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Localization, Hopping, and Diffusion of Electrons in Molten Salts

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The electronic states and dynamical properties of dilute liquid K-KCl solutions are studied by simultaneous integration of the coupled time-dependent Schrödinger equation for the excess electrons and classical equations of motion for the ions. Excess electrons are found to spend most of their time in localized F-center states, whose size and shape can fluctuate significantly. Transport is mostly due to jumps between localized states, with a jumping rate $\simeq 3\times10^{12}\ \mathrm{s}^{-1}$. The optical excitation spectrum and the electron diffusion coefficient are calculated and found to be in agreement with the experimental data.

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Recent theoretical and experimental efforts have focused on the properties of electrons dissolved in molten alkali halides in the limit of extremely high dilution.[1] The validity of the F-center model, in which the electron sits in a fluid cavity surrounded mostly by cations, has been proved by several experimental findings.[2] Numerical path integral (PI) calculations have confirmed the F-center model and clarified the nature of the electronic states.[3] This numerical method, however, does not provide information on the dynamics of the electrons. The experimental NMR and conductivity data are consistent with a picture in which the electron hops between different localized states.[1,4] However, no universal consensus on a model for the solvated-electron dynamics has yet emerged. In order to clarify this issue we introduce here an approach which can be very useful for the study, within the adiabatic approximation, of static and dynamical properties of many-body systems containing a few quantum degrees of freedom. In particular we show that it is possible to obtain quantitative information on the optical spectrum and the diffusion process of the excess electrons.

We adopt a mixed quantum-classical approach in which the electron is described by its wave function $\psi(\mathbf{r},t)$ and the ions by their positions $\{\mathbf{R}\}$. The time evolution of $\psi(\mathbf{r},t)$ is obtained from the time-dependent Schrödinger equation:

$$i\hbar\,\partial\psi(\mathbf{r},t)/\partial t = H_{el}(\{\mathbf{R}\})\psi(\mathbf{r},t), \tag{1}$$

with $H_{el}=T+V_{el}$, where T is the kinetic energy operator, and $V_{el}=V_{el}(\mathbf{r},\{\mathbf{R}\})$ the total electron-ion interaction. Because of the ionic motion, the operator $H_{el}(\{\mathbf{R}\})$ changes in time and has time-dependent eigenvalues $E_n(\{\mathbf{R}\})$ and eigenvectors $\phi_n(\mathbf{r},\{\mathbf{R}\})$. In turn the ionic motion is coupled to the electronic degrees of freedom by

$$M_I\ddot{\mathbf{R}}_I = -\partial V_{II}(\{\mathbf{R}\})/\partial\mathbf{R}_I - \int d^3r\,|\psi(\mathbf{r},t)|^2\,\partial V_{el}(\mathbf{r},\{\mathbf{R}\})/\partial\mathbf{R}_I, \tag{2}$$

where M_I is the ionic mass and $V_{II}(\{\mathbf{R}\})$ the interionic potential.

The model defined by Eqs. (1) and (2) has been extensively discussed in the literature.[5-8] According to it, each ion moves along a single, well-defined classical trajectory. This is justified if the motion of the system is adiabatic, i.e., the electron is always in a single Born-Oppenheimer state. In contrast, Eqs. (1) and (2) are not generally valid in situations where electronic transitions occur. Although alternative approaches might be considered in order to handle such situations,[6,7,9,10] we are concerned here with the case of adiabatic motion where the electronic system is in the Born-Oppenheimer ground state. This was found to be adequate to describe the behavior of our system, since at equilibrium the temperature is much smaller than the energy gap between ground and excited electronic levels.

The coupled set of Eqs. (1) and (2) is numerically solved and—assuming the ergodic hypothesis to be valid—static and dynamical properties evaluated as temporal averages. In our procedure $\psi(\mathbf{r},t+\Delta t)$ is obtained from $\psi(\mathbf{r},t)$ as

$$\psi(\mathbf{r},t+\Delta t) = \exp\left[-\frac{i}{\hbar}\int_t^{t+\Delta t} H_{el}dt'\right]\psi(\mathbf{r},t) \approx \exp\left[-\frac{iT\Delta t}{2\hbar}\right]\exp\left[-\frac{iV_{el}\Delta t}{\hbar}\right]\exp\left[-\frac{iT\Delta t}{2\hbar}\right]\psi(\mathbf{r},t)+O(\Delta t^3). \tag{3}$$

The matrix multiplication in (3) is performed by a fast-Fourier-transform method.[11] Equation (2) is instead solved by standard means.[12] The difference in time scale between ions and electrons requires the use of a rather small Δt. We found that a Δt of 2.4×10^{-17} s, while conserving the total energy to better than 10^{-3} over extremely long integration times ($\simeq 10^6 \Delta t$), still allows averages over several typical ionic periods to be performed.

