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 TWO-ELECTRON STATES IN  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$  VIA DISCRETIZED PATH INTEGRAL MOLECULAR DYNAMICS

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We report for the calculation of the electronic singlet and triplet states in  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$  by a discretized path integral molecular dynamics which includes quantum indistinguishability. We show that two nonpolarized electrons form a bound complex within a single Bi ion. Two polarized electrons are located on different Bi sites. The singlet–triplet splitting is found to be  $\sim 0.6$  eV. © 1997 Published by Elsevier Science Ltd

$\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$  is an electronically simple example of a high temperature superconducting perovskite oxide. It is therefore more amenable to theoretical studies of electronic behavior in the ceramic superconductors.

In a previous publication [1], we have reported calculations of the electron–phonon coupling constant in  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$  using a discretized quantum path integral (DQPI) molecular dynamics. This model consisted of a classical rigid ion representation of the  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$  lattice [2] and a single electron mapped onto a discretized set of spatial states. The method of molecular dynamics was employed to sample the states of the system. Electron correlations are expected to play a significant role in the electronic structure of superconducting perovskites. A more realistic simulation of the electronic states in  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$  requires a study of systems containing more than one single electron.

Exchange effects have been successfully incorporated into QPI techniques [3] for the simulation of bosonic particles [4]. To reduce this problem, state sampling can be done with a weighted function based on the density matrix [5]. A high temperature alternative is to bypass the Fermi Disease altogether by restricting the sampled region of phase space to those portions where the density matrix is always positive [6]. Several years ago, it has been shown that by writing the density matrix as a Boltzman factor of an effective potential [7, 8], state sampling based on the density matrix will actually favor phase space sampling where the matrix is positive [9]. Calculations using this approach compare extremely well with local spin density approximation (LSDA) [9] based results.

In this paper we present the calculation of the singlet and triplet states of two electrons in  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$  by using discretized path integral molecular dynamics. Quantum indistinguishability is tackled through effective potentials defined exactly for nonpolarized electrons and approximately for a two-electron polarized system.

Here, we report the formation of an electronic complex, localized on a single Bi ion in the case of two electrons with antiparallel spin. In contrast, the polarized system remains in the form of two localized electrons on neighboring Bi ions. Finally, a singlet–triplet energy splitting is calculated.

The partition function of  $N$  interacting quantum electrons in some external potential can be approximated by

$$Z_P = \left[ \frac{1}{N!} \right]^P \left[ \frac{Pm}{2\hbar^2\beta} \right]^{3NP/2} \int \prod_{j=1}^N \prod_{i=1}^P \text{d}\mathbf{r}_i^{(j)} \\ \times \prod_{k=1}^P M[A_{k,k+1}] \exp \left( \frac{\beta}{P} \sum_{j=1}^N \sum_{i=1}^P \phi(\mathbf{r}_i^{(j)}) \right) \\ \times \exp \left( \frac{-\beta}{P} \sum_{j>1}^N \sum_{l=1}^P \phi_{jl}(r_i^{(j)} - r_l^{(l)}) \right),$$

where  $\phi(\mathbf{r}_i^{(j)})$  is the external potential and  $\psi_{ji}$  is an interaction term between the particles.  $\beta$  is the usual Boltzman term  $1/kT$ . In this expression, the electrons are mapped on  $P$  discrete sets of spatial states.  $Z_P$  approaches the exact partition function as  $P$  tends to infinity. In order to approach the statistical way, a

high temperature approximation for a two-electron  $M[A_{k,k+1}]$  gives

$$M[A_{k,k+1}] = \exp\left(-\beta \frac{C}{2} \{(\mathbf{r}_k^{(1)} - \mathbf{r}_{k+1}^{(1)})^2 + (\mathbf{r}_k^{(2)} - \mathbf{r}_{k+1}^{(2)})^2\}\right) + \zeta \exp\left(-\beta \frac{C}{2} \{(\mathbf{r}_k^{(1)} - \mathbf{r}_{k+1}^{(2)})^2 + (\mathbf{r}_k^{(2)} - \mathbf{r}_{k+1}^{(1)})^2\}\right),$$

where  $C = Pm/\hbar^2\beta^2$  with  $\zeta$  taking the value of +1 or 0 for the singlet state (symmetric orbital part of the wave function) and -1 for the triplet state (antisymmetric orbital part of the wave function).

