Influence of correlated electrons on the paramagnetism of DNA

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We address the fundamental role of electronic and vibrational interactions on the magnetization of the homogeneous and randomly sequenced DNA. We find several important magnetic properties of DNA: the intrastrand electron-electron interaction enhances magnetization, while the interstrand interaction suppresses it. Renormalization of the hopping integrals due to electron-vibration interactions results in a paramagnetic to diamagnetic transition as a function of temperature. The influence of interelectron interactions is therefore to transform the diamagnetic system into a paramagnetic one while the temperature can reverse that behavior. Being entirely intrinsic, these properties would not be influenced by the environment.

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I. INTRODUCTION

Magnetization of disordered systems and disordered mesoscopic rings, in particular, has been studied extensively during the past few decades. In these systems, magnetization is determined by the closed trajectories, where a magnetic flux passing through the loop will influence the electron dynamics along the trajectory. Both disorder and interelectron interactions are known to play an important role in the magnetic properties of the electron systems.[1–4] In a quantum ring the repulsive on-site Hubbard interaction gives a paramagnetic contribution to the magnetization, while the nearest-neighbor interaction results in a diamagnetic contribution.[4] In a two-dimensional tight-binding model of the electronic system, both the paramagnetic and diamagnetic behaviors have been reported.[1–3] In this context, the DNA molecule is an unique system to study magnetism in nanostructures. It has a helix structure and consists of two base pairs: guanine (G) cytosine (C) and adenine (A) thymine (T). The low-energy properties of DNA can be described by a double-stranded model.[5,6] In poly-DNA, the two strands correspond to highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of the base pairs, and the model takes into account both the interstrand and intrastrand electron hoppings. The hopping integrals correspond to the overlap between the HOMO and LUMO orbitals of the nearest base pairs within DNA. The value of the hopping integral depends on the type of the base pair. As a result, the properties of DNA can be controlled by building it with a special sequence of base pairs. One such property that is strongly affected by the actual DNA sequence, as shown below, is the magnetic susceptibility. Therefore, DNA is truly a novel system to study the magnetic properties of low-dimensional structures.

Recently, Nakamae *et al.*[7] reported a noninvasive probe of the intrinsic electronic properties of DNA. Their low-temperature experiments uncovered some unusual magnetic properties under different experimental conditions.[7] For example, it was found that the genomic-length λ-DNA molecule in the B form[8] (wet DNA) at low temperatures ($T \leq 20$ K) is paramagnetic, while at higher temperatures it becomes diamagnetic. The DNA molecule in the A form (dry DNA) remains diamagnetic at all temperatures.[9] There are various issues related to those observations that are yet to be resolved. The role of electron-electron interactions needs to be understood since in A and B forms of DNA, the interaction potentials differ by almost 0.5 eV.[10] Here we report on some important effects of the electron-electron interaction on the magnetization of DNA. Additionally, we introduce the electron-vibration interaction, which modifies the intrastrand hopping integrals and is crucial for the temperature dependence of DNA magnetization. We show below that a combination of the interelectron and the electron-vibration interactions can in fact explain the magnetic behavior observed in Ref. 7.

This paper is organized as follows. In Sec. II, we introduce our model for DNA and discuss how we incorporate the electron-vibration interactions in this model. In Sec. III, we discuss the results on the effects of electron-electron and electron-vibration interactions on magnetization of homogeneously sequenced DNA. We then consider also the case of a random DNA sequence in Sec. III. We close with conclusions and a brief discussion on the possible significance of this work in future nanodevices.

II. DOUBLE-STRANDED MODEL FOR DNA IN A MAGNETIC FIELD

We consider a double-stranded tight-binding model,[5,11] which includes the interstrand and intrastrand hoppings and the electron-electron and the electron-vibration interactions. We focus on the homogeneous DNA sequence, which can either be a poly(dG)-poly(dC) or poly(dA)-poly(dT) DNA. Based on the results of these systems, we also estimate the magnetic susceptibility of a generic DNA. In what follows, we assume that all HOMO states are fully occupied while all the LUMO states are empty. The Hamiltonian of our model consists of the tight-binding Hamiltonian $\mathcal{H}_t$, the electron-electron interaction term $\mathcal{H}_{ee}$, the vibration Hamiltonian, and the electron-vibration interaction Hamiltonian. The tight-binding Hamiltonian has the following form:

$$\mathcal{H}_t = \sum_{i,K,\sigma} \epsilon_K n_{K,i,\sigma} + \sum_{i,K,\sigma} t_K a^\dagger_{K,i,\sigma} a_{K,i+1,\sigma} + \sum_{i,\sigma} t_\perp a^\dagger_{H,i,\sigma} a_{L,i,\sigma} + \text{H.c.}, \quad (1)$$