The present calculation was performed on a periodically repeated system of 1 electron, 31 Cl^- anions, and 32 K^+ cations. The electronic wave function was represented on a mesh of 16^3 points. V_{el} and V_{II} were the same as those of Ref. 3, except for some additional smoothing of the electron-ion pseudopotentials. We have explicitly checked that the average static properties calculated by the PI[3] and present approaches do not significantly differ within statistical errors.

Several computations were performed with different initial conditions. A typical run was as follows. First a well equilibrated liquid of 32 K^+ and 31 Cl^- in a neutralizing uniform negative background was generated at a temperature of about 1300 K and a density of 1.52 g/cm^3. A typical liquid configuration was stored, and for such a fixed ionic configuration the background removed and replaced by a quantum electron. The ground state ϕ_0 of the electron was determined and used together with the stored ionic configuration as the initial condition for the run.

Initially the electronic energy $E=\langle\psi|H_{el}|\psi\rangle$ decreased steadily. This was found to correspond to an adiabatic localization of the electron from an initial fairly delocalized state into an *F*-center-like state, structurally very similar to the one described in Ref. 3. The amount of localization can be measured via the participation ratio,[13] which decreased from $\simeq 0.25$ for an initial state to $\simeq 0.06$ for a typical localized state. In some of our runs we found departures from adiabaticity. This was indicated by a sudden change in the probability $|c_0|^2$ of finding the electron in the instantaneous ground state ϕ_0. In the worst case $|c_0|^2$ dropped from 1 to 0.76 in about $600\Delta t$. After such events the calculations were stopped and resumed with $\psi=\phi_0$. The details of this operation were similar to what is done in the surface hopping model[6] in order to preserve the relevant conservation laws. In all the cases we have studied, with a variety of initial conditions, at most one such manipulation was needed since the electronic motion remained adiabatic (in the worst case $1-|c_0|^2 \simeq 0.01$) over all the remaining part of our rather long calculations ($10^6\Delta t$). From this we infer that the behavior of the system is ground-state dominated in agreement with PI calculations, and that nonadiabatic events occur with low probability. Hence we believe that for the calculation of most physical properties the neglect of these nonadiabatic effects is justified.

In Fig. 1 we show a typical electronic configuration which exhibits the localized *s*-like nature of the ground state ϕ_0. In the same picture the electronic density of the first excited state ϕ_1 is presented. In this case ϕ_1 is *p* type. However, ϕ_0 and ϕ_1 can fluctuate substantially, leading to configurations where the *s* or *p* character is temporarily destroyed. Also shown in Fig. 1 is the imaginary part of the dielectric function, which was calculated from the Fourier transform of the velocity-velocity correlation function. The gap in energy between ϕ_0 and ϕ_1 is typically $\simeq 1.2$ eV, all the higher excited states being more closely spaced in energy. Correspondingly the optical spectrum shows a peak at about 1.6 eV, since transitions to higher states shift the maximum to higher energies, and lead to an asymmetric curve. This is in