In the case  $\zeta = 0$ , distinguishability between the electron is implicit. For  $\zeta = +1$ , electron swapping is allowed. Writing  $M[A_{k,k+1}]$  as  $e^{\beta V_{eff}}$  provides a definition for a classical effective potential. This effective potential is exact in the case of  $\zeta = +1, 0$ . The possibility of negative values for  $M[A_{k,k+1}]$  in the triplet state makes us to restrict the effective classical potential to those electronic states which are giving  $M[A_{k,k+1}] > 0$ . For  $\zeta = -1$ , we employ the following prescription:

$$V_{eff} = \frac{1}{2}C(\mathbf{r}_k^{(1)} - \mathbf{r}_{k+1}^{(1)})^2 + \frac{1}{2}C(\mathbf{r}_k^{(2)} - \mathbf{r}_{k+1}^{(2)})^2 - \frac{1}{\beta} \ln[1 - \exp\{-\beta C\{(\mathbf{r}_k^{(1)} - \mathbf{r}_{k+1}^{(2)})^2 + (\mathbf{r}_k^{(2)} - \mathbf{r}_{k+1}^{(1)})^2 - (\mathbf{r}_k^{(1)} - \mathbf{r}_{k+1}^{(1)})^2 - (\mathbf{r}_k^{(2)} - \mathbf{r}_{k+1}^{(2)})^2\}\}]$$

if  $M[A_{k,k+1}] > 0$  and

$$V_{eff} = \frac{1}{2}C(\mathbf{r}_k^{(1)} - \mathbf{r}_{k+1}^{(1)})^2 + \frac{1}{2}C(\mathbf{r}_k^{(2)} - \mathbf{r}_{k+1}^{(2)})^2,$$

if  $M[A_{k,k+1}] \leq 0$ .

This corresponds to effectively setting  $\zeta = 0$  when  $M[A_{k,k+1}] \leq 0$ . We have shown that if the number of states  $P$  and the temperature are sufficiently large, the contribution to the partition function of states with  $M[A_{k,k+1}] \leq 0$  is extremely small and the preceding approximate effective potential valid [9].

The total energy of two electrons given by  $\langle E \rangle = -\partial \ln Z_p / \partial \beta$  is calculated from

$$\langle E \rangle = 2 \times \frac{3P}{2\beta} - C \left\langle \sum_{k=1}^P f [(\mathbf{r}_k^{(1)} - \mathbf{r}_{k+1}^{(1)})^2 + (\mathbf{r}_k^{(2)} - \mathbf{r}_{k+1}^{(2)})^2] + (1-f) [(\mathbf{r}_k^{(1)} - \mathbf{r}_{k+1}^{(2)})^2 + (\mathbf{r}_k^{(2)} - \mathbf{r}_{k+1}^{(1)})^2] \right\rangle + \left\langle \sum_{k=1}^P \frac{\phi_{12}(\mathbf{r}_k^{(1)} - \mathbf{r}_k^{(2)})}{P} \right\rangle + \left\langle \sum_{i=1}^2 \sum_{k=1}^P \frac{\phi(r_k^{(i)})}{P} \right\rangle,$$

where

$$f = \frac{1}{1 + \zeta e^{-\beta CK}};$$

$$K = [(\mathbf{r}_k^{(1)} - \mathbf{r}_{k+1}^{(2)})^2 + (\mathbf{r}_k^{(2)} - \mathbf{r}_{k+1}^{(1)})^2 - (\mathbf{r}_k^{(1)} - \mathbf{r}_{k+1}^{(1)})^2 - (\mathbf{r}_k^{(2)} - \mathbf{r}_{k+1}^{(2)})^2].$$

The sum of the first two terms is the kinetic energy. The last two terms correspond to the electron/electron Coulomb energy (or Hartree energy) and the electrons potential energy, respectively.

