

CONF-830233--1

Final

CONF-830233--1

DE83 014736

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May 1983

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For proceedings of Conference on "Monte Carlo Methods in Quantum Problems"
Edited by Prof. M. Kalos, N.Y. University, held in Orsay, France, Feb. 9-11,
1983, Sponsored by C.E.C.A.M. (European Center for Atomic and Molecular
Calculations)

* Work supported in part by the U.S. Department of Energy and by the Italian
Ministry for Public Education.

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STUDY OF AN F CENTER IN MOLTEN KCl*

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ABSTRACT

It is shown that a discretized version of Feynman's path integral provides a convenient tool for the numerical investigation of the properties of an electron solvated in molten KCl. The binding energy and the pair correlation functions are calculated. The local structure around the solute electron appears to be different from that of an F center in the solid.

I. INTRODUCTION

Solutions of alkali metals in their liquid halides (M-MX) display an intriguing variety of behavior as a function of temperature and concentration.(1,2) In the present investigation we shall restrict our attention to extremely small concentration of metals. The most accepted picture in this dilute limit is that the added metal atom dissociates into M^+ and e^- . Based on a variety of different experiments a model has been proposed which is known as the F center model.(3) The physical picture underlying the model is that the e^- substitutionally occupies in the liquid structure, the place of an X^- . This, of course, parallels what occurs in solid alkali-halides where the occurrence of F centers is a well known and well studied phenomenon.(4) However, in the liquid state, particles are not only

*Work supported in part by the U.S. Department of Energy and by the Italian Ministry for Public Education.

free to relax but they can also diffuse and the local environment around the solute electron can be substantially different from that in a solid. A theoretical approach to the problem presents great difficulties since quantum mechanics and statistical physics are here interwoven in a complicated way. However a discretized version of Feynman's path integral formulation of quantum statistical mechanics(5) may provide a convenient framework for solving this problem. This approach has been pioneered by Fosdick and coworkers(6) and more recently has attracted considerable interest from the numerical and theoretical point of view.(7-11) In this scheme the quantum problem is shown to be isomorphic to an appropriate classical problem. In our case the solvated electron is mapped onto a closed flexible polymer of P points. The isomorphism becomes more and more exact as $P \rightarrow \infty$. Such a limit cannot be taken on the computer, thus the practical applicability of the method relies heavily on the possibility of achieving convergence with a manageable value for P . It is the purpose of this note to report a preliminary study of the convergence of the method when applied to a model for a single electron in molten KCl. We have calculated the binding energy of the electron as well as the pair correlation between the electron and the ions in the molten solvent. In a more detailed paper we shall present data related with the effect of the e^-K^+ potential; there we will also present a compelling justification for the F center model(3) of e^- in molten salts by showing the details of the hole digging process. We are also in the process of calculating the diamagnetic susceptibility of the electron and the behavior of 2 electrons in the molten salt system.

II. THE ISOMORPHISM

Let us first consider the case of a single electron in an external potential $\phi(\underline{r})$. The partition function for such a system is:

$$Z = \text{Tr } e^{-\beta H} \quad , \quad (1)$$

where $H = -\frac{\hbar^2}{2m} \nabla^2 + \phi(\underline{r})$ and $\beta = 1/k_B T$ is the inverse temperature. Eqn. (1) can be rewritten as:

$$Z = \text{Tr } (e^{-\beta H/P})^P \quad . \quad (2)$$

Inserting P complete sets of states Eqn. (2) becomes:

$$Z = \int d\underline{r}_1 \dots d\underline{r}_P \langle \underline{r}_1 | e^{-\beta H/P} | \underline{r}_2 \rangle \dots \langle \underline{r}_P | e^{-\beta H/P} | \underline{r}_1 \rangle . \quad (3)$$

Eqn. (3) is of course exact but impractical. To proceed further one has to make the high temperature expansion:

$$\langle \underline{r}_1 | e^{-\beta H/P} | \underline{r}_2 \rangle = \rho_0(\underline{r}_1, \underline{r}_2; \beta/P) e^{-\beta[\phi(\underline{r}_1) + \phi(\underline{r}_2)]/2P}, \quad (4)$$

where $\rho_0(\underline{r}_1, \underline{r}_2; \beta/P)$ is the free particle propagator relative to the temperature β/P :

$$\rho_0(\underline{r}_1, \underline{r}_2; \beta/P) = (Pm/2\pi\hbar^2\beta)^{3/2} e^{-Pm(\underline{r}_1 - \underline{r}_2)^2/2\hbar^2\beta}. \quad (5)$$

