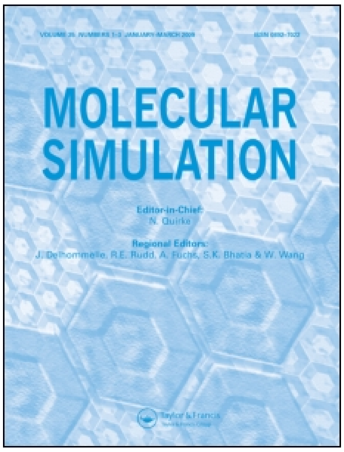

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Path Integral Monte Carlo Simulation of an Electron Pair in a Cavity, Paramagnetic Susceptibility and Other Canonical Properties

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PATH INTEGRAL MONTE CARLO SIMULATION OF AN ELECTRON PAIR IN A CAVITY, PARAMAGNETIC SUSCEPTIBILITY AND OTHER CANONICAL PROPERTIES

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The PIMC method is used to simulate an electron pair located in a spherical cavity in equilibrium with a thermal bath over a wide temperature range. Permutational symmetry, electron spin and interelectron Coulomb interaction are accounted for explicity. Spin "pairing" at low temperatures results in a fall in paramagnetic susceptibility in qualitative accordance with the experimental data for electrides. The method proves to be promising in solving various quantum statistical many electron problems.

KEY WORDS: Path Integral, Monte Carlo, permutational symmetry, spin, magnetic susceptibility.

1. INTRODUCTION

In the traditional Schroedinger description of the permutational symmetry in many particle quantum systems based on the single particle approximation, the contribution from exchange "interactions" is presented by exchange integrals over the overlapping areas of the single particle wave functions. Complete symmetrization of the N-particle wave function produces 2-, 3-, ..., N-particle exchange integrals. In quantum statistical problems dealing with mixed states the localization of a single particle is determined by thermal de Broglie wave length, so with the increase of temperature the localization area of a particle contracts and overlapping of wave functions becomes weaker. At intermediate degrees of degeneracy when the thermal wave length has an order of the mean interparticle distance there should survive only the lowest, two particle exchanges — the system can be treated as divided into virtual pairs. The spin of each pair being a result of statistical mechanic averaging over spin states of pair of nondistinguishable particles depends on temperature and density of the system. Temperature dependence of the "quasispin" of such a pair can alter the conventional paramagnetic behavior of the magnetic susceptibility ($\sim 1/T$) of the system breaking its monotonous character. Such a dependence with a maximum was experimentally observed in certain types of electrides [1] — crystals with ionic structure in which anions are substituted by electrons. These electrons are localized in cavities with the size of several angstroms connected by channels thus providing partial overlapping of electron wave functions.

The most developed numerical methods for multielectron systems at present are methods of quantum chemistry (SCF, LCAO MO etc.). Calculation of characteristics of each pure quantum state represents here a specific and complicated problem. In spite of the single electron approximation (with possible corrections and semi-phenomenological description of the permutational symmetry) used in quantum chemistry it appeared to be successful in obtaining good results for some molecules if a sufficiently large and appropriate expansion basis were used. For application of these methods in quantum statistical problems one should initially determine the excited state spectrum that is practically unattainable due to the enormous amount of necessary calculations. While for description of quantum dynamics of an electron system in the strong field of nuclei the single particle approximation which does not account for interelectron correlations could appear to be satisfactory, in the case of weak fields when the character of electron motion is mainly determined by their mutual interactions such an approximation is not adequate.

For correct treatment of the spin state of the many electron system accurate and explicit account of the permutational symmetry is necessary. It results in catastrophic growth of computational difficulties (faster than N!) with the increase of the system. These and other obstacles can be overcome with the aid of a nontraditional quantum approach based on path integrals [2,3]. In recent years a major effort has been made to create stochastic quantum statistical methods based on Feynman formalism of path integrals for distinguishable [4–13] and spinless [14] particles. In preprint [15] there was suggested and developed a general approach to description of nondistinguishable fermions with the spin 1/2 and proposed the corresponding Monte Carlo scheme.

In section 2 of the present paper we shortly discuss the general scheme of application of the path integral Monte Carlo (PIMC) method to calculation of paramagnetic characteristics of the N-electron system in the zero magnetic field limit with the account of permutational symmetry. The case of two electrons is then discussed in detail and general principles of the computer programme operation is being described (section 3). Methodological PIMC data for energy characteristics of two electrons in the field of two fixed nuclei (hydrogen molecule) are presented in section 4. In section 5 PIMC results for equilibrium properties of an electron pair in a cavity with the radius 10 A in the temperature interval $300 < T < 2000$ K are presented and discussed: paramagnetic susceptibility and electrical polarizability; canonical averages of the square of the spin operator in the zero field, of kinetic and potential energy operators; radial distribution function. Section 6 — short conclusion.

2. METHOD

The quantum state of an electron system is described by a set of quantum numbers S, M, R where S ($S = 0, 1, \ldots, N/2$ for even number of electrons N and $S = 1/2, 3/2, \ldots, N/2$ for odd N) ennumerate eigenvalues of the square of spin operator for the N-electron system; $M = 0; \pm 1, \pm 2, \ldots, \pm S$ (even N) $M = \pm 1/2, \pm 3/2, \ldots, \pm S$ (odd N) — the quantum number of the complete spin projection; R represents all the remaining quantum numbers corresponding to the complete set of the eigenfunctions. The Hamiltonian of the nonrelativistic system does not explicitly include the spin variables S and the dependence on M in the presence of the external magnetic field H is represented by the term $-J_M B = Me\hbar m^{-1} B$, where $B = \mu_0 H$ (μ_0 being the magnetic permittivity of vacuum) $\hbar$ — Planck constant, e — elementary charge, m — electron mass, J_M — projection of the spin magnetic moment on **H**. The canonical partition function can now be written as:

$$Q = \sum_S \sum_M \exp(-\beta M e\hbar B/m) \sum_R \langle S, R | \exp(-\beta \hat{H}) | S, R \rangle, \qquad (1)$$

where $\beta = (\mathrm{kT})^{-1}$ is the reciprocal temperature, $\hat{H}$ — Hamiltonian of the system of spinless particles.