We employ a classical molecular dynamics method to sample the system phase space [10]. The interactions between ions in the Ba<sub>0.6</sub>K<sub>0.4</sub>BiO<sub>3</sub> lattice are modelled with simple Bohn–Mayer–Huggins type interionic potentials [2]. The simulation cell contains a total of 320 ions. The cation–electron interactions are represented by local pseudopotentials. The core radii of K and Ba are taken at 1.96 Å [1]. The core radius of Bi is chosen to be 1.75 Å which gave an electron/phonon coupling constant  $\sim 1$  at room temperature in the simulation of a single electron in Ba<sub>0.6</sub>K<sub>0.4</sub>BiO<sub>3</sub> [1]. We neglect the core correlations for oxygen because of the repulsive nature of the electron/O<sub>2</sub>-interaction. The system is simulated at room temperature and constant volume. We use periodic boundary conditions and the Ewald summation method for the calculation of long range Coulombic potential and forces for both electrons and ions. A number of intermediate spatial states  $P = 400$  is chosen to ensure the validity of the different approximations leading to the electrons effective potential. Monitoring states for which  $M[A_{k,k+1}] \leq 0$  for  $\zeta = -1$  similar to Monte Carlo simulation [5] shows a frequency of occurrence less than one out of 400 every 10 000 molecular dynamics integration steps (one step =  $2.68 \times 10^{-15}$  s).

The two electron necklaces are inserted into an already equilibrated ionic lattice. Subsequently we subtract equivalent charges from each individual Bi ion to ensure charge neutrality in the simulation cell. The initial positions of the two electrons are within the core of two second nearest neighbor Bi ions (Fig. 1A).

We present here the results of three simulations for electrons with antiparallel ( $\zeta = +1, 0$ ) and parallel ( $\zeta = -1$ ) spins.

Projections of the electrons in their various states are shown in Fig. 1. The  $\zeta = 0$  and  $\zeta = -1$  states (Fig. 1B and D respectively) indicate the retention of two spatially separated and localized electrons on second nearest neighbor bismuth sites. Note that since periodic boundary conditions are used, the two electrons in Fig. 1B are effectively neighbors. In contrast, the singlet ( $\zeta = +1$ ) state is characteristic of a complex composed of two overlapping electrons. Both electrons are located within the core of a single bismuth ion. The two electrons with antiparallel spins form a bound state.

For  $\zeta = -1$  the Pauli exclusion principle requires two electrons to be in different spatial states. For  $\zeta = +1$  an attractive force between the two electrons resulting from the effective potential leads to a paired state. For  $\zeta = 0$  the absence of a swapping attractive force in