Inserting Eqn. (4) into Eqn. (3) one finds for Z the approximate expression

$$Z = Z_P = (Pm/2\pi\hbar^2\beta^2)^{3P/2} \int d\underline{r}_1 \dots d\underline{r}_P e^{-\beta V_{\text{eff}}(\underline{r}_1, \dots, \underline{r}_P)}, \quad (6)$$

with

$$V_{\text{eff}}(\underline{r}_1, \dots, \underline{r}_P) = \sum_{i=1}^P \left\{ \frac{Pm}{2\hbar^2\beta^2} (\underline{r}_i - \underline{r}_{i+1})^2 + \frac{1}{P} \phi(\underline{r}_i) \right\}. \quad (7)$$

In the above equation it is understood that in the first summation when $i = P$, $\underline{r}_{P+1} \equiv \underline{r}_1$ and a similar convention will be adopted throughout the paper. This periodic condition reflects the fact that the trace has to be taken in evaluating Z. Equation (6) and (7) establish an approximate isomorphism between the original quantum problem and the classical problem defined by Eqn. (7). In this isomorphism the quantum particle is mapped onto a flexible closed chain polymer or necklace. Each point on the necklace interacts with its first neighbors in the chain through a harmonic potential of spring constant $Pm/\hbar^2\beta^2$ and with the external potential through the appropriately scaled potential $\phi(\underline{r})/P$.

The accuracy of the isomorphism increases with the value of P and in the limit one has:

$$Z = \lim_{P \rightarrow \infty} Z_P. \quad (8)$$

In practical applications of the isomorphism P is a finite number such that

$$Z \approx Z_P. \quad (9)$$

At high temperature and/or for smooth potentials Eqn. (9) can be satisfied with a manageable value for P.

Neglecting exchange, the isomorphism is easily generalized to the many particle case of N quantum particles and the effective classical potential reads in this case:(12)

$$\begin{aligned}
V_{\text{eff}} = & \sum_{\nu=1}^N \sum_{i=1}^P P m (\underline{r}_{-i}^{\nu} - \underline{r}_{-i+1}^{\nu})^2 / 2\hbar^2 \beta^2 \\
& + \sum_{\nu > \mu}^N \sum_{i=1}^P \psi_{\nu\mu} (\underline{r}_{-i}^{\nu} - \underline{r}_{-i}^{\mu}) / P \\
& + \sum_{\nu=1}^N \sum_{i=1}^P \phi_{\nu} (\underline{r}_{-i}^{\nu}) / P ,
\end{aligned} \tag{10}$$

where \underline{r}_{-i}^{ν} is the i -th point of the necklace onto which the ν -th quantum particle has been mapped, $\psi_{\nu\mu}(\underline{r})$ is the interparticle potential between the quantum particles ν and μ , and $\phi_{\nu}(\underline{r})$ is the external potential felt by particle ν .

Once the isomorphism has been established one has to find ways of calculating the quantities of interest. Such quantities are represented in quantum theory by operators and it is by no means obvious how operators can be expressed in the classical isomorphism. (9) Let us consider first the energy E . In principle it can be evaluated from the exact relation:

$$E = - \frac{\partial}{\partial \beta} \ln Z . \tag{11}$$

Substituting Z_p for Z , this leads to: (4)

$$\begin{aligned}
E = & 3P/2\beta - P m \left\langle \sum_{i=1}^P (\underline{r}_{-i} - \underline{r}_{-i+1})^2 \right\rangle / 2\hbar^2 \beta^2 \\
& + \sum_{i=1}^P \langle \phi(\underline{r}_{-i}) \rangle / P ,
\end{aligned} \tag{12}$$

where the averages are taken over the Boltzman distribution defined in Eqns. (6) and (7). The last term in Eqn. (12) can be clearly identified with the average potential energy. Thus one finds for the kinetic energy the following estimator:

$$K = 3P/2\beta - P m \left\langle \sum_{i=1}^P (\underline{r}_{-i} - \underline{r}_{-i+1})^2 \right\rangle / 2\hbar^2 \beta^2 . \tag{13}$$

This estimator for K , though formally exact for $P \rightarrow \infty$, has two major numerical disadvantages. It gives K as the difference between two large quantities and its variance grows with P . The way out from this difficulty has been suggested in a paper by

Herman et al., (9) where it is shown that by appropriate integration by parts Eqn. (13) can be reexpressed in the equivalent form

$$K = 3/2\beta + \left\langle \sum_{i=1}^P \frac{\partial \phi}{\partial r_i} \cdot \underline{r}_{iP} \right\rangle / 2P \quad (14)$$

$$= K_{\text{free}} + K_{\text{int}} ,$$

where \underline{r}_{iP} denotes $\underline{r}_i - \underline{r}_P$.