The permutational symmetry of the coordinate wave function $|S, R\rangle = \psi_s(R; X)$ is determined by the value of S; matrix elements in (1) are $2S + 1$ times degenerate with respect to M. In the position representation R becomes a 3N-dimensional set of continuous values of cartesian coordinates $R = \{r_i\}$, and $\psi_s(\{r_i\}; \{x_i\})$ becomes linear combinations of multidimensional Dirac delta functions symmetrized over particle transpositions and composed of products of 3-dimensional delta functions of the type $\delta(x_i - r_i)$ (it should be stressed here that 3-dimensional delta function factorization in coordinate representation does not mean a single electron approximation which we do not intend to introduce in our approach). Matrix elements in (1) in the coordinate representation could be expressed in the form of Feynman continual integrals [2] if $H = 0$. Their finite dimensional approximation by integrals over K vertex positions of cyclic broken line trajectories is:

$$\langle \{r_i\} | \exp(-\beta \hat{H}) | \{r_j\} \rangle = \int \ldots \int d\{r_i^{(1)}\} \ldots d\{r_i^{(K-1)}\} \langle \{r_i\} | \exp(-\beta \hat{H}/K) | \{r_i^{(1)}\} \rangle$$
$$\langle \{r_i^{(1)}\} | \exp(-\beta \hat{H}/K) | \{r_i^{(2)}\} \rangle \ldots \langle \{r_i^{(K-1)}\} | \exp(-\beta H/K) | \{r_j\} \rangle. \qquad (2)$$

Here $\{r_j\} = \hat{P}_n\{r_i\}$, $\hat{P}_n$ — index permutation operator.

Expression (2) can be used for the creation of a stochastic procedure for numerical estimation of canonical averages.

MC simulation consists of a random walk in the space of broken line trajectories with the distribution weight function proportional to the integrand in (2) with the known asymptotics of the matrix elements $\langle \{r_i^{(k)}\} | \exp(-\beta \hat{H}/K) | \{r_i^{(k+1)}\} \rangle$ for $K \to \infty$. The structure of the integrand in (2) depends on the type of the permutation $\hat{P}_n$. As far as (1) contains summation over S, the computation of canonical averages requires also a random walk in the space of various trajectory linkings with the appropriate transition probabilities. To each spin state S there corresponds its proper specific set of topological structures of trajectory linkings $\hat{P}_n$ with the corresponding set of weight factors. And vice versa, each topological structure $\hat{P}_n$ simultaneously includes contributions to several spin states; hence each Markov microstate, which is being characterized by coordinates of vertices and a definite structure of trajectory linkings, contributes to a certain distribution over spin $W_n(S)$, rather than to a single state ($W_n(S)$ depends only on topological structure of trajectories linkings and is independent of vertex cooridinates). Markov random walk over these distributions yields an average normalized distribution over spin states $\bar{W}(S)$ thus yielding to the average spin magnetic moment of the system:

$$\langle J \rangle = \sum_S \bar{W}(S) \left[\sum_{-S \leqslant M \leqslant S} J_M \exp(\beta J_M B) / \sum_{-S \leqslant M \leqslant S} \exp(\beta J_M B) \right] \qquad (3)$$

The initial (zero magnetic field) susceptibility then can be expressed as follows:

$$\kappa = d\langle J \rangle / dB|_{B=0} = \sum_S \bar{W}(S) \sum_{-S \leqslant M \leqslant S} \beta (J_M)^2 / (2S + 1) = 2\beta(e\hbar/m)^2 = \qquad (4)$$

$$\sum_S \bar{W}(S)/(2S + 1) \sum_{1 \leqslant M \leqslant S} M^2 = \beta \langle J^2 \rangle \tag{4}$$

It has been accounted in (4) that for $B = 0$ after summation over M there survives only the term with the second power of J_M (in accordance with the fluctuation theorem). It should be stressed that $\bar{W}(S)$ both in (4) and in (3) are to be calculated in absence of the magnetic field.

3. THE SYSTEM OF TWO ELECTRONS

The general approach to the construction of topological structures of linked trajectories for arbitrary numbers of electrons N was formulated and carried out in [15]. In the case of two electrons, incorporation of permutational symmetry into the general scheme of Feynman integrals is considerably simplified. Nonsymmetrized two-particles eigenfunctions of the coordinate operator and of the spin projection operator have the form:

$$f(r_1, r_2; x_1, x_2) = \delta(x_1 - r_1)\, \delta(x_2 - r_2) \tag{5}$$

$$x(m_1, m_2; \sigma_1, \sigma_2) = \chi(m_1; \sigma_1)\, \chi(m_2; \sigma_2)$$

where $\chi(1/2; 1/2) = 1$, $\chi(1/2; -1/2) = 0$, $\chi(-1/2; 1/2) = 0$, $\chi(-1/2; -1/2) = 1$. There exist two irreducible representations corresponding to singlet ($S = 0$) and triplet ($S = 1$) spin states [3]. Accordingly the two-particle wave function could be symmetrized in two ways:

$$\begin{gathered} \psi_{S=(0,1)}(m_1, m_2, r_1, r_2; \sigma_1, \sigma_2, x_1, x_2) = \\ (1/2)\, [\chi(m_1, m_2; \sigma_1, \sigma_2) \mp \chi(m_1, m_2; \sigma_2, \sigma_1] \times \\ [f(r_1, r_2; x_1, x_2) \pm f((r_1, r_2; x_2, x_1)] = \\ (1/2)[\chi(m_1, m_2; \sigma_1, \sigma_2) \mp \chi(m_2, m_1; \sigma_1, \sigma_2)] \times \\ [f(r_1, r_2; x_1, x_2) \pm f(r_2, r_1; x_1, x_2)] \end{gathered} \tag{6}$$