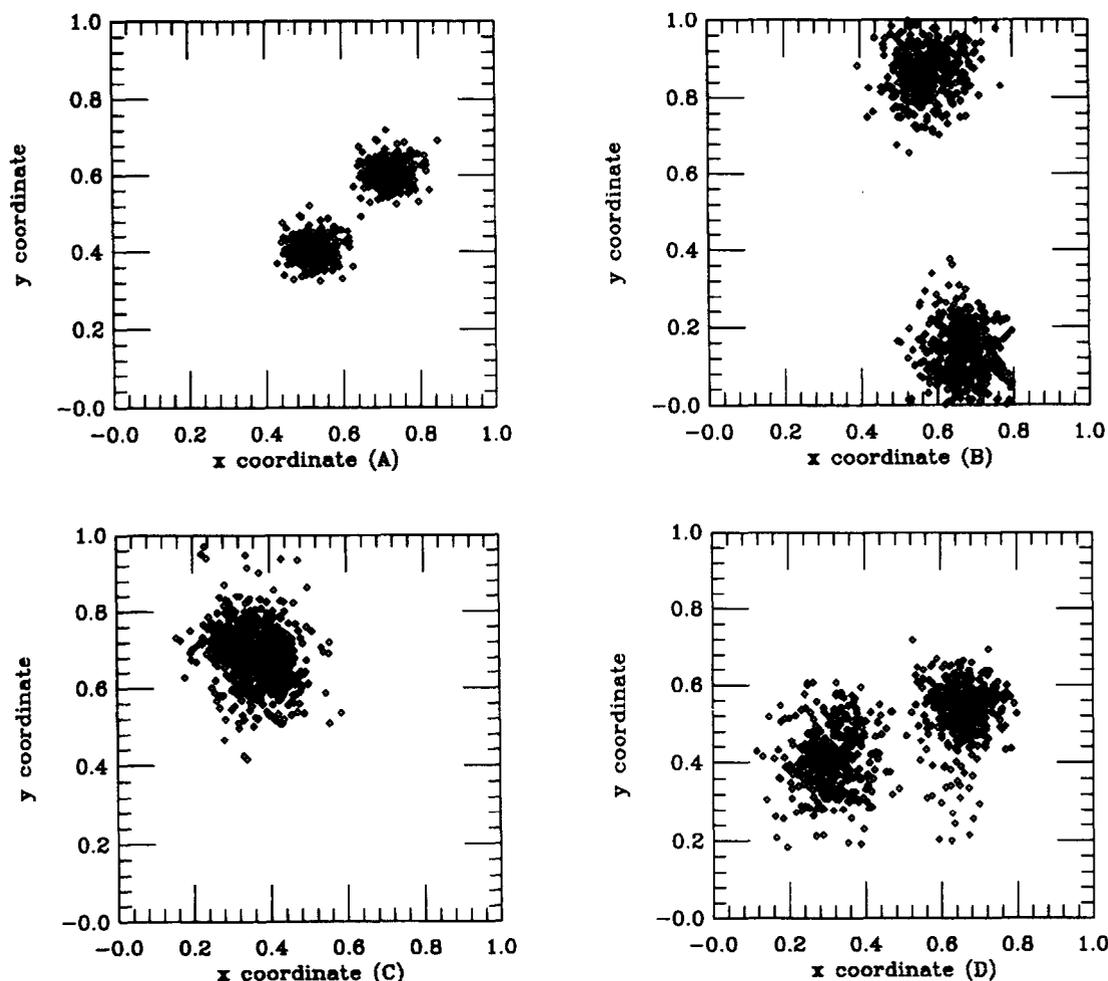


Fig. 1. Projections of the initial configuration of the two electrons (A), equilibrium configurations of the singlet states  $\zeta = 0$  (B),  $\zeta = +1$  (C) and triplet state  $\zeta = -1$  (D). The coordinates are reduced to the size of the simulation cell.

the effective potential prevents the electrons to overcome the energy barrier to form a bound state, retaining the initial state. These observations are strongly supported by the electron–electron correlation functions for  $\zeta = +1$  and  $\zeta = -1$  states of Fig. 2A and B.

Various temporal average energies characteristic of the two electron states are also reported in Table 1. An average electron–electron distance of approximately  $2 \text{ \AA}$  in the two electron complex is consistent with the very high Hartree energy of  $6.5 \text{ eV}$ . The lower Hartree energy of the  $\zeta = -1, 0$  states  $\sim 2.2$  to  $2.5 \text{ eV}$  reflects the electrons separation distance of  $\sim 6 \text{ \AA}$ .

Despite the larger Hartree energy, the total energy of the  $\zeta = +1$  state is lower than that of the  $\zeta = -1$  and  $\zeta = 0$  states. The stability of the two-electron complex arises from the very low potential energy balancing its large Coulomb repulsion. The estimated singlet–triplet splitting energy is  $E \sim 0.6 \text{ eV}$ .

In conclusion, we have demonstrated that the method of DQPI molecular dynamics with quantum

indistinguishability can be used to calculate properties of many electron systems in crystals. The results of our study on two electrons in  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$  show that two electrons with antiparallel spin form a bound complex in the vicinity of a single bismuth ion. In contrast, two polarized electrons remain on separated bismuth ions. The difference in energy between these two states is in the singlet–triplet splitting. Our model gives a value of on the order of half an eV for this energy.

Table 1. Kinetic (K.E.), potential (P.E.), Hartree (H.E.) and total energy (T.E.) of the singlet state ( $\zeta = +1$  and  $\zeta = 0$ ) and triplet state ( $\zeta = -1$ ). The zero of energy is for infinitely separated particles and the unit of energy is eV. The uncertainty is less than  $0.1 \text{ eV}$

	K.E.	P.E.	H.E.	T.E.
$\zeta = +1$	4.8	-22.9	6.5	-11.5
$\zeta = 0$	4.0	-17.2	2.5	-10.7
$\zeta = -1$	3.7	-16.7	2.0	-10.9