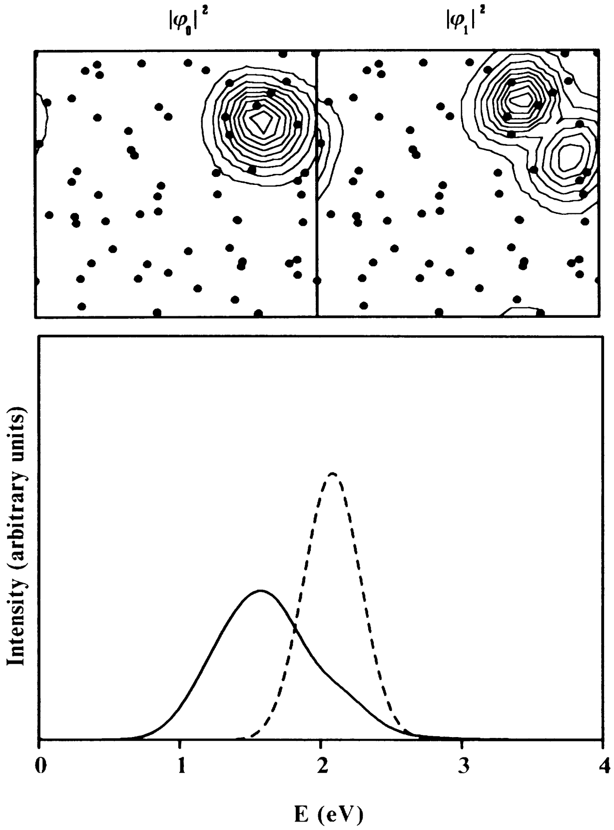

FIG. 1. Top panel: Contour plots of the electronic density (integrated along the sight line) of a typical *F*-center state ϕ_0 (left), together with the corresponding excited state ϕ_1 (right). The dots are the projections of the ionic positions. Bottom panel: Optical spectrum for the *F* center in liquid (solid line) and crystalline (dashed line) KCl. These spectra have been calculated by division of the Fourier transform of Eq. (5) by ω^2 and use of 45 and 18 ionic configurations for the statistical average for the liquid and crystal, respectively. A Gaussian broadening (FWHM $=0.3$ eV) has been used in both cases. Curves have been normalized to the same area.

good agreement with the experimental absorption data,[2] considering the limited statistics and the modest quality of our pseudopotentials. In the same picture the result of a similar calculation for solid KCl at 550 K is shown. This exhibits a peak of smaller width shifted towards the blue in accordance with experiment.[1] We evaluate the electron velocity-velocity correlation function starting from

$$\Phi(t)=\lim_{T\to\infty}\frac{1}{T}\int_0^T dt_1\langle\psi(t_1)\,|\,U^\dagger(t)\mathbf{v}U(t)\mathbf{v}\,|\,\psi(t_1)\rangle, \tag{4}$$

where $\mathbf{v}=-(i\hbar/m)\nabla$ and $U(t)$ is the time evolution operator. Using the Franck-Condon approximation $\Phi(t)$ becomes

$$\Phi(t)\cong\lim_{T\to\infty}\frac{1}{T}\int_0^T dt_1\langle\phi_0(\{\mathbf{R}(t_1)\})\,|\exp[iH_{el}(\{\mathbf{R}(t_1)\})t/\hbar]\mathbf{v}\exp[-iH_{el}(\{\mathbf{R}(t_1)\})t/\hbar]\mathbf{v}\,|\,\phi_0(\{\mathbf{R}(t_1)\})\rangle. \tag{5}$$

We evaluate this expression by approximating the temporal average with an average over a finite number of ionic configurations and by calculating the time evolution of $\mathbf{v}\phi_0$ with the same numerical techniques used to solve Eq. (1). The usual expression for the **v**-**v** response function in terms of the spectral representation of H_{el} can be obtained with trivial manipulations.

Use of the Franck-Condon approximation is inadequate to describe the mobility of the electron. For the calculation of this quantity we monitor the expectation value of the electron position[14] $\langle\mathbf{r}(t)\rangle=\langle\psi(t)\,|\,\mathbf{r}\,|\,\psi(t)\rangle$ and evaluate the mean square displacement as

$$r^2(t)=\lim_{T\to\infty}\frac{1}{T}\int_0^T dt'[\langle\mathbf{r}(t'+t)\rangle-\langle\mathbf{r}(t')\rangle]^2. \tag{6}$$

As shown in Fig. 2, the long-time part of $r^2(t)$ is approximately linear, indicating a diffusive motion. Furthermore, since the wave packet is well localized, the diffusion constant associated with $\langle\mathbf{r}(t)\rangle$ coincides with the electronic diffusion constant D_e, and one can use the asymptotic relation

$$r^2(t)\underset{t\to\infty}{=}6D_et$$

to determine $D_e\simeq2\times10^{-3}$ cm^2 s^{-1}. This compares favorably with the value 3×10^{-3} cm^2 s^{-1} that can be deduced from the experimental mobility[15] and is consistent with very recent results on picosecond recombination dynamics.[16]