The upper sign in (6) and further in (7), (8) corresponds to $S = 0$ and the lower one — to $S = 1$. For the antisymmetric over m_1 and m_2 function (with $S = 0$) there exist two nonzero spin functions with $m_1 = 1/2$, $m_2 = -1/2$ and $m_1 = -1/2$, $m_2 = 1/2$, differing only in their sign and representing the same quantum state with $M = m_1 + m_2 = 0$. In another case ($S = 1$) the function (6) is symmetrical over m_1 and m_2 and hence two of the four possible combinations of values of m_1, m_2 $(1/2, 1/2)$, $(1/2, -1/2)$, $(-1/2, 1/2)$, $(-1/2, -1/2)$ (the second and the third) yield to the same wave function. There remain three states with $M = 1, 0, -1$. Diagonal matrix elements of the density matrix do not depend on sets of m_i $\{m_i = \pm 1/2\}$ and hence on M since the simultaneous inversion of the sign of m_1 and σ_1 according to (5) yields to the same spin eigenfunction, but the sign inversion for σ_i effects only the summation order over $\{\sigma_i = \pm 1/2\}$, with no change in the result:

$$\begin{gathered} \langle S = (0,1), M, r_1, r_2 | \exp(-\beta \hat{H}) | S = (0,1), M, r_1, r_2 \rangle = \\ (1/2)\, (\langle r_1, r_2 || r_1, r_2 \rangle \pm \langle r_1, r_2 || r_2, r_1 \rangle \pm \\ \langle r_2, r_1 || r_1, r_2 \rangle + \langle r_2, r_1 || r_2, r_1 \rangle) \end{gathered} \tag{7}$$

According to (5) simultaneous transposition of arguments x_1 and x_2 and parameters r_1 and r_2 does not effect the coordinate eigenfunctions; so the first and the fourth term, as well as the second and the third, in (7) coincide:

$$\langle S = (0,1), M, r_1, r_2 || S = (0,1), M, r_1, r_2\rangle = \langle r_1, r_2 || r_1, r_2\rangle \pm \langle r_1, r_2 || r_2, r_1\rangle \tag{8}$$

The partition function now can be written in the following way:

$$\begin{aligned} Q &= (3/2!)\int dr_1 dr_2(\langle r_1, r_2 || r_1, r_2\rangle - \langle r_1, r_2 || r_2, r_1\rangle) \\ &+ (1/2!)\int dr_1 dr_2(\langle r_1, r_2 || r_1, r_2\rangle + \langle r_1, r_2 || r_2, r_1\rangle) \\ &= \int dr_1 dr_2(2\langle r_1, r_2 || r_1, r_2\rangle - \langle r_1, r_2 || r_2, r_1\rangle) \end{aligned} \tag{9}$$

Factor 1/2! in (9) accounts for the fact that transposition of r_1 and r_2 transfers the function (6) into itself (with the only change in the sign); factor 3 accounts for equal contributions of the three states — $M = 1, 0, -1$ (for $S = 1$). Expression (9) shows that diagonal elements of the density matrix in symmetrized representation are expressed as a linear combination of the diagonal and nondiagonal elements of the nonsymmetrized representation. Both of them can be expressed as Feynman continual integrals. The nondiagonal element yields for instance:

$$\begin{aligned} \langle r_1, r_2 | r_2, r_1\rangle &= \langle r_1, r_2 | \exp(-\beta \hat{H}) | r_2, r_1\rangle \\ &= \iint \exp(-\beta G([r_1(t)], [r_2(t)]))\, Dr_1(t)\, Dr_2(t), \end{aligned} \tag{10}$$

where $G([r_1(t)], [r_2(t)])$ is the functional calculated on linked trajectories $r_1(t)$, $r_2(t)$ [2] with fixed end points (r_1, r_2) and (r_2, r_1):

$$\begin{aligned} G([r_1(j)], [r_2(j)]) = \lim_{K\to\infty} \Bigg(\sum_{1 \leqslant j \leqslant K} ((\mathrm{Km}/2\beta^2 \hbar^2)\, ((r_1(j+1) - r_1(j))^2 + \\ (r_2(j+1) - r_2(j))^2 + (1/K)\,(e^2/(|r_1(j) - r_2(j)|) + U(r_1(j)) + U(r_2(j))))\Bigg) \end{aligned} \tag{11}$$

$U(r)$ — potential energy operator for an electron in the external electric field. The measure in the functional integral (10) is determined by the condition that for a free particle the density matrix in the coordinate representation $\rho(r, r') = \langle r | \exp(-\beta \hat{H}) | r'\rangle$ in the limit of $\beta \to 0$ tends to a delta function — $\rho(r, r') \to \delta(r - r')$ [2]:

$$Dr(t) = \lim_{K\to\infty} (2\pi \hbar^2 \beta/\mathrm{mK})^{-3K/2} dr^{(1)} \ldots dr^{(K)}$$

Nonlinked ring trajectories with $r_1(K+1) = r_1(1)$; $r_2(K+1) = r_2(1)$ correspond to diagonal elements $\langle r_1, r_2 || r_1, r_2\rangle$; the linked ring trajectories with $r_1(K+1) = r_2(1)$; $r_2(K+1) = r_1(1)$ correspond to nondiagonal elements $\langle r_1, r_2 || r_2, r_1\rangle$.

Hence the two-particle partition function has the following structure:

$$Q = \int Dr_1(t) Dr_2(t)\, (2(r_1 \circlearrowright\ r_2 \circlearrowright) - r_1 \rightleftarrows r_2) \tag{12}$$

The normalized spin state distribution probabilities corresponding to the first (diagonal) term in (12) are $W_1(0) = 1/4$, $W_1(1) = 3/4$; the corresponding probabilities for the nondiagonal term are:

$$W_2(0) = -1/2,\ W_2(1) = +3/2.$$

Using the statistical thermodynamical expressions [16] it is easy to obtain from Q any canonical average of the quantum mechanical observable quantity

$$\langle F\rangle = Q^{-1}\int Dr_1(t)\, Dr_2(t)\, F([r_1(t), [r_2(t)])\, (2(r_1 \circlearrowright\ r_2 \circlearrowright) - r_1 \rightleftarrows r_2) \tag{13}$$

In the discretized approximation the functional $F([r_1(t)], [r_2(t)])$ yields the function of 6K variables

$$F(r_1^{(1)}, \ldots, r_1^{(K)}, r_2^{(1)}, \ldots, r_2^{(K)}),$$

which is usually called the estimator of the corresponding physical quantity. For the energy there exist several estimators [7,13], with different magnitudes of dispersion.

