{2} (D_a + D_b), \quad (9)$$

where

$$D_i = \langle n_{i\uparrow} n_{i\downarrow} \rangle = -\frac{1}{\beta} \frac{\partial}{\partial U_i} \ln Z(\beta, \mu), \quad (10)$$

is the average number of double occupation of electrons at site i .

As much as the average number of electrons at each site $\langle n_i \rangle$, D_i is important for investigate the effect of the translational non-invariance in a molecule AB .

In the limit of $U_a = U_b = 0$, $D = 1/4$. In this case, the four possible configurations of occupation of each site are equally probable and the double occupation is only one between four possibilities. However, for a molecule AB , with $U_a > U_b$, the probability of the different configurations of occupation are not equal at each site. In this case, the double occupation at site a is less probable than at site b . In the limit of $U_b = 0$, any value of U_a , with $U_a > U_b$, makes the configuration with double occupation more probable at site b and thus, $D_b > 1/4$. In Fig. 3 (b), on the curve for (4;0), D_b exceeds the value $1/4$.

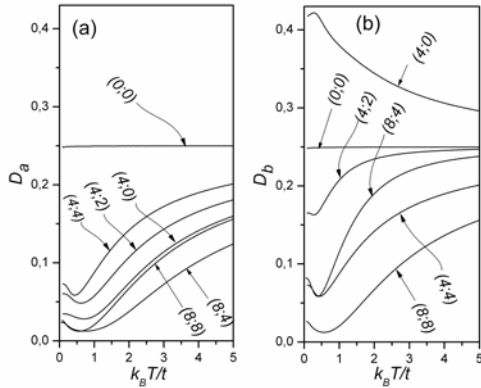


Figure 3. Average number of double occupation of electrons at each site versus $k_B T/t$. (a) At site a and (b) at site b. The numbers labeling the curves refer to the values of $(U_a/t; U_b/t)$.

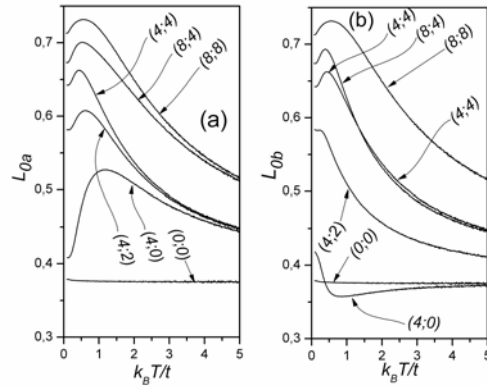


Figure 4. Magnitude of spin at each site versus $k_B T/t$. (a) At site a and (b) at site b. The numbers labeling the curves refer to the values of $(U_a/t; U_b/t)$.

MAGNITUDE OF AT EACH SITE

In order to obtaining information about the temperature dependence of the magnitude of spin at each site we determine the functions L_{0a} and L_{0b} .

$$L_{0i} = \langle \mathbf{S}_i^2 \rangle = 3 \langle (S_i^z)^2 \rangle, \quad i = a, b. \quad (11)$$

\mathbf{S}_i and S_i^z are, respectively, the spin operator and the spin component on the z-direction operator at site i . As

$$S_i^z = \frac{1}{2} (n_{i\uparrow} - n_{i\downarrow}), \quad (12)$$

then, using the Eqs. (6) and (10) we can rewrite Eq. (11) as

$$L_{0i} = \frac{3}{4} n_i - \frac{3}{2} D_i. \quad (13)$$

Two typical values of L_{0i} can occur: (i) $U_a = U_b = 0$, that causes $n_i = 1$ and $D_i = 1/4$, consequently $L_{0i} = 3/8$; (ii) $U_a = U_b = \infty$, that produces $n_i = 1$ and $D_i = 0$, then $L_{0i} = 3/4$. Figure 4 shows curves of L_{0a} and L_{0b} versus $k_B T/t$. It is observed that when $U_a > U_b$ occurs, $L_{0a} > L_{0b}$. This fact is consistent with the observed behavior of n_i (Fig. 2) and D_i (Fig. 3), where, $n_a < 1$, $n_b > 1$, and $D_a < D_b$.

SPIN CORRELATION ON SITES

In order to completing information about the magnetic structure of the diatomic molecule we determine the temperature dependence of the spin correlation function L_1 , defined by

$$L_1 = \frac{1}{2} \langle \mathbf{S}_a \cdot \mathbf{S}_b \rangle, \tag{14}$$

where \mathbf{S}_a (\mathbf{S}_b) is the spin operator at the site a (b).

The derivation this physical quantity requires, also, the use of an auxiliary field in the Hamiltonian. Thus, we rewrite the Hamiltonian of the system as

$$\tilde{H} = H - \lambda \mathbf{S}_a \cdot \mathbf{S}_b, \tag{15}$$

where H is the Hamiltonian (2) and λ is an auxiliary field.