where $K=H$ and L, and $a_{H,i,\sigma}$ and $a_{L,i,\sigma}$ are the annihilation

operators of an electron with spin $\sigma=\pm 1$ on site i at the HUMO and LUMO strands, respectively. ϵ_H and ϵ_L are the corresponding on-site energies, $n_{K,i,\sigma}=a^{\dagger}_{K,i,\sigma}a_{K,i,\sigma}$, t_H and t_L are intrastrand hopping integrals between the nearest base pairs (sites), and $t_\perp$ is the interstrand hopping integral. We considered only the direct Hartree interactions between the nearest neighbors and introduce the corresponding interaction potentials,[12]

$$\mathcal{H}_{\rm ee}=\sum_{i,K,\sigma}V_{K,0}n_{K,i,\sigma}n_{K,i,-\sigma}+\sum_{i,K,\sigma,\sigma_1}[V_{K,1}n_{K,i,\sigma}n_{K,i+1,\sigma_1}+V_{\rm HL}n_{H,i,\sigma}n_{L,i,\sigma_1}]. \quad (2)$$

We introduce the magnetic field through the Peierls substitution,[13] which modifies the hopping integral between the two sites i and j as

$$t_{ij}\rightarrow t_{ij}\exp\left[i(2\pi/\Phi_0)\int_i^j\vec{A}(\vec{r})d\vec{r}\right],$$

where $\vec{A}$ is the vector potential, $\vec{B}=\nabla\times\vec{A}$ is the magnetic field, and Φ_0 is the magnetic-flux quantum. The magnetic field is orthogonal to the DNA helix axis and we choose the vector potential in the Landau gauge and assume it to be orthogonal to the DNA helix axis. The magnetic field then affects only the interstrand hopping integral, which depends on the base-pair index. Taking into account the helix structure of DNA we present the interstrand hopping integral as[14,15]

$$t_{\perp,i}(H)=t_\perp\exp[2i\pi f\Theta_i].$$

Here $f=adB/\Phi_0$ is the magnetic flux in units of the flux quantum through the untwisted plaquette of size $a=0.34$ nm (base-pair spacing) and $d=1$ nm (DNA radius); $\Theta_i=\Sigma_{j=1}^{i-1}\cos(\theta_0 j)+\frac{1}{2}\cos(\theta_0 i)$, where $\theta_0=36^\circ$ is the equilibrium twist angle of the bases. As the interaction Hamiltonian (2) contains only the Hartree terms the magnetic field does not alter the interaction potentials.

We did not take into account the Zeeman splitting of the energy levels due to electron spin. At experimental values of the magnetic field the Zeeman splitting is small (less than 1 meV). Therefore both electron-spin levels will be occupied and the corrections to magnetization due to electron spin are exponentially small even at room temperature.

The low-frequency vibrations introduce a low-energy scale into the problem, which can result in a low-temperature dependence of DNA magnetization. The coupling of electron and vibration dynamics is introduced through the electron-vibration interaction, which can modify both the on-site energy[16] and the hopping integral in Eq. (1).[17,18] Since magnetization of DNA is more sensitive to the hopping integral than to the on-site energy, we consider below only the effect of the vibrations on the intrastrand hopping integrals. Due to the bosonic nature of the vibrations it is very difficult to consider a coupled electron-vibration dynamics exactly especially for a many-electron system. Therefore we introduce the following simplifications into the problem. We consider the twist angles, θ_i, between adjacent base pairs of the DNA molecule as the vibration variables. Here θ_i is the twist angle between ith and $(i+1)$ base pairs. We assume that the twist angles, θ_i, are independent variables and their dynamics is described by the semiclassical Hamiltonian $\mathcal{H}_{ph}(\theta_i)$. Therefore, at a finite temperature we consider the deviations of the twist angles from the equilibrium value, $\delta\theta_i$, as independent random variables, which are characterized by a Gaussian probability distribution function,

$$P(\delta\theta_i)=\frac{1}{\Delta(T)\sqrt{2\pi}}\exp[-\delta\theta_i^2/2\Delta(T)^2] \quad (3)$$

with the standard deviation $\Delta(T)=\sqrt{\beta T}$. We choose the coefficient β to be $(8^\circ)^2/(300\ \mathrm{K})$, which corresponds to a twist angle of 8° at room temperature.[19]