As it is seen from (13) the linked trajectories should be accounted for with the negative weight, which hinders creation of a standard Markov random walk procedure which implies existence of the positively determined measure of microstates. The problem is resolved by a redetermination of the measure together with the parallel compensatory redetermination of estimators. Let $\langle F\rangle$ be the average of $F(X)$ in the space of microstates X:

$$\langle F\rangle = \int dX F(x)\, \omega(X) \tag{14}$$

where $\omega(X)$ can change its sign. Let us determine the normalized $\Omega(X)\rangle\, 0$

$$\Omega = |\omega(X)| / \int dX |\omega(X)| \tag{15}$$

Then in terms of $\Omega(X)$ (14) can be rewritten as:

$$\begin{aligned}\langle F\rangle &= \int dX \operatorname{sign}(\omega(X))\, F(X)\, \Omega(X) / \int dX \operatorname{sign}(\omega(X))\, \Omega(X)\\ &= \langle \operatorname{sign}(\omega(X))\, F(X)\rangle_+ / \langle \operatorname{sign}(\omega(X))\rangle_+\end{aligned} \tag{16}$$

where $\langle\ldots\rangle_+$ denotes averaging with the positively determined weight function $\Omega(X)$. The relative dispersion of (16) calculated on a finite set of Markov microstates in MC sampling is the sum of relative dispersions of numerator and denominator in (16), it tends to infinity if $\langle \operatorname{sign}(\omega(X))\rangle_+ \to 0$. So the presence of negative contributions in the partition function (9) inserts complications into the calculation procedure. In the case of two electrons the lowest value of $|\langle \operatorname{sign}(\omega(X))\rangle_+|$ is attained at zero temperature ($\beta \to \infty$) when the length of the Feynman trajectory becomes infinite and the difference between the "managing" functional G in $\exp(-\beta G)$ for linked and nonlinked trajectories averaged over the configurational space vanishes. The combinatorial weights (see (13)) provide the ratio for realization frequencies of nonlinked and linked configurations 2:1, i.e. for each three Markov steps in two cases $\operatorname{sign}(\omega(X)) = 1$ and in one case $\operatorname{sign}(\omega(X)) = -1$ with the average value $\langle \operatorname{sign}(\omega(X))\rangle_+ = 1/3$. In this zero temperature limiting case the distribution of spin values S is:

$$\langle W(S)\rangle_+ = (\langle W(0)\rangle_+, \langle W(1)\rangle_+) = 2W_1(S) - W_2(S)$$

$$= (2(1/4) - (-1/2), 2(3/4) - (3/2)) = (1,0)$$

with the average square of spin $\langle S(S+1)\rangle_+ = 0$

The problem of negative contributions becomes much more severe for systems including more than two electrons. The direct counting of the combinatorial weights of all possible linkings of Feynman trajectories yields zero [15], which reveals the impossibility of creating a Junge scheme for the coordinate part of the wave function with more than two cells in each row [15]. Presence of negative contributions in the partition function results in elimination of nonphysical electron configurations (due to the Pauli principle) and simultaneous decrease of the denominator in (16) $|\langle \text{sign}\,(\omega(X))\rangle_+|$. To accelerate the procedure in conditions of strong degeneracy vast areas of the configuration space with such compensated contributions can be preliminarily excluded from averaging. In our algorithm it is achieved by "switching on" an additional (to G) managing functional of a special type which simulates exchange interaction; however in the system of two electrons there is no necessity for such a measure. In systems with moderate degrees of degeneracy calculations without such a correlation functional are possible for any number of electrons because, in this case Feynman trajectories are localized in areas smaller than the mean distance between particles; the combinatorial distribution of various ways of trajectory linkings in this case is modified due to the influence of the weight factor $\exp(-\beta G)$, which breaks the accurate balance between positive and negative contributions and hence results in $|\langle \text{sign}\,(\omega(X))\rangle_+| \neq 0$

4. TEST OF THE METHOD

Numerical realization of the Markov process discussed above has been carried out by a special algorithm in which the number of electrons is the input parameter. Managing tables [15] for the calculation of transition probabilities and distributions over spin states in the space of various trajectory linkings have been preliminarily prepared and joined to the main programme. Markov steps included shifts of single trajectory vertices, rotations and shifts of the trajectory as a whole, linkings and "dislinkings" of trajectories. A selfregulated algorithm establishes the optimal parameters of the Markov steps according to the results of the initial nonstationary piece of the MC chain (excluded from further averaging). This initial nonstationary interval comprised also special "macroscopic" relaxational moves of trajectories (with continuous transfer to stationary regime) that accelerates the establishing of the thermal equilibrium by several orders of magnitude. The experience of simulations showed that attempts of linking and dislinking of trajectories by means of simple "rethrowing" of links from one pair of vertices to another without special additional measures rarely results in a successful move, due to considerable (compared with kT) change of the exponent G (11) in the weight function. For attaining the optimal ratio of "successful" and "unsuccessful" Markov steps there has been introduced into the programme a fast random search of neighbouring vertices in trajectories which are to be linked or dislinked. Depending on the distance between vertices, linkage or dislinkage is attained either by a plain "rethrowing" of two links or by "pulling" together the ends to each other. In the latter case a piece of the trajectory is deformed; this piece is chosen so that the kinetic (quadratic over difference $(r(j+1) - r(j))$) part of the function (11) should gain variation of the order of kT.

For each T-point we generated a Markov chain of about 1.6×10^6 of steps including 10^6 of configurations and 10^5 of trials to alter the trajectory linkings. After each 40 attempts to move an arbitrary chosen vertex there followed an attempt to move the trajectory as a whole (two of them together if they are linked) and three attempts to rotate the trajectory around the axes with the origin in the centre of mass. There occurred about 5×10^3 adopted linkings and dislinkings of the electron trajectories. Initial 4×10^5 steps (interval of termolization) were excluded from averaging.

