GEOMETRICAL PERSPECTIVES OF A SOLVATED ELECTRON

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The path integral formulation of quantum theory provides a framework to describe the behavior of solvated electrons. Feynman used the approach to treat the slow moving electron in ionic crystals -- the prototypical polaron problem. We have extended this theory, drawing on theories of the liquid state, to analyze the localization transition and related phenomena found with excess electrons in fluids.

Excess electrons in liquids exhibit a strikingly wide variety of behaviors. For example, the mobilities of e\(^-\) in two very similar liquids, neo- and normal pentane, differ by a factor of 500. To understand this variability -- akin to phase transition behavior -- it is helpful to transcribe the physical issues into those of a mathematically isomorphic problem, that of a classical Gaussian ring polymer dissolved in the liquid as illustrated in Fig. 1. This isomorphism is derived from the Feynman path integral formulation of quantum mechanics (Feynman and Hibbs, 1965; Feynman, 1972). Wolynes and I have written at length about this isomorphism (Chandler and Wolynes, 1981). A tutorial is given in my 1984 article (Chandler, 1984). This paper outlines my lecture reviewing the principal ideas and some of the literature pertaining to this approach. It is a recent and very rapidly growing literature.

The units (or beads) of the isomorphic ring polymer (or necklace) correspond to the possible positions of the single quantal electron. That is, the configuration of the isomorphic necklace corresponds to a quantum path of the electron. Farrinello and Rahman (1984) used this perspective in their study of the solvated electron in molten potassium chloride. Their simulation calculations illustrate the power of this methodology in studying the transition between extended and self-trapped states. Many groups have followed. For example, Klein and coworkers
Fig. 1. Electron "polymer" in a fluid of classical atoms.

have examined e− in liquid ammonia (Sprik et al., 1985), Schnitker and Rossky (1987) have studied e− in water, Berne and coworkers have studied e− in water clusters (Wahlqvist et al., 1986), and also in the nonpolar liquids helium and xenon (Coker et al., 1987). In the latter cases, the results are well understood in terms of the hard-sphere models studied earlier by Klein and coworkers (Sprik et al., 1985; Laria and Chandler, 1987). These examples are not all inclusive, but serve to illustrate the recent activity in this area.

When studying this literature, the reader should be aware of a significant detail that must be addressed before one can be confident with the accuracy of the simulation results. In particular, the isomorphic polymer becomes an exact representation only in the limit of a continuum of points on the ring. A discrete number of beads is an approximation to path integrals analogous to numerical quadrature of ordinary integration. As with ordinary integration, one must devise checks of the accuracy of discretization; further, to accurately approach the continuum limit, efficient numerical procedures are often crucial in the implementation. The so-called "staging" algorithm introduced by Sprik et al., (1985) was historically the first application of a new algorithm to the path integral study of the solvated electron. A modification of that procedure was adopted with great success by Coker et al., (1987), and in their application to helium, they describe inaccuracies of earlier work which did not correctly approach the continuum limit.

By examining through simulation the structures of the isomorphic polymers, researchers gain a geometrical perspective of electronic states in a liquid environment. It is a perspective that Feynman usefully exploited long ago in his treatment of the slow moving electron in an
ionic crystal -- the original polaron problem (Feynman, 1955; Feynman and Hibbs, 1965; Feynman, 1972). It is a perspective very different than the earlier theories created by Jortner, Rice, Cohen and others in their treatments of electrons in liquids (Davis and Brown, 1975; Jortner and Kestner, 1973; Kevan and Webster, 1976).

The interpretation of the new simulations have been guided by analytical theory and its focus on a particular class of correlation functions. In particular, the analysis of the electronic structure is conveniently described in terms of the mean square displacement

\[ R^2(t-t') = \langle |\xi(t) - \xi(t')|^2 \rangle \]

\[ = \sum_n A(Q_n) \left\{ 1 - \cos [Q_n(t-t')] \right\}, \quad Q_n = 2\pi n/\beta \kappa. \quad (1) \]

Here, \( \xi(t) \) is the position on the path of the electron at the imaginary time \( t \). (Imaginary time in quantum theory corresponds to real time for the classical isomorphic system.) The periodicity of the polymer implies the quantized frequencies, \( Q_n \). On analytical continuation, \( A(i\omega) = \Phi(\omega) \), where \( \omega\Phi'(\omega) \) is the absorption spectrum for the electron (Baym and Mermin, 1961).

Approximate theoretical calculations based on the RISM-polaron theory (Chandler et al., 1984) have shown how the behavior of \( R^2(t-t') \) provides the signature of self trapped localization and the dominance of a ground state (Nichols et al., 1984; Nichols and Chandler, 1986; Malescio and Parrinello, 1987). These behaviors as predicted by the theory have been observed in simulation work as well (Sprik et al., 1985; Schnitker and Rossky, 1987; Coker et al., 1987; Sprik et al., 1985). The connections between ground state dominance and low mobility and other spectral features have been analyzed with theory (Nichols and Chandler, 1987), but here simulation work has not yet proved entirely successful. In the real time domain, the sampling of quantum paths involves oscillating positive and negative weights which are problematic for any currently known Monte Carlo procedure. Thus we must await new developments in time-dependent path integral quantum Monte Carlo.

The mechanism for self trapped localization is treated in the RISM-polaron theory in terms of the influence functional contribution to the action:

\[ S_{\text{inf}} = \frac{1}{2} \int_0^\beta \frac{\delta \Phi}{\delta t} \int_0^\beta \frac{\delta \Phi}{\delta t'} \nu[\xi(t) - \xi(t')] dt dt', \quad (2) \]

where \( \nu[\xi(t) - \xi(t')] \) has the diagrammatic structure of a reaction field or self energy,
\[ v(\xi - \xi') = \frac{(\xi - \xi')}{r - r'} \]

(The reader may consult my first lecture in this volume for the meaning of this picture.) With the convolution theorem, we can consider separately the different wave vector contributions to \( v(\xi - \xi') \). Each is proportional to the response function or density-density correlation function, \( \chi \), at that particular wave vector. Thus, we arrive at the familiar physical picture that confinement or localization is a measure of the disorder in the material. The RISM-polaron theory adds to this picture, in that it provides the quantitative means for estimating the importance of different types of randomness in a topologically disordered system within the context of a single theoretical approach.

There is still much to be done before this theory, and also the recent simulation work, will provide fully satisfactory descriptions of the experimental phenomena. To date, few realistic systems and few experimentally observed properties have been analyzed. There are unresolved and important issues concerning the correct single-electron or pseudo-potential models for electron-solvent particle interactions. Perhaps an even more difficult and significant issue is that of analytic continuation. Without its resolution, computer simulation studies will be limited to the analysis of equilibrium structural properties, and only the more approximate theoretical approaches will provide information about dynamics.

REFERENCES