To incorporate the electron-vibration interaction we introduce the dependence of the interstrand hopping integrals at each base pair i on the deviations of the twist angle from the equilibrium values[20] $t_H(\delta\theta_i)$ and $t_L(\delta\theta_i)$. We assume that at low temperatures the hopping integrals have linear dependence on $\delta\theta_i$,[19]

$$t_H(\delta\theta_i)=t_H+\gamma_H\delta\theta_i, \quad (4)$$

$$t_L(\delta\theta_i)=t_L+\gamma_L\delta\theta_i. \quad (5)$$

The slope in this dependence has the following values:[19] $\gamma_H\approx-0.01$ eV/deg and $\gamma_L\approx 0.0075$ eV/deg for the poly(G)-poly(C) DNA, and $\gamma_H\approx-0.008$ eV/deg and $\gamma_L\approx 0.0075$ eV/deg for the poly(A)-poly(T) DNA.

To describe the complete electron-vibration system we separate the electron and vibration dynamics assuming that the motion of the base pairs, i.e., the vibration dynamics, is much slower than the motion of the electrons. It means that for given values of the variables $\delta\theta_i$ we can calculate the electronic states and find the energy spectra of the electronic system $E_n(\delta\theta_1,\delta\theta_2,\ldots)$, where the variables $\delta\theta_i$ should be considered as parameters in this expression. As we mentioned above, at finite temperature the variables $\delta\theta_i$ are the random variables that are described by the probability distribution function (3). Then the energy of the electron system should be averaged over the random variables $\delta\theta_i$.

We therefore describe the electron-vibration system as a two-stranded electron model with nondiagonal dynamical disorder. The strength of disorder depends on the temperature. Within this model we calculate the average magnetization.

III. MAGNETIC PROPERTIES OF DNA: RESULTS

A. Effect of interelectron interaction

We first disregard the electron-vibration interaction and study the effect of interelectron interaction on the magnetic properties of DNA.

In a noninteracting electron system, if all the hopping integrals are much smaller than the HOMO-LUMO gap ($E_{\rm HL}=\epsilon_L-\epsilon_H$) then from the standard perturbation theory, the susceptibility is proportional to $t_H t_L t_\perp^2$.[14,15] Therefore, whether the DNA molecule is paramagnetic or diamagnetic is determined by the sign of the product $t_H t_L$. If t_H and t_L have the same sign then DNA is paramagnetic, while if t_H

TABLE I. Parameters for the hopping Hamiltonian (1) (Ref. 21) and the interaction Hamiltonian (2) (Ref. 22). All energies are in units of meV.

	ϵ_H	ϵ_L	t_H	t_L	$t_\perp$
GC	−4278	−1065	−115	−61	63
AT	−5245	−931	21	−23	34
	V_{H0}	V_{L0}	V_{H1}	V_{L1}	V_{HL}
GC	5879	5227	1844	2455	2.7×10^3
AT	5681	5270	1625	2378	2.6×10^3

and t_L have opposite signs, it is diamagnetic. In what follows, we used the parameters of the two-stranded DNA model from Ref. 21 (Table I). Obviously, if we ignore the electron-electron interactions, poly(G)-poly(C) DNA is always paramagnetic while poly(A)-poly(T) DNA is diamagnetic.[23]

We then ask the question: Can the interelectron interaction change the sign of susceptibility, i.e., transform the paramagnetic system into a diamagnetic one and vice versa? To answer that, we have studied numerically a finite-size system: It has 6 base pairs and 12 electrons, and hence all the HOMO states are occupied by electrons. The system is then described by the Hamiltonian $\mathcal{H}_t+\mathcal{H}_{\mathrm{ee}}$ with the values of all the parameters summarized in Table I. With these parameters we calculate a few lowest eigenvalues E_i of the finite Hamiltonian matrix by the Arnoldi-Lanczos method. At a given temperature the free energy of the system is derived from the expression $F=-k_BT\ln[\Sigma_i\exp(-E_i/k_BT)]$. We then calculate the magnetization of DNA, $M(B)=-\partial F(B,T)/\partial B$, and the susceptibility $\chi=\partial M(B)/\partial B$.