Calculations for a single T-point on a computer with the efficiency of 1 million op/sec required several hours of processor time and was divided into pieces ("quants") with the output of the intermediate results onto a disk to protect them from possible computer failure that could result in interruption of the calculation process.

Test computations with the aid of this method were carried out for the hydrogen molecule in which the exchange "interaction" is most clearly expressed in a system with a minimal number of electrons. It should be pointed out for comparison that for instance in the helium atom the exchange "interaction" lowers the energy of the atom by about 0.5 eV i.e. 0.5 % of the total energy. In the hydrogen molecule the neglect of the exchange symmetry results in an error for the dissociation energy of about an order of magnitude. In traditional Schroedinger formalism this feature of exchange "interaction" is explained by the fact that a simple product of coordinate single electron wave functions of the helium atom $f_1^{\mathrm{He}}(x_1)\, f_1^{\mathrm{He}}(x_2)$ already possesses the necessary property of symmetry — the exchange integral is absent. In the hydrogen molecule single electron wave functions are centered on different nuclei and their product $f_1^H(x_1 - a/2)\, f_1^H(x_2 + a/2)$ needs further symmetrization that results in emergence of the exchange integral.

In terms of Feynman integrals the exchange symmetry results in the emergence of "stretches" between atoms. Fragments of trajectories in the interatomic space appear to be in an expanded state and their contribution into the partition function differs from that of the internal atomic trajectories.

In order to get rid of effects caused by movement of nuclei their coordinates were fixed at the equilibrium distance $a = 0.7416$ Å [17]. Calculations were carried out for $T = 2500$ K (0.17 eV), the number of vertices in each trajectory was $K = 640$. The nonphysical singularity of the nuclei potential ($1/r$) caused by the finite number of vertices K was avoided by continuous distribution of the electrical charge along the trajectory links. The average energy and distribution picture of the electron density were obtained. Calculation with the virial estimator [7] resulted in the following data for the energy characteristics of the electron subsystem: kinetic energy $\langle K \rangle = (+28.5 \pm 0.1)$ eV; potential $\langle U \rangle = (-79.8 \pm 0.1)$ eV; total $\langle C \rangle = (-51.3 \pm 0.1)$ eV. Total energy of the molecule without the kinetic energy of the nuclei movement $\langle E \rangle = (-31.9 \pm 0.1)$ eV. The latter value corresponds to the total energy of the molecule in the ground state minus energy of the zero vibrations $(1/2)\,h\nu_{\mathrm{nucl}}$ and can be estimated from the experiment [17]:

$$E^{\mathrm{exp}} = 2E_H - E_{\mathrm{dis}}^{\mathrm{exp}} - (1/2)\,h\nu_{\mathrm{nucl}}^{\mathrm{exp}} = -2\cdot 13.598 - 4.478$$
$$-(1/2)\cdot 4.1357\cdot 10^{-15}\; 1.3181\cdot 10^{14} = -31.946\,(\mathrm{eV})$$

where E_H — the ground state energy of the hydrogen atom, $E_{\mathrm{dis}}^{\mathrm{exp}}$ — the experimental value of the dissociation energy of the hydrogen molecule. Our result reproduces the experimental value of energy with the accuracy of 0.2 % and yields the dissociation energy of the hydrogen molecule $E_{\mathrm{dis}} = \langle E \rangle - 2E_H = (4.4 \pm 0.1)$ eV in accordance with the experimental result $E_{\mathrm{dis}}^{\mathrm{exp}} = 4.478$ eV.

Calculations showed that cooling of the system results in a steep fall of dispersion for the main energy estimator [7] obtained by direct differentation of the free energy over reciprocal temperature; so for $T = 2500$ K the main estimator becomes competitive with the virial estimator. Averaging of the main estimator has given: $\langle K \rangle = (28.5 \pm 0.5)$eV, $\langle C \rangle = (-51.3 \pm 0.5)$eV, $\langle E \rangle = (-31.9 \pm 1)$eV.

The partition function of the system includes two spin states $S = 0$ and $S = 1$. In our simulation the hydrogen molecule occupied the state with $S = 0$ 98 % of the effective Markov "time".

Analysis of the fluctuation behavior of S allows to suppose that the increase of the random sampling volume would result in a more accurate and a lower (than $\langle S \rangle = 0.02$) value of the average spin number $\langle S \rangle$.

5. NUMERICAL RESULTS FOR THE ELECTRON PAIR IN A CAVITY

We simulated two electron inside a spherical cavity with rigid walls and radius $L = 10$ Å in equilibrium with the thermal bath at temperature T ($300 < T < 2000$ K). Simulation conditions correspond to intermediate degree of degeneracy — the thermal de Broglie wave length is comparable with the mean distance between electrons. Electrostatic interaction of electrons is presented by the Coulomb potential thus rigorously accounting for interelectronic correlations. Feynman trajectories included $K = 40$ vertices for each electron that corresponds to the mean distance between the neighbouring (along the chain) vertices $\overline{\Delta r} = \lambda/(2\pi K^{1/2}) = (0.5 \div 1)$A.

Correct control of the discretized approximation is based upon the smallness of the contributions in the potential part of the energy in G (the managing weight function (11) in the exponent (10)) proportional to the square of $\overline{\Delta r}$:

$$\beta \delta^2 G \langle (1/2)\, d^2 u(r)/dr^2 |_{r=\bar{r}} (\overline{\Delta r})^2/(kT) = 0.01 \div 0.005, \tag{17}$$

where $u(r)$ — Coulomb potential and $\bar{r} = 10 \div 15$ Å — has an order of the mean distance between electrons.