Equation (14) is obtained from the equality:

$$\frac{3}{2\beta} (P-1) - \frac{Pm}{2\hbar^2 \beta^2} \left\langle \sum_{i=1}^P (r_i - r_{i+1})^2 \right\rangle = \frac{1}{2P} \left\langle \sum_i \underline{r}_{iP} \cdot \frac{\partial \phi}{\partial r_i} \right\rangle, \quad (14')$$

which is a consequence of the integration by parts alluded to above. Note that the identity

$$\sum_i (\underline{r}_i - \underline{r}_P) \cdot (\underline{r}_i - \underline{r}_{i+1}) + (\underline{r}_i - \underline{r}_{i-1}) \cdot (\underline{r}_i - \underline{r}_{i-1}) \equiv \sum_i (\underline{r}_i - \underline{r}_{i+1})^2$$

is used in the derivation of these results. Note also that in Eqn. (14'), for the special case $\phi=0$ i.e., in the case of a free particle the two large terms on the left side exactly cancel each other. We will explicitly show in the following that Eqn. (14) is numerically more convenient form to use.

III. MODEL CALCULATION

We now turn to the description of the calculation that we have performed for a model of an electron solvated in KCl. In the model the ions K^+ and Cl^- that compose the melt are treated purely classically and interact through a Born-Meyer potential

$$\phi_{IJ}(r) = A_{IJ} e^{-r/\rho_{IJ}} + \frac{Z_I Z_J e^2}{r}, \quad (19)$$

and the parameters of the potential are those fixed by Fumi and Tosi. (12)

As to the interaction potential between the electron and Cl^- we have taken it to be purely Coulombic at all distances:

$$\phi_{eCl^-}(r) = \frac{e^2}{r}. \quad (20)$$

Equation (20) neglects all corrections due to repulsion from the

Cl⁻ core. Since an electron is already repelled by the Coulombic potential such corrections are expected to be of small consequence. In contrast core corrections are very important in the e-K⁺ interactions. These will be dealt with through the following local pseudopotential(13)

$$\begin{aligned}\phi_{eK^+}(r) &= -e^2/R \quad r \leq R \\ &= -e^2/r \quad r > R ,\end{aligned}\tag{21}$$

where quite tentatively we have taken $R = 1.96\text{\AA}$. While non-locality and other effects are of quantitative importance, the potential in Eqn. (21) has the merit of being slowly varying. This is instrumental in obtaining a rapid convergence of the isomorphism.

Summing up all the contributions the effective potential for the problem at hand becomes:

$$\begin{aligned}V_{\text{eff}} &= \sum_{i=1}^P P_m (r_{\underline{i}} - r_{\underline{i+1}})^2 / 2\hbar^2 \beta^2 \\ &+ \sum_{i=1}^P \sum_{J=1}^N \phi_{eJ}(r_{\underline{i}} - R_{\underline{J}}) / P \\ &+ 1/2 \sum_{I=1}^N \sum_{J=1}^N \phi_{IJ}(R_{\underline{I}} - R_{\underline{J}}) ,\end{aligned}\tag{22}$$

where the $R_{\underline{I}}$ are the ionic coordinates, ϕ_{eJ} and ϕ_{IJ} are defined in Eqn. (20), (21) and (19) respectively, and N is the total number of ions in the system. Statistical sampling of the classical problem defined by the potential in Eqn. (22) can be performed on a microcanonical ensemble. The numerical equivalence of the two procedures has been demonstrated in ref. 14. The microcanonical ensemble sampling is performed by averaging over the trajectories generated by the classical Hamiltonian

$$H = \sum_{i=1}^P \frac{1}{2} m^* \dot{r}_{\underline{i}}^2 + \sum_{I=1}^N \frac{1}{2} M_I \dot{R}_{\underline{I}}^2 + V_{\text{eff}} ,\tag{23}$$

where M_I are the ionic masses and m^* is some arbitrary mass attributed to the points on the necklace. The trajectories generated by H are obtained by employing the methods of constant pressure molecular dynamics (MD).(15) Strictly speaking, the

time trajectories thus obtained have no real meaning and are a mere computational device for exploring the properties of V_{eff} at various temperature density conditions. Furthermore, since this part of the calculation is merely classical the static properties obtained will be independent of the values of M_I and m^* . In the present calculation we have taken for M_I the ionic masses as it is natural to do, while fairly arbitrarily, we have put $m^* =$ one atomic unit of mass.