The electron-electron interactions modify the energy spectrum of DNA molecule compared to a single-electron tight-binding model. We have found that the presence of the interelectron interaction enhances the HOMO and LUMO bandwidths by ~10%–15%, while it suppresses the HOMO-LUMO gap by 20%. These values are within the range of *ab initio* calculations of the energy spectra of the DNA molecule. Since there are many parameters, which determine the final energy spectra of the many-electron system, we did not try to adjust the parameters of single-electron tight-binding Hamiltonian to obtain the electron energy spectra of DNA molecule in complete consistency with *ab initio* calculations.[24]

We vary one of the parameters in Eq. (2) while keeping the other parameters fixed. The variation of the interaction parameters is done through the coefficient $\alpha\leq1$. The susceptibility is weakly dependent on the interaction strength between the LUMO states, i.e., $V_{L,0}$ and $V_{L,1}$. This is due to a large HOMO-LUMO gap, and hence the mixture between the HOMO and LUMO states is small. Magnetization however depends strongly on $V_{H,0}$, $V_{H,1}$, and V_{HL} (Fig. 1). The sign of susceptibility is not affected by the interaction. It is entirely determined by the relative signs of the hopping integrals t_H and t_L. Therefore, poly(G)-poly(C) DNA is paramagnetic for all values of the interaction strength while poly(A)-poly(T) is diamagnetic.

Another specific feature of the interaction is that the parameters $V_{H,0}$, $V_{H,1}$, and V_{HL} have different qualitative effects on the magnitude of the susceptibility. The on-site interaction (Hubbard interaction), $V_{H,0}$, enhances the magnetic properties. For both paramagnetic [Fig. 1(a)] and diamagnetic [Fig. 1(b)] states the absolute value of the susceptibility increases. The nearest-neighbor interaction within the HOMO states, $V_{H,1}$, also enhances magnetization, while the nearest-neighbor interaction between the HOMO and the LUMO states, V_{HL}, suppresses the magnitude of the susceptibility for both paramagnetic and diamagnetic systems. But this suppression never results in a change of sign of the magnetization. The arrows in Fig. 1 show the susceptibility of the noninteracting system. In all cases the net effect of interaction is an enhancement of magnetization of the system.

The reason for such specific dependence of the magnetization of the DNA molecule on the interstrand and intrastrand electron-electron interactions is in the mixture of the HOMO and LUMO states. Namely, the intrastrand interaction, i.e., the interaction between the electrons at the HOMO states, introduces an additional mixing between the HOMO and LUMO levels. This mixture results in extra sensitivity of the electron states to the external magnetic field. The interstrand interaction, i.e., the interaction between the electrons

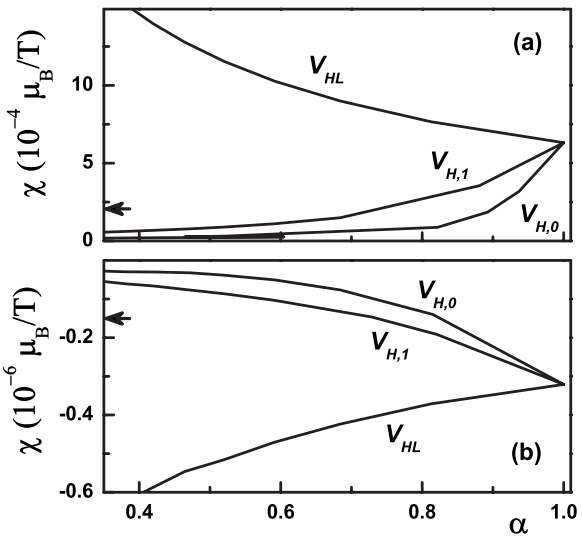

FIG. 1. (a) Magnetic susceptibility of the poly(G)-poly(C) DNA molecule as a function of α, which characterizes the suppression of the corresponding interaction potential, i.e., the interaction potential (2) is $\alpha V_{x,x}$. The potentials $V_{x,x}$ are shown next to the corresponding lines. The susceptibility of DNA without the electron-electron interaction is indicated along the left axis (as an arrow). (b) Same as in (a) but for the poly(A)-poly(T) DNA molecule.

at the HOMO and LUMO states, suppresses mixing between the HOMO and LUMO levels. Then the corresponding electron states become less sensitive to the magnetic field. Since the strength of intrastrand interaction is larger than the strength of interstrand interaction, the final effect of electron-electron interaction is to enhance the magnetic properties of the DNA molecule.

The results in Fig. 1 were obtained for a six-base-pair DNA molecule. Although this is a small-size system we already observe some saturation of DNA susceptibility. For example, for poly(G)-poly(C) system the magnetic susceptibility at $\alpha=1$ is $3.2\times10^{-4}\mu_B/T$ for four base pairs, $5.6\times10^{-4}\mu_B/T$ for five base pairs, and $6.3\times10^{-4}\mu_B/T$ for six base pairs.