For estimation of the statistical error of averages $\langle F \rangle$ caused by finite sampling the Markov chain was divided into equal intervals ($n = 10$) and partial averages $\langle F \rangle_i$ were calculated. The error for $\langle F \rangle$ was estimated in the usual way:

$$\delta \langle F \rangle = ((\langle \langle F \rangle_i^2 \rangle - \langle \langle F \rangle_i \rangle^2)/(n-1))^{1/2}. \tag{18}$$

The mixed spin state of the system is characterized by the mean square of spin (Figure 1, Table 1). The greatest rate of spin "pairing" while cooling of the system occurs at about $T = 500$ K for which the thermal wave length $\lambda \simeq 3.3\,\bar{r}$($\bar{r}$ – 12 Å — the mean interelectron distance). For $T = 2000$ K (Figure 1) the spin of the system differs from its high temperature limit ($(3/2)^{1/2}\hbar$) within 1.5 %. Hence at the degeneracy edge $\lambda = \bar{r}(T = 4000\,\mathrm{K})$ this difference should be practically negligible. It is evidently caused by weak wave function overlapping as a result of repulsive Coulomb correlations of electrons. The mean square of spin appears to be higher compared with the case of noninteracting particles — coupling of the magnetic moments occurs at lower temperatures.

Paramagnetic susceptibility (Figure 2, Table 1) passes through maximum at temperature $T = 650$ K ($\lambda = 2.5\,\bar{r}$). For $T \rightarrow 0$ it falls to zero due to coupling of magnetic moments in the singlet state; at $T \rightarrow \infty$ it asymptotically follows the conventional paramagnetic dependence $1/T$ for distinguishable particles. The statistical error

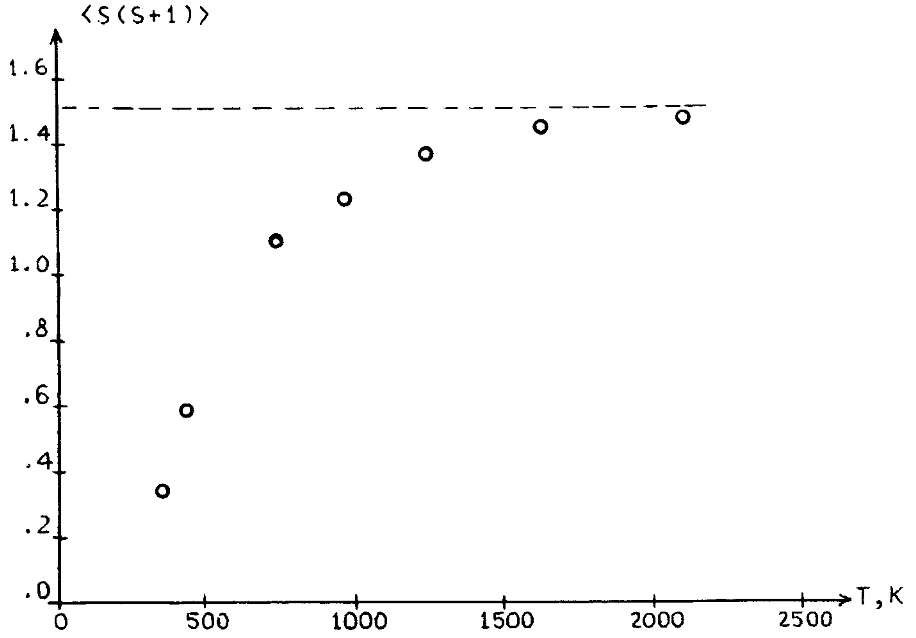

Figure 1 Temperature dependence of the mean square of spin for the electron pair in the spherical cavity with the radius $L = 10$ Å in the heat bath.

in calculations of spin and of magnetic susceptibility grows with the decrease of T; so for $T < 300$ K it was already difficult to obtain reliable results and another simulation scheme should be used in this region.

The magnetic permittivity of the corresponding macrosystem can be calculated from κ in the usual way — $\mu = 1 + \rho\kappa$ where ρ is the number of the electron pairs in the unit volume.

Our temperature dependence for κ with the maximum, Figure 2, qualitatively corresponds to paramagnetic susceptibility experimental data [17] for electrides. The difference is in the temperature scale — experimental curve has its maximum at

Table 1 Temperature dependences for the electron pair in the spherical cavity with radius $L = 10$ Å. $\langle S(S+1)\rangle$ — mean square of spin, $\langle K\rangle$ — mean kinetic energy, $\langle U\rangle$ — mean potential energy, κ — zero field paramagnetic susceptibility, α — electrical polarizability.

T, K	$\langle K\rangle$ (eV)	$\langle U\rangle$ (eV)	$\langle S(S+1)\rangle$	$\kappa\,10^3$ (Å^3)	$\alpha\,10^{-3}$ (Å^3)
338	0.65 ± 0.01	1.242 ± 0.004	0.34 ± 0.06	11 ± 2	0.99
439	0.75 ± 0.01	1.250 ± 0.005	0.58 ± 0.06	14 ± 1	0.95
742	0.85 ± 0.02	1.286 ± 0.006	1.10 ± 0.06	15 ± 1	0.82
965	0.92 ± 0.02	1.304 ± 0.006	1.23 ± 0.02	13.3 ± 0.2	0.79
1255	1.02 ± 0.03	1.304 ± 0.007	1.37 ± 0.01	11.4 ± 0.1	0.78
1631	1.03 ± 0.04	1.327 ± 0.005	1.446 ± 0.004	7.25 ± 0.03	0.76
2121	1.21 ± 0.05	1.329 ± 0.007	1.478 ± 0.002	7.27 ± 0.01	0.74