The product $\mathbf{S}_a \cdot \mathbf{S}_b$ can be write as

$$\mathbf{S}_a \cdot \mathbf{S}_b = S_a^x S_b^x + S_a^y S_b^y + S_a^z S_b^z = \frac{1}{2} (S_a^+ S_b^- + S_a^- S_b^+) + S_a^z S_b^z. \tag{16}$$

Expressing the raising and lowering spin operators in terms of creation and annihilation operators,

$$\begin{aligned} S_i^+ &= c_{i\uparrow}^+ c_{i\downarrow} \\ S_i^- &= c_{i\downarrow}^+ c_{i\uparrow} \end{aligned} \tag{17}$$

and using (12), Eq. (16) can be rewritten as

$$\mathbf{S}_a \cdot \mathbf{S}_b = \frac{1}{2} (c_{a\uparrow}^+ c_{a\downarrow} c_{b\downarrow}^+ c_{b\uparrow} + c_{a\downarrow}^+ c_{a\uparrow} c_{b\uparrow}^+ c_{b\downarrow}) + \frac{1}{4} (n_{a\uparrow} n_{b\uparrow} + n_{a\downarrow} n_{b\downarrow} - n_{a\uparrow} n_{b\downarrow} - n_{a\downarrow} n_{b\uparrow}) \tag{18}$$

Following, again, the standard procedure, we get the new 16 energy eigenvalues that are given in Table IV.

Table IV. Eigenvalues of the Hamiltonian (14).

N	Eigenvalues	S^z
0	$E_1 = 0$	0
1	$E_{2,4} = t$	$\pm 1/2$
	$E_{3,5} = -t$	$\pm 1/2$
2	$E_{6,7} = -\lambda/4$	± 1
	$E_8 = -\lambda/4$	0
	E_9, E_{10}, E_{11} are the roots of $\begin{vmatrix} \kappa - E & 0 & \tau \\ 0 & \frac{3}{4}\lambda - E & -2t \\ \tau & -2t & \kappa - E \end{vmatrix} = 0$	
3	$E_{12,14} = \sqrt{t^2 + \tau^2} + \kappa$	$\pm 1/2$
	$E_{13,15} = -\sqrt{t^2 + \tau^2} + \kappa$	$\pm 1/2$
4	$E_{16} = 2\kappa$	0

The inclusion of the auxiliary field permits L_1 to be determined by

$$L_1 = \frac{1}{2\beta} \frac{\partial}{\partial \lambda} \ln Z(\beta, \mu, \lambda) \Big|_{\lambda=0}, \quad (19)$$

where $Z(\beta, \mu, \lambda)$ is the partition function obtained as in (3), but with the eigenvalues of the Hamiltonian (15). Naturally,

$$Z(\beta, \mu, 0) = Z(\beta, \mu). \quad (20)$$

Figure 5 shows the temperature dependence of L_1 for some typical values of $(U_d/t; U_b/t)$. The temperature dependence with negative sign of L_1 demonstrates how far the antiparallel ordering of the magnetic moments on different sites persist when the temperature is raised.

The analysis of Figures 4 and 5 makes possible the constructing of a physical picture as follows: the magnetic moments of the sites have different magnitudes, and exhibit an antiferromagnetic correlation between them. The direct consequence of this phenomenon is that the diatomic molecule AB of Hubbard presents a liquid magnetic moment, that is, it exhibits a ferrimagnetic behavior.

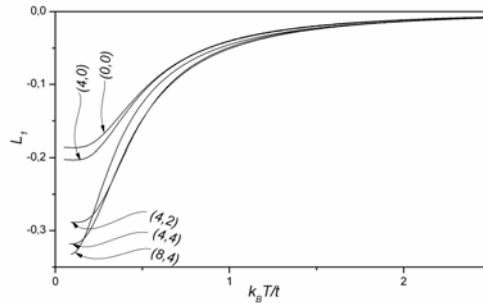


Figure 5. Spin correlation on different sites L_1 versus $k_B T/t$. The numbers labeling the curves refer to the values of $(U_d/t; U_b/t)$.

INTERNAL ENERGY, SPECIFIC HEAT, ENTROPY AND MAGNETIC SUSCEPTIBILITY

The internal energy per site u is determined by

$$u = \frac{1}{N_S} \sum_v \frac{E_v \exp[-\beta(E_v - \mu N_v)]}{Z(\beta, \mu)}. \quad (21)$$

The specific heat c can be calculated by

$$c = \frac{\partial u}{\partial T}. \quad (22)$$

The entropy per site s can be obtained from grand potential thermodynamic per site Ω ,

$$\Omega = u - Ts - \mu n = -\frac{1}{N_S} k_B T \ln Z(\beta, \mu), \quad (23)$$

or,

$$s = \frac{1}{N_S} k_B \ln Z(\beta, \mu) + \frac{1}{T} (u - \mu n). \quad (24)$$

Finally, the magnetic susceptibility χ per site can be calculated by

$$\chi = \frac{1}{N_S} \beta g^2 \mu_B^2 \left(\langle (S^z)^2 \rangle - \langle S^z \rangle^2 \right), \quad (25)$$

where μ_B is the Bohr magneton, g is the gyromagnetic factor, and

$$\langle (S^z)^\alpha \rangle = \sum_v \frac{(S_v^z)^\alpha \exp[-\beta(E_v - \mu N_v)]}{Z(\beta, \mu)}, \quad \alpha = 1, 2. \quad (26)$$

Figures from 6 to 9 show the temperature dependences of the internal energy, specific heat, entropy and magnetic susceptibility.