B. Effect of electron-vibration interaction: Dynamical disorder

Since the system has a large HOMO-LUMO gap, the temperature dependence of magnetization is of activated type, i.e., $M(T)\propto\exp(-E_{\mathrm{HL}}/k_BT)$, and therefore we should not expect any change in the magnetization up to the room temperature.[14,15] To obtain the proper behavior of DNA magnetization at low temperatures we need to introduce excitations into the DNA model that have the low-frequency scale, which are the vibrations.

As we mentioned above we describe the electron-vibration system as a two-stranded electron model with nondiagonal disorder, where the strength of disorder depends on the temperature. Within this model we calculate the average magnetization. The results for an electron system without the electron-electron interaction are shown in Fig. 2(a), where we consider a system with 100 base pairs, and the magnetization is averaged over 5000 realizations of the disorder. Clearly, a transition from the paramagnetic state to the diamagnetic state occurs for the poly(G)-poly(C) DNA at ~70 K. The poly(A)-poly(T) DNA remains diamagnetic at all temperatures. We can understand the temperature effect of the vibration on the DNA magnetization from Eqs. (4) and (5). Assuming that the hopping integrals are much smaller than the HOMO-LUMO gap, we obtain from the perturbation approach that the DNA susceptibility for a given realization of the twist angles is proportional to $\chi\propto\Pi_i t_H(\delta\theta_i)t_L(\delta\theta_i)$. Taking into account expressions (4) and (5), we obtain

$$\chi\propto\prod_i(t_H+\gamma_H\delta\theta_i)(t_L+\gamma_L\delta\theta_i). \tag{6}$$

We need to find the average of the expression (6) over the random variables, $\delta\theta_i$, which are characterized by the probability distribution function (3). Since we assumed that the twist angle at different base pairs are independent, then

$$\langle\chi\rangle\propto t_Ht_L+\gamma_H\gamma_L\Delta(T)^2. \tag{7}$$

Since $\gamma_H\gamma_L$ is negative the vibrations provide a diamagnetic contribution to DNA magnetization. Therefore, since at zero temperature the poly(A)-poly(T) DNA is diamagnetic, it remains diamagnetic at all temperatures. The poly(C)-poly(G), being paramagnetic at zero temperature, becomes diamagnetic at high temperatures.

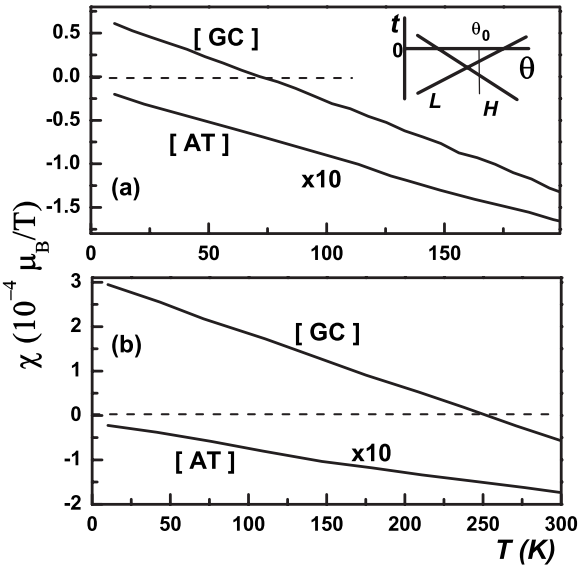

FIG. 2. (a) Magnetic susceptibility of DNA versus the temperature shown for the double-stranded DNA model with electron-vibration interaction included. The electron system is noninteracting. The labels [GC] and [AT] correspond to the poly(G)-poly(C) and the poly(A)-poly(T) DNAs, respectively. The susceptibility of the poly(A)-poly(T) DNA is multiplied by 10. The inset shows schematically the hopping integrals as functions of the twist angle for the HOMO and LUMO strands of the poly(G)-poly(C) DNA. Here $\theta_0=36°$ is the equilibrium twist angle. (b) Same as in figure (a) but with electron-electron interactions included.

In Fig. 2(b) we present the results for the system with electron-electron interactions included. Now the magnetization is averaged over 100 realizations of the disorder and the system consists of five base pairs. Just as for the system without disorder (Fig. 1) the interelectron interaction enhances magnetization of DNA. This fact results in an increase in the transition temperature for the poly(G)-poly(C) DNA, which is now 250 K. The poly(A)-poly(T) remains diamagnetic at all temperatures.