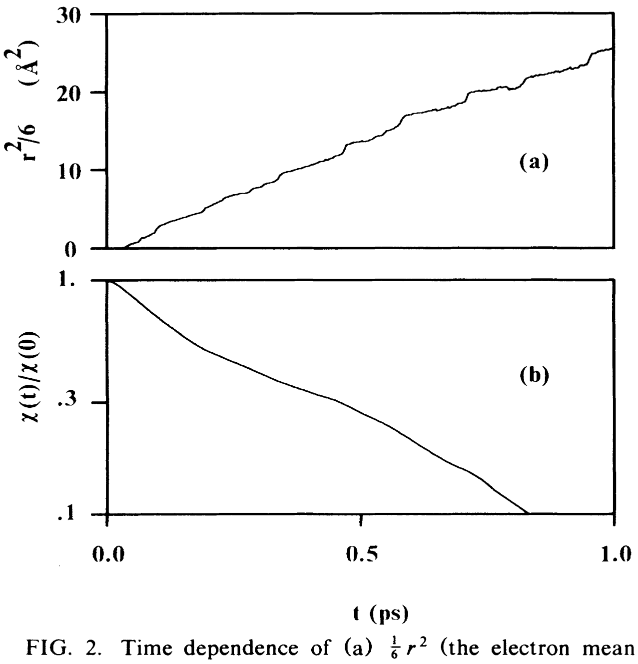

FIG. 2. Time dependence of (a) $\frac{1}{6}r^2$ (the electron mean square displacement) [see Eq. (6)] and (b) $\chi(t)/\chi(0)$ [see Eq. (7)].

We can also address the question of the lifetime of an F center in the liquid. The F center has a finite lifetime because of the ionic and electronic diffusion. The characteristic time for these processes can be measured with NMR.[4] In our simulation we study the following

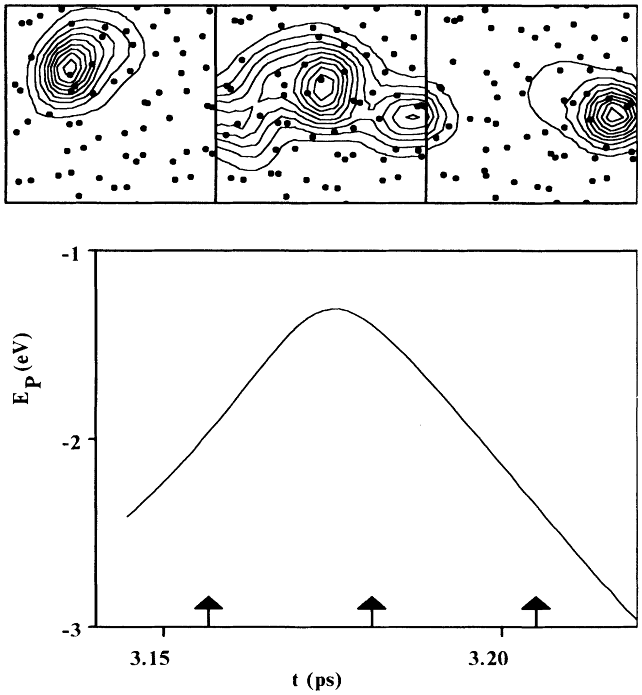

FIG. 3. Top panel: Contour plots of the electronic density at three successive times, just before, during, and just after a hopping event. Lower panel: Time dependence of E_P during the jump. The arrows on the time axis indicate the instants of the three snapshots in the upper panel.

correlation function:

$$\chi(t)=\sum_{I^+}\langle |\psi(\mathbf{R}_{I^+},t_0+t)|^2 |\psi(\mathbf{R}_{I^+},t_0)|^2\rangle, \qquad (7)$$

where the sum is performed over all the N_{I^+} cations. This quantity is plotted in Fig. 2. Its decay time is an estimate of the average residence time τ of the electron on a given ion. We find $\tau \simeq 3\times 10^{-13}$ s, in reasonable agreement with experiments on related systems.[4]

Finally, the mechanism of the electron diffusion is illustrated in Fig. 3. This shows a typical process in which the electron in a short time jumps between two spatially separated sites. The frequency of occurrence of these events, which can also be described as disruption and formation of an F center, is compatible with the time τ estimated from $\chi(t)$. The splitting of the wave function at intermediate times suggests that quantum effects are significant for electronic diffusion. During this process the electron remains in the ground state while the energy gap decreases substantially (for instance, this reduces to 0.38 eV during the event in Fig. 3). It is possible that the energy gap can decrease to such an extent that transitions to excited states may occur. This is the case in the rare nonadiabatic events mentioned above. In Fig. 3 we also show the time variation of the electronic potential energy $E_P = \langle\psi(t)|V_{eI}|\psi(t)\rangle$ during the jumping process. It appears that a potential barrier separates the initial and final localized states. As a rough estimate of the average barrier height one can take the rms fluctuation of E_P, which is of the order of 0.7 eV.

To conclude, we stress that the approach discussed in this paper, although limited to the description of adiabatic motion, can be very useful in studying dynamical systems where few quantum degrees of freedom interact with a many-body classical medium. With this approach one cannot only evaluate static properties, as in the PI approach, but also obtain direct information on the dynamics of the system. Extension of the present approach to many-body quantum systems is practicable by the use of the time-dependent density-functional method[17] and is currently being pursued.

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