The calculations have been performed at 1000 K and 10.4 kb with 150 K^+ , 149 Cl^- and a varied number of P. As usual periodic boundary conditions were imposed; the long range nature of the Coulomb potential imposes consideration of the interaction between different images of the MD cell. This was handled by the Ewald method of summation. Some care is needed here since the isomorphism described in sec. II leads to peculiar rules for the interaction between different points on the necklace; see Eqn. (10). When these are taken into account we find for the total Coulomb energy of the system:

$$V_{\text{Coulomb}} = 1/2 \sum_{I=1}^N \sum_{J=1}^N \sum_{\underline{v}}' z_I z_J e^2 / |R_I - R_J + \underline{v}|$$

$$- \sum_{i=1}^P \sum_{J=1}^N \sum_{\underline{v}} e^2 z_{J/P} / |r_i - R_J + \underline{v}| + 1/2 \sum_{\underline{v} \neq 0} e^2 / |\underline{v}|,$$
(24)

where \underline{v} runs over all the translations of the MD cell and the prime in the summation over \underline{v} implies exclusion of the term $I = J$ if $\underline{v} = 0$.

For later purposes we introduce the Coulomb interaction for the electron:

$$V_{eI} = V_{\text{Coulomb}} - V_{II},$$
(25)

where V_{II} , the interionic Coulomb potential is given by the first term in Eqn. (24), made convergent by the introduction of a charged background of density $-e/\Omega$, Ω being the MD cell volume. This definition of V_{eI} implies that we measure the electronic energy relative to a state in which the electron is uniformly spread over the whole volume. In the language of quantum mechanics this corresponds to a plane wave state of infinite wavelength. The sums in Eqn. (24) and (25) have been evaluated by the usual Ewald method.

IV. THE KINETIC ENERGY ESTIMATOR AND THE BINDING ENERGY OF THE ELECTRON

As seen from Eq. (13), in the limit of large P the kinetic energy of the electron is obtained by taking the difference between two large numbers. In the special case of a free particle, by calculating the "necklace energy" i.e., the 2nd term on the right side of Eqn. (13) one learns that the condition of the necklace closing on itself gives the value $3(P-1)/2\beta$ to the necklace energy and hence $K = 3/2\beta$.

When an analytical solution of the type alluded to above is not possible and Eqn. (13) is used in making numerical estimates difficulties will arise because both terms in Eqn. (13) grow with increasing P. This is obviously not the case when Eqn. (14) is used for estimating K. Note that in Eqn. (14) we see a separation of the kinetic energy into physically meaningful parts. The first term is the free particle contribution and the second due to the interaction of the electron with the medium.

Table I. Value (variance) of e^- kinetic energy (Ryd. units) estimator calculated according to Eq. (13) and Eq. (14). $3/2\beta = .0095$ Ryd. The last three rows correspond to 3 independent calculations with $P=201$.

P	$P[3/2\beta - \langle \Sigma \rangle]$	$\frac{1}{2P} \langle \Sigma \frac{\partial \phi}{\partial r_i} \cdot \underline{r}_{iP} \rangle$
12	.091 (.008)	.077 (.024)
25	.100 (.022)	.103 (.026)
50	.109 (.034)	.108 (.024)
100	.120 (.050)	.111 (.029)
201	.142 (.031)	.095 (.027)
201	.118 (.055)	.099 (.028)
201	.113 (.071)	.095 (.029)

In Table I we show the values of K when it is calculated using Eqn. (13) and also K_{int} appearing in Eqn. (14); in each case we also show the variance. It is clear that the kinetic energy estimator in Eqn. (14), i.e., K_{int} , has a variance independent of P. This is not so for the variance of the kinetic energy calculated from Eqn. (13).

From Eqns. (12) and (22) we see that in our model system the potential energy of the electron is to be identified with the average

$$V_{\text{int}} = \left\langle \sum_{i=1}^P \sum_{I=1}^N P^{-1} \phi_{eI} (r_i - R_I) \right\rangle, \quad (26)$$

where ϕ_{eI} depending on whether I is K^+ or Cl^- is given by Eqn. (21) or Eqn. (20) respectively.