C. Magnetic properties of generic DNA

In order to simulate the situation for a generic DNA (for example, the λ DNA for which experimental results have been reported[7]), we assume that the DNA consists of η fraction of A-T base pairs and $(1-\eta)$ fraction of G-C base pairs. The susceptibility is then estimated from

$$\chi_\eta(T)=(1-\eta)\chi_{\mathrm{GC}}(T)+\eta\chi_{\mathrm{AT}}(T), \tag{8}$$

where $\chi_{\mathrm{GC}}(T)$ and $\chi_{\mathrm{AT}}(T)$ are shown in Fig. 2. The function $\chi_\eta(T)$ describes the transition from the paramagnetic to the diamagnetic states at some transition temperature, T_{tr} $[\chi_\eta(T_{\mathrm{tr}})=0]$. The transition temperature depends on the composition of DNA, η [Fig. 3(a)]. Clearly, a change in the DNA composition can alter the transition temperature. In Fig. 3(a) there are two special values of DNA composition, $\eta_0\approx0.97$ and $\eta_1\approx0.99$, which determine the boundary between paramagnetic and diamagnetic states at low temperatures for the noninteracting and the interacting systems, re-

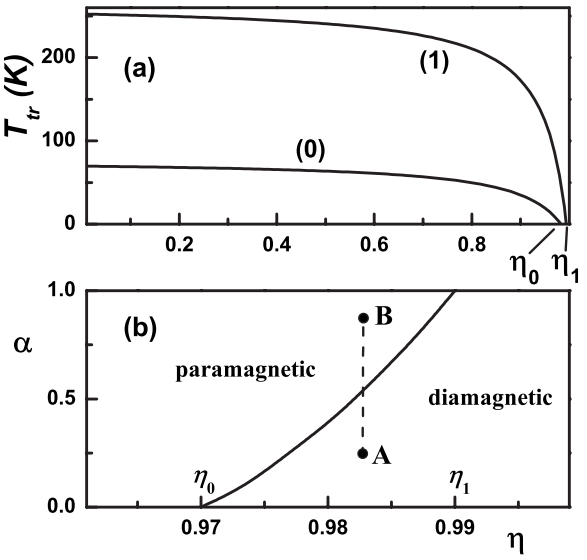

FIG. 3. (a) The transition temperature versus the DNA composition. The labels (0) and (1) next to the lines correspond to noninteracting and interacting electron systems, respectively. (b) The paramagnetic and diamagnetic phases are shown in the α-η plane (see text). The line AB marks the transition from A DNA to B DNA, which occurs at a fixed value of the DNA composition.

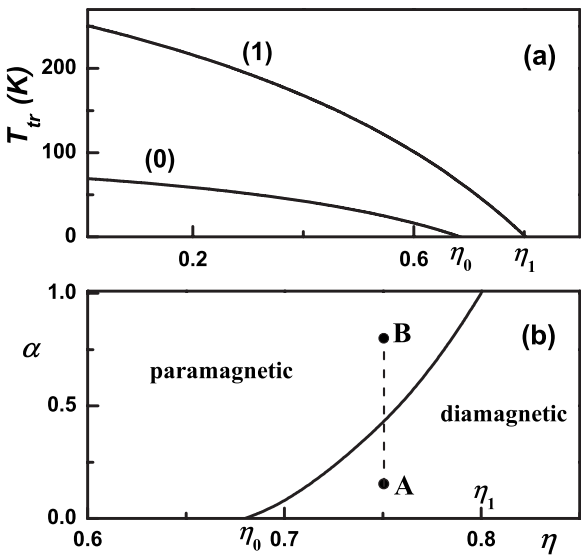

FIG. 4. (a) The transition temperature is shown as a function of DNA composition with modified hopping integrals for poly(A)-poly(T) DNA: $t_H=-0.15$ eV, $t_L=0.08$ eV, and $t_{\mathrm{LH}}=0.06$ eV. The labels (0) and (1) next to the lines correspond to noninteracting and interacting electron systems, respectively. (b) Two different phases, paramagnetic and diamagnetic, are shown in the plane $U-\eta$. Here U characterizes the interaction strength, and η determines DNA composition. The line AB illustrates the transition from A DNA to B DNA. The transition occurs at fixed value of DNA composition.

spectively. For example, if $\eta > \eta_0$, the noninteracting system is always diamagnetic, and if $\eta > \eta_1$ the interacting system is always diamagnetic. To illustrate the transition from the noninteracting to the interacting systems we introduce a parameter α $(1 > \alpha > 0)$ of the same type as in Fig. 1, but now this parameter corresponds to the strength of the whole electron-electron interaction, i.e., for both poly(G)-poly(C) and poly(A)-poly(T) DNAs, we multiply all the interaction parameters in Eq. (2) by α. Then, at low temperatures there are two domains in the α-χ plane: One corresponds to the paramagnetic state of DNA while the other to the diamagnetic state. The domains are shown in Fig. 3(b) and are separated by a line, which starts at η_0 with $\alpha=0$ and ends at η_1 with $\alpha=1$.