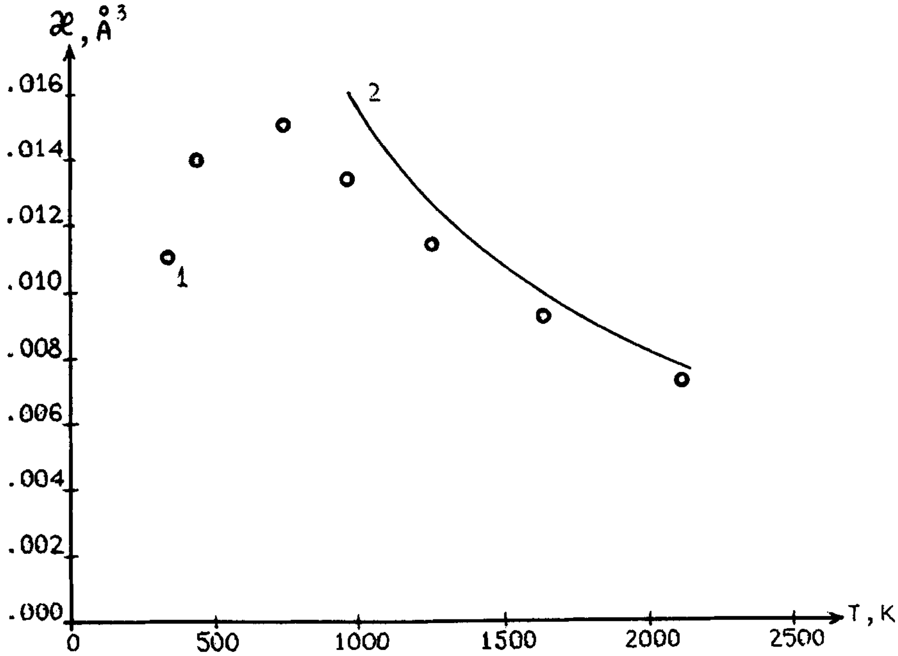

Figure 2 Temperature dependence for the zero field spin paramagnetic susceptibility of the electron pair: 1 — present PIMC simulation; 2 — classical paramagnetic curve for distinguishable particles.

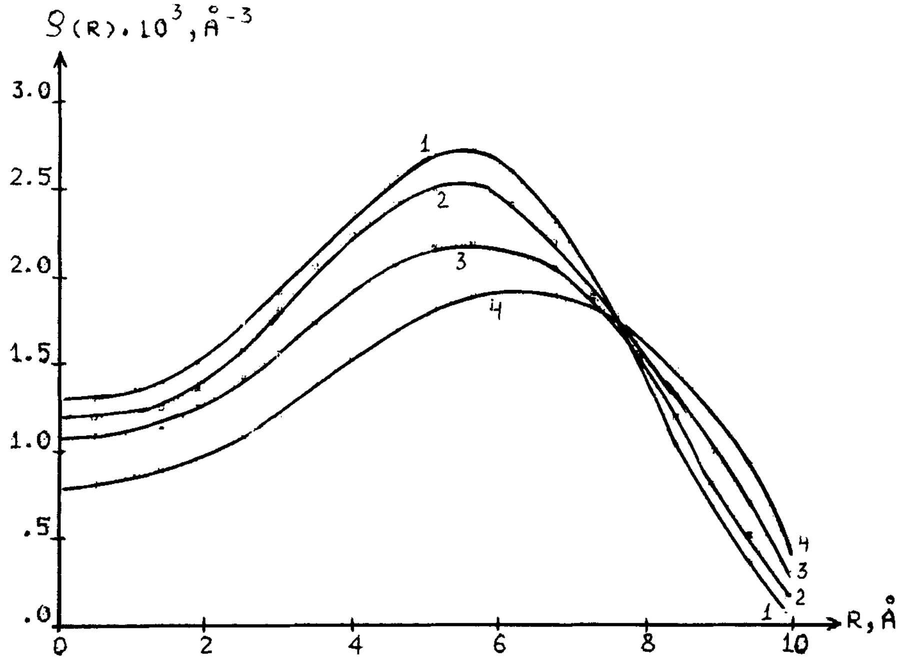

Figure 3 Electron density as a function of distance from the centre of the sphere (normalized on the number of electrons, $N = 2$). Values of temperature in Kelvins: 1 — 1631; 2 — 742; 3 — 338, 4 — 200.

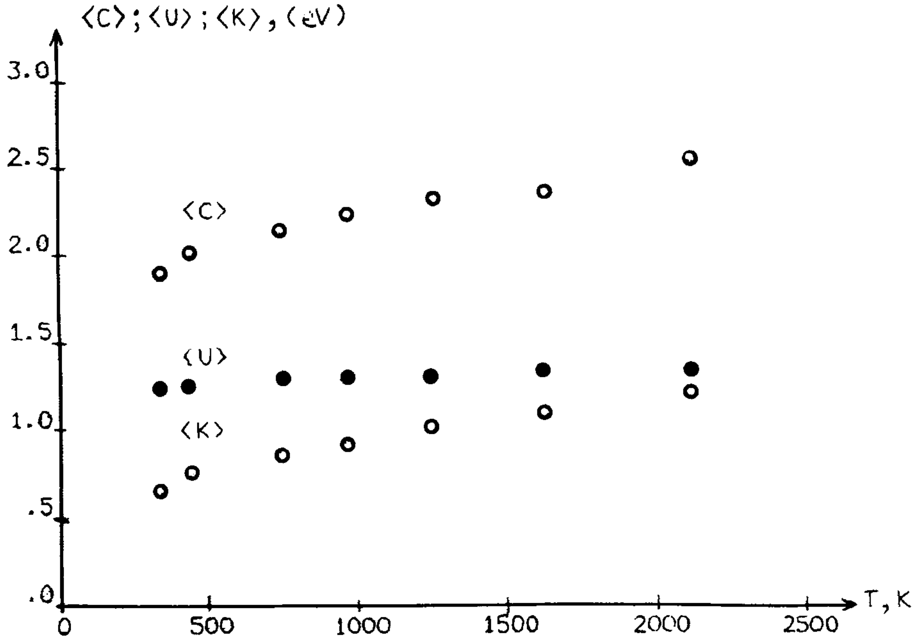

Figure 4 Temperature dependence for canonical averages of energies for the electron pair: total, $\langle C\rangle$ potential, $\langle U\rangle$, kinetic, $\langle K\rangle$.