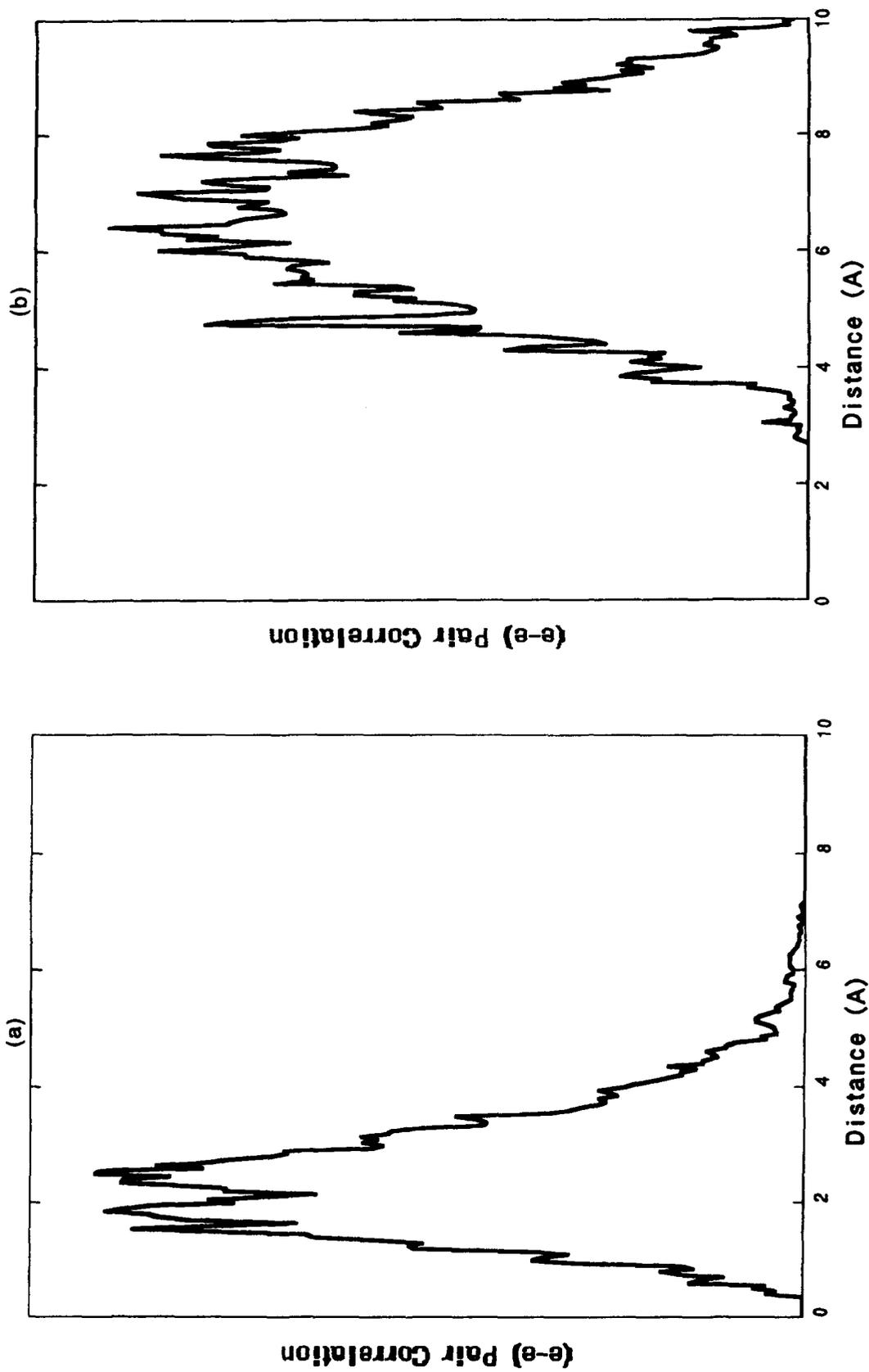


Fig. 2. Electron-electron correlation functions of the  $\zeta = +1$  (A) and  $\zeta = -1$  (B) systems. The vertical axis is expressed in arbitrary units.

We are currently extending this type of calculation to more than two electrons with the aim of studying electronic collective effects.

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