Figure 3(b) provides a plausible explanation of the transition from the diamagnetic A DNA to the paramagnetic B DNA. Indeed, the transition from A to B DNAs occurs at the same DNA composition η. It has been noted earlier[10,25] that the interelectron interactions in B DNA are stronger than in A DNA. Therefore, during the transition from A to B DNAs we increase the interaction strength, α, keeping η constant. This transition corresponds to a vertical line in the α-η plane as shown schematically by the line AB for the DNA composition within the interval $\eta_1 > \eta > \eta_0$. The figure clearly reveals the possible mechanism of transition from the diamagnetic A DNA to the paramagnetic B DNA.

The interval between η_0 and η_1 can in fact be large for a real DNA and can perhaps be simulated by an appropriate choice of values of the hopping integrals. To illustrate this property we now consider the modified parameters of poly(A)-poly(T) DNA. Namely, we change only the hopping integrals and introduce the following values: $t_H=-0.15$ eV, $t_L=0.08$ eV, and $t_{\mathrm{LH}}=0.06$ eV. The magnetization is very sensitive to the values of the hopping integrals. At the same time the actual values of the hopping integrals are not well known for a DNA molecule. With the modified parameters of poly(A)-poly(T) DNA we repeat the calculations of the transition temperature as functions of DNA composition η. The results of our calculations are shown in Fig. 4(a). From this figure we can see that if $\eta > \eta_0 \approx 0.67$ then the noninteracting system is always diamagnetic, and if $\eta > \eta_1 \approx 0.8$ the interacting system is always diamagnetic. The transition from the diamagnetic A DNA to the paramagnetic B DNA can then be illustrated by the line AB in Fig. 4(b). Accurate determination of the parameters in Eqs. (2) and (3) is therefore important in determining the magnetic behavior of DNA.

D. Random DNA sequences

In Sec. III C we used expression (8) to find the magnetic properties, i.e., susceptibility of generic DNA, which consists of η fraction of A-T base pairs and $(1-\eta)$ fraction of G-C base pairs. This expression means that the DNA molecule consists of a mixture of poly(dG)-poly(dC) and poly(dA)-poly(dT) blocks. Of course, the real DNA (for example, λ DNA) is the random mixture of the different base pairs. In this case expression (8) cannot provide a good estimation of the magnetic properties of DNA. To check the accuracy of Eq. (8) we evaluated numerically the susceptibility of DNA for an arbitrary mixture of A-T and G-C base pairs. Since the size of the system with electron-electron interaction is relatively small to accommodate different combinations of DNA base pairs, we consider only a noninteracting system. We also disregard the electron-vibration

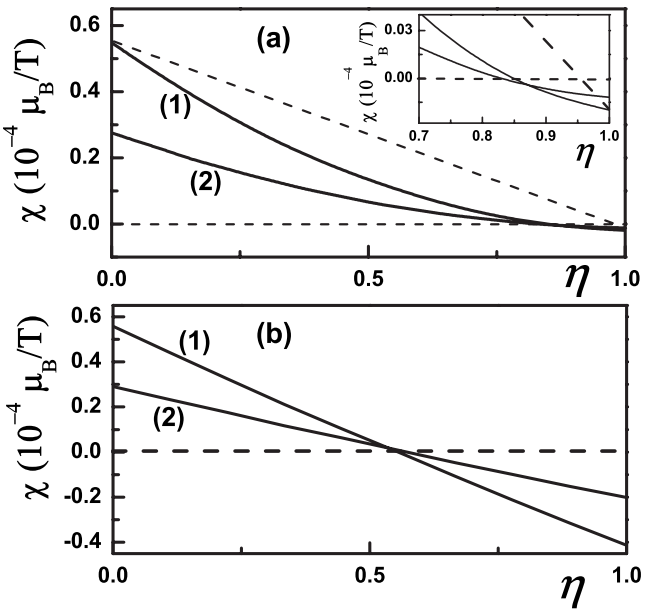

FIG. 5. (a) The susceptibility of generic DNA is shown as a function of DNA composition η. The dashed lines illustrate the linear dependence described by Eq. (8). The labels (1) and (2) next to the lines correspond to partially random and random DNA sequences, respectively. The inset shows the effect of the random structure on the value of η_0. (b) The susceptibility of generic DNA is shown as a function of DNA composition, η, with modified hopping integrals for A-T base pairs: $t_H=-0.15$ eV, $t_L=0.08$ eV, and $t_{\mathrm{LH}}=0.06$ eV. Labels (1) and (2) next to the curves correspond to partially random and random DNAs, respectively.

interaction, i.e., we study the low-temperature case. The system contains 100 base pairs. Each base pair can be A-T base pair with probability η or G-C base pair with probability $(1-\eta)$. The base pairs are randomly distributed within the system. The average susceptibility is then calculated where the average was taken over 5000 random realizations of the DNA sequence.