Table II: Value (variance) of e^- kinetic and potential energy (Ryd. units). The sum is also shown.

P	K · E	P · E	B · E
12	.087(.024)	-.549(.068)	-.462
25	.113(.026)	-.417(.054)	-.304
50	.118(.024)	-.401(.050)	-.283
100	.121(.029)	-.396(.062)	-.275
201	.104(.027)	-.413(.069)	-.309
201	.108(.028)	-.428(.032)	-.320
201	.105(.029)	-.445(.043)	-.340

In Table II is shown the kinetic energy $3/2\beta + K_{\text{int}}$, the potential energy V_{int} of Eqn. (26), and the sum of the two which we refer to as the binding energy.

We notice from Tables I and II that except for $P=12$ all other values of P give a consistent set of values for the energy of the electron. We therefore believe that calculations with $P=100$ or 201 are reliable from the point of view of the convergence with respect to P . The uncertainties are statistical and are related to the lengths of runs and other factors that are an inherent part of all such computer simulations.

In this content the questions of the 'correct' estimator is still open inspite of the data in Table I. As has been reported by Jacucci(8) in this volume the persistence of correlations in long Monte Carlo or molecular dynamics chains of configurations can alter, in rather unexpected ways, the above apparently obvious conclusions about estimators and their variances.

V. SOLVATION SHELL AROUND e^- DESCRIBED THROUGH PAIR CORRELATIONS

For an F center in solid KCl, i.e., an e^- trapped at a Cl^- vacancy, the geometrical description of the surroundings of the e^- presents neither any difficulty or challenge. The e^- is surrounded by 6 K^+ ions in an octahedral configuration and then by 12 Cl^- etc. Of course the relaxation of the mean thermal positions away from the ideal lattice sites of the surrounding ions is an interesting problem, specially in its dependence on temperature and on the assumed e^-K^+ pseudopotential.

For an e^- in liquid KCl however one has to adopt procedures borrowed from the well established methods of analysis in terms of pair correlation functions to describe the solvation shell of K^+ ions around the e^- cloud.

The formal procedures, using functional derivations, has been given by Chandler and Wolynes.(10) The pair correlation between e^- and K^+ , to be written $g_{e^-K^+}(r)$ is simply a suitably normalized average $\langle n_i^i \rangle$ where n_i^i , in a given configuration, is the number of K^+ in a shell of radius $r = (\ell-1)\Delta r$ and thickness Δr around a prescribed point i on the electron necklace. $\langle \rangle$ of course denotes averaging over configurations.

In fact since all the points on the necklace are statistically equivalent there is an enormous gain in efficiency in averaging further over all points of the necklace. Thus we get