The internal energy presents, normally, as expected, larger values when the Coulomb repulsion is more intense. Some small variations of this behavior are explained as due to changes in magnetic ordering when the temperature is raised.

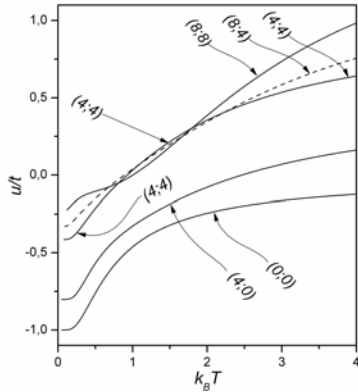


Figure 6. Internal energy per site versus $k_B T/t$. The numbers labeling the curves refer to the values of $(U_a/t; U_b/t)$.

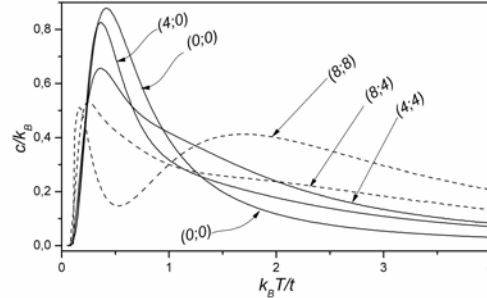


Figure 7. Specific heat versus temperature. The numbers labeling the curves refer to the values of $(U_a/t; U_b/t)$.

The behavior of the specific heat with the temperature elucidates the non-monotonic variation of the internal energy with the Coulomb repulsion. Comparing the curves of c vs. T with each other one can notice that the specific heat has a peak at a slightly lower temperature than t/k_B when the magnitude of U_i is small, while when U_i is increased, the peak splits in two. The low-temperature peak arises from the antiferromagnetic ordering and the high-temperature peak comes from the gradual formation of local moments [7].

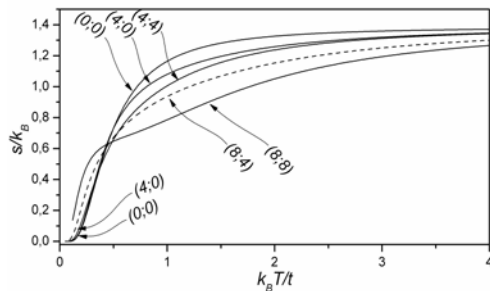


Figure 8. Entropy per site versus temperature. The numbers labeling the curves refer to the values of $(U_a/t; U_b/t)$.

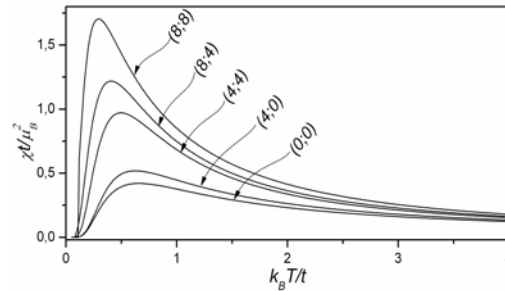


Figure 9. Magnetic susceptibility per site versus $k_B T/t$. The numbers labeling the curves refer to the values of $(U_a/t; U_b/t)$.

Figure 8 shows curves of the entropy versus temperature for the same values of $(U_a/t; U_b/t)$ as before. The general behavior follows what is expected. When the temperature is raised all curves tend to $k_B \ln 4$ which is the maximum value of the entropy per site. The change of curvature when U_i is increased, how explained before, corresponds to changes in magnetic ordering.

All curves of the magnetic susceptibility versus temperature present a peak at the same temperature in which the specific heat presents the low-temperature peak and, naturally, it also arises from the antiferromagnetic ordering.

4. CONCLUSIONS

We have studied, with a pedagogical approach, the thermodynamic properties of the Hubbard model for a diatomic molecule AB , that is, we consider a translationally non-invariant case. We apply the grand canonical ensemble method for allowing the analysis of a general

situation of any average electron number per site. In the applications we consider, in particular, the case in which the average electron number per site is one.

The analysis of the average number of electrons at each site, of the average number of doubly occupied sites, of the magnitude of spin at each site and the spin correlation on different sites makes possible the constructing of a physical picture as follows: the magnetic moments of the sites have different magnitudes, and exhibit an antiferromagnetic correlation between them. The direct consequence of this phenomenon is that the diatomic molecule AB of Hubbard presents a liquid magnetic moment, that is, it exhibits a ferrimagnetic behavior.

The studied system presents a conceptual and mathematical structure accessible to undergraduate students of physics in their last year, and the results show a rich variety of physics phenomena with details that make feasible a deeper comprehension of the quantum mechanisms involved in the thermodynamics properties and of the methods employed to obtain such properties.

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