We consider two types of random sequences. In the first type, one strand of DNA contains only adenines and guanines, for example, *AGGAAGAGGG*. In the second type, each DNA strand can have any nucleobase, for example, *AGGTTCAGCG*. We call the first type a partially random sequence and the second type a random sequence. In our calculations, we use the values of the hopping integrals from Ref. 21. The results of calculations are shown in Fig. 5(a). The dashed line illustrates the linear approximation described by Eq. (8). A deviation from the linear behavior is clearly seen here. As we see from the inset, the effect of this deviation is that the value of η_0 becomes smaller. For a linear dependence, $\eta_0 \approx 0.97$, while for the random sequence, $\eta_0 \approx 0.83$. Another tendency that we observe in Fig. 5(a) is the suppression of the susceptibility of a random sequence [curve (2)] compared with a partially random sequence [curve (1)].

In Fig. 5(b) we change the hopping integrals corresponding to the coupling between A-T base pairs and use the same values as in Fig. 4, namely, $t_H=-0.15$ eV, $t_L=0.08$ eV, and $t_{\mathrm{LH}}=0.06$ eV. In this case we can see that the dependence of the susceptibility of a random DNA on DNA composition, η, is almost linear. Similar to Fig. 5(a), there is a suppression of the magnetic properties of the random DNA compared to the partially random DNA.

IV. CONCLUSIONS

The temperature dependence of DNA magnetization in our approach is due to modulation of the electron hopping integrals by vibrations of the DNA molecule. In our calculations we considered only the linear regime of vibrations of the molecule. As a result, we obtained only the almost linear temperature dependence of magnetization and did not observe any saturation of magnetization with temperature. To obtain a saturation of DNA magnetization with temperature within the present model we need to introduce the nonlinear dynamical model of DNA vibrations.[26] The nonlinear dynamics should be taken into account when the internal motions of DNA molecule have large amplitudes, which is realized at high temperatures. The nonlinear dynamics of DNA manifests itself in phenomena such as conformational transitions between different DNA forms, opening of base pairs, and denaturation processes. While the formalism presented here is valid at all values of the magnetic field, here the DNA magnetization was studied only at low magnetic fields. We introduced this limitation on the values of the magnetic field to clearly illustrate the unique effects of electron-vibration interaction on DNA magnetization. The saturation of magnetization at high magnetic fields is not addressed here and should be a topic of future research.

In our present approach the only effect of water on the magnetic properties of DNA was the modulation of the interelectron interaction strength in wet and dry DNAs. The other effects of the water molecules and counterions on the parameters of the DNA molecule were not taken into account, but they can also affect the magnetic properties of DNA. It has been found recently that hydrogen bonding to water molecules changes the electron structure of the bases. In particular, the covalent structure is converted to the ionic type. An interesting outcome of this is the creation of unbound electrons and suppression of the HOMO-LUMO gap.[27]

Although the interval of DNA composition, within which the paramagnetic to diamagnetic transition can be observed (see Figs. 3 and 4), strongly depends on the parameters of effective Hamiltonian [Eqs. (2) and (3)], the interval is still relatively narrow. This indicates that to describe quantitatively the experimental data, some additional factors and the processes should be taken into account.

In conclusion, we have analyzed the magnetization of DNA chains both homogeneous and randomly sequenced. We found several unique magnetic properties of DNA, in particular, the important role of electron-electron and electron-vibration interactions on the magnetization of this biomolecule. We have also considered mechanisms for magnetic transitions in DNA. These should be of interest not only to the DNA community but also to a broader

condensed-matter community interested on the behavior of correlated electrons in reduced dimensions. Finally, we wish to point out that, in addition to being of fundamental importance, the magnetic behavior of DNA found here might also lead to interesting developments on DNA-based devices. As an example, it would perhaps be possible to design a DNA molecule with given magnetic properties that would depend entirely on the composition and the operating temperature. This would clearly admit the possibility of magnetic nanodevices with DNA as a building block.

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