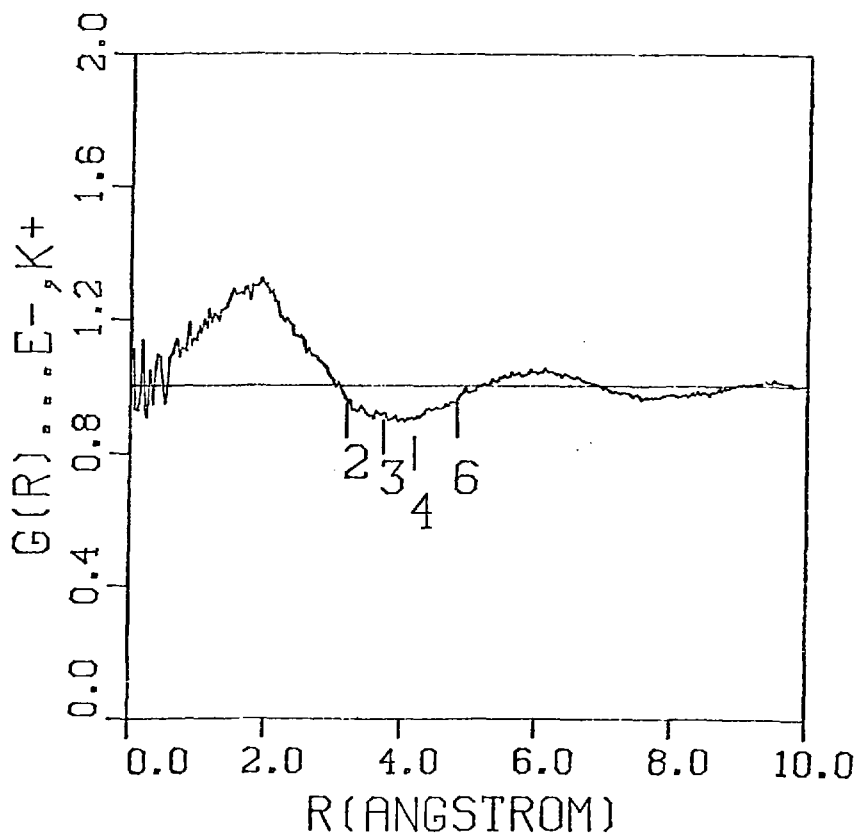


Fig. 1. Solvation shell structure around the electron. The core radius in e^-K^+ pseudopotential is 1.96Å. The coordination number is estimated to be between 3 and 4.

$$\langle n_\ell \rangle = \frac{1}{P} \sum_i \langle n_\ell^i \rangle = 4\pi r^2 \Delta r N^+ / \Omega g_{e^-, K^+}(r), \quad (27)$$

where $r = (\ell-1) \Delta r$ and N^+ / Ω is the number density of K^+ ions in the system. The coordination number up to distance $s = \sigma \Delta r$ will then be

$$N(s = \sigma \Delta r) = \sum_{\ell=1}^{\sigma} \langle n_\ell \rangle \quad (28)$$

The function g_{e^-, K^+} is shown in Fig. 1. The values of $N(s)$ is also shown in a suitable manner. For comparison g_{Cl^-, K^+} is shown in Fig. 2. It is clear that the coordination number in Fig. 2 is clearly 6 as is to be expected in molten KCl but in Fig. 1 it is definitely less than 6 and is closer to 4. Thus we conclude that (for the case of $R = 1.96 \text{ \AA}$ in the pseudopotential) the coordination number is tetrahedral rather than octahedral. However this average coordination number is itself an average of a distribution of coordination numbers. This is being studied and it appears that in this distribution of coordination numbers up to the distance 4 \AA there may very well be a peak at 3 and a longish tail with larger values giving an average of 4.

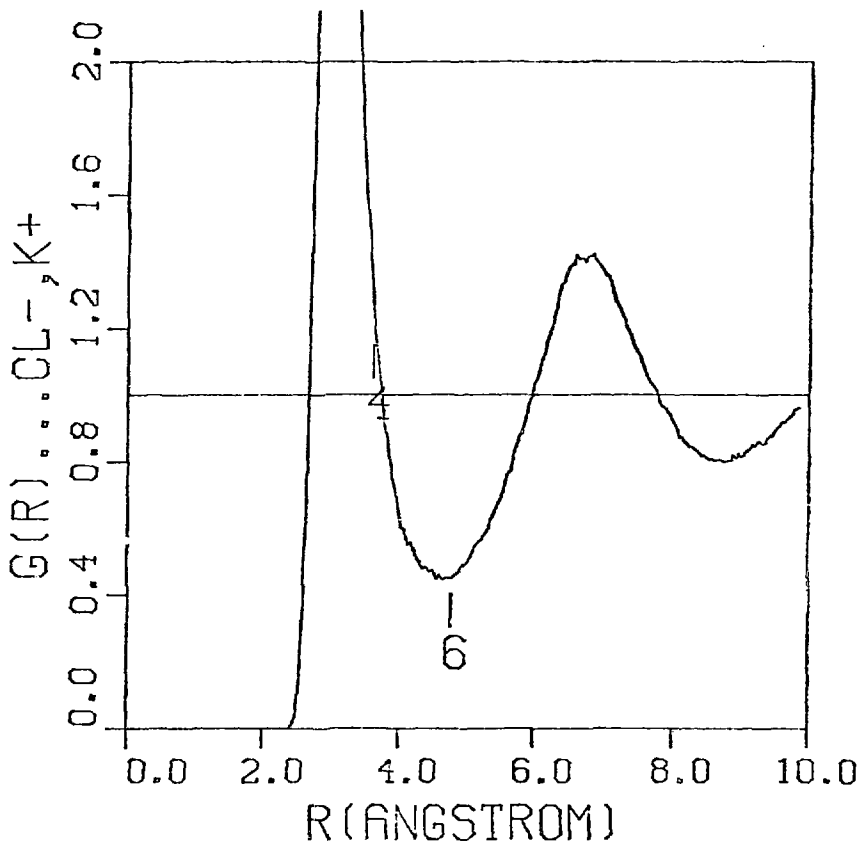


Fig. 2. Cation-anion pair correlation.

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