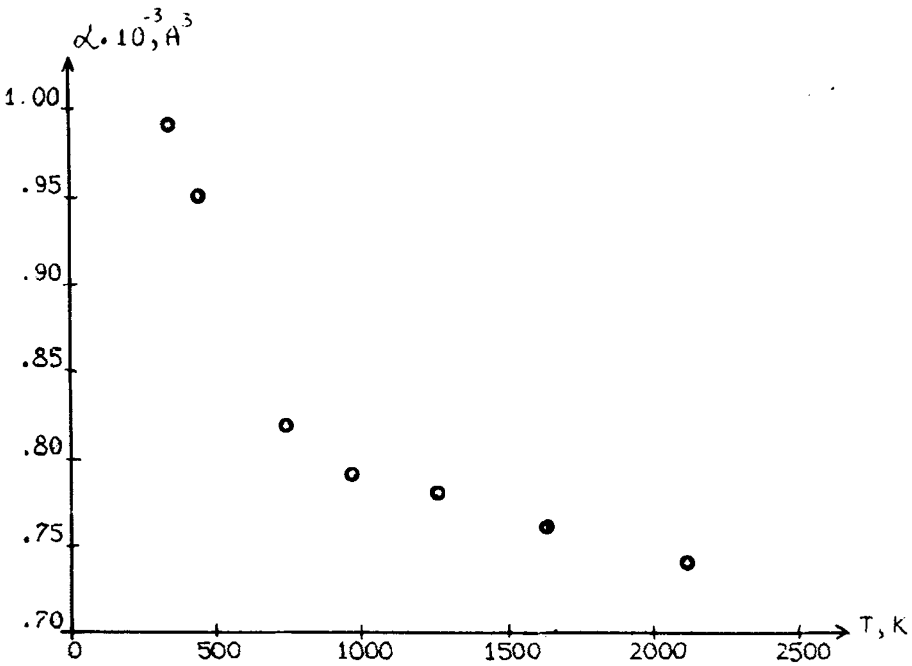

Figure 5 Temperature dependence for the zero field electrical polarizability of the electron pair.

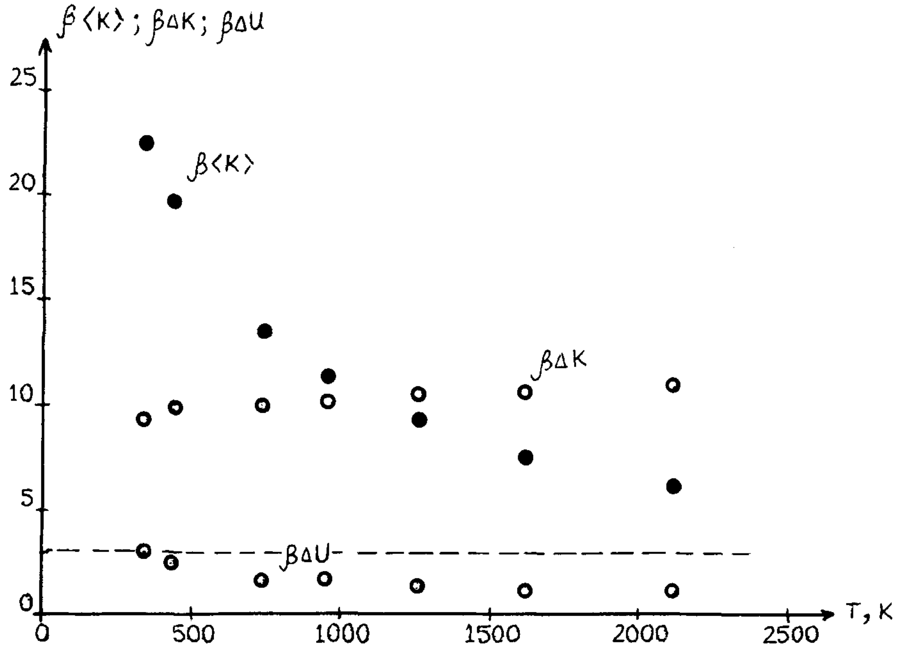

Figure 6 Temperature dependence for mean square deviations of kinetic, ΔK, and potential, ΔU, energies in kT units. Mean kinetic energy, $\langle K \rangle$, is also shown.

$T \sim 20$ K while in our case it is at $T \sim 700$ K. The cause is in the size and profile of cavities and in other possible factors (external electric field existing in the experimental systems). In this study we do not attempt to reproduce specific experimental parameters but rather try to demonstrate facilities of the method which then can be readily applied to simulation of electron systems in specific conditions.

On Figure 3 electron radial distribution functions inside the sphere are presented. The area of low density in the centre is caused by Coulomb repulsion of electrons. The dependence of the electron density profiles on temperature testifies that "pairing" of spins does not denote mutual localization of electrons in space. On the contrary, with the decrease of temperature electron density maximum is shifted to the periphery — the mean distance between electrons increases (though insignificantly) that is confirmed by the temperature behavior of the electron interaction energy (Figure 4, Table 1). Total energy $\langle C \rangle$ is decreasing with the fall of temperature mainly on the account of its kinetic part $\langle K \rangle$.

Parallel to the decrease of the magnetic susceptibility with $T \to 0$ the polarizability $\alpha = d\langle p \rangle / dE|_{E=0}$ (p-induced dipole moment, E — external electric field) is increasing, tending to the finite limiting value of about 1.1 10^3 Å^3 (Figure 5, Table 1). For $T < 700$ K its temperature dependence becomes more steep, that probably is associated with the transition to the singlet state as a result of the symmetry of the wave function.

The mean square deviation for the main kinetic energy estimator ΔK has an almost linear dependence on temperature ($\beta \Delta K$ is almost constant, Figure 6) while the kinetic energy itself tends to a finite limite as $T \to 0$; so the relative fluctuation of the main estimator lowers with the decrease of temperature. It is seen on Figure 6 that in the investigated temperature interval (up to 2000 K) kinetic energy is several times higher than its classical limit $(2(3/2)kT)$ that testifies the essentially quantum behavior of the system even after decoupling of the electron spins.

6. CONCLUSION

We have discussed the PIMC method for calculation of magnetic and other equilibrium characteristics of an N-electron system in a heat bath with an explicit and correct account of permutational symmetry and Coulomb interaction. The case of two electrons was then presented in detail and the corresponding PIMC procedure was tested on the hydrogen molecule. For an electron pair in a cavity detailed calculations of zero field magnetic susceptibility and other canonical properties were carried out. It should be stressed that for a system of two fermions the situation appears to be much simplified (compared with the general case of $N > 2$). The general case requires a special and detailed presentation which we plan to make in future publications.

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