Ground and excited states of an impurity-bound surface optical polaron

Ashok Chatterjee
School of Physics, University of Hyderabad, Central University P.O., Hyderabad 500 134, India

Shreekantha Sil
Solid State and Molecular Physics Division, Saha Institute of Nuclear Physics, Sector-1, Block-AF, Bidhannagar, Calcutta 700 064, India

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The ground and the first two excited states of an extrinsic surface optical polaron bound to a Coulomb impurity near the surface are studied by using a variational method for all ranges of the coupling parameters. It is shown that for large electron-impurity coupling the phonon-induced Lamb shift is quite significant and is opposite in sign as compared to the corresponding shift in the bulk material.

Recent advances in fabrication techniques such as molecular-beam epitaxy have made it possible to grow extremely thin films of polaron semiconductors and tailor-mode polar-polar interfaces of supreme quality. Consequently, much attention (see Ref. 1 for references) has lately been focused on polaronic properties of electron systems at surfaces and interfaces and in quantum wells, heterojunctions, and multilayered superlattices of polar semiconductors. These studies are interesting from the point of view of fundamental physics and also for their importance in device technology. Theoretical and experimental studies have revealed that the surface optical (SO) phonons play a dominant role in determining the optical as well as the transport properties of quasi-two-dimensional electrons. At low temperatures the presence of impurities in any polar material has a very significant effect on various polaronic properties. The problem of an impurity state in a bulk polar material was originally considered by Platzman[2] and Nettel.[3] Bhattacharya, Mukhopadhyay, and Mitra[4] have studied the ground state (GS) of an extrinsic SO polaron bound to a surface Coulomb impurity using a canonical transformation method. Their work is, however, particularly suited for the strong-coupling regime. Farias, Degani, and Hipolito[5] have recently obtained the GS energy and the average distance from the interface of a weakly coupled extrinsic polaron in the presence of an external electric field.

In the present paper we address the extrinsic polaron problem in the presence of the Coulomb field of a surface-bound hydrogenic impurity for the entire range of the electron-phonon coupling constant and the Coulomb binding parameter. We calculate the GS energy and the average width of the extrinsic polaron, using Huybrechts' modification[6] of the Lee-Low-Pines variational method,[7] which has been shown[8] to give fairly accurate results for the entire range of α and β. We also calculate the $2s$ and $2p$ excited-state energies and obtain the phonon-induced Lamb shift corrections.

The model we consider is as follows. The material under study is a polar crystal and fills the space $z \leq 0$ with the plane $(x,y,0)$ defining the surface. An electron lying outside the surface is then considered to interact with the longitudinal surface optical phonons which are assumed to be dispersionless. We also consider a positive Coulomb impurity localized on the material surface which can bind the electron forming what is commonly called a bound polaron. The form of the electron-surface-optical-phonon interaction has been given by several authors.[9] Following those works, the Hamiltonian of our present system can be written after eliminating the impurity-phonon interaction by a canonical transformation[2] as

$$H = h_e + h_p + h_{e\text{-}p} \ , \tag{1}$$

with

$$h_e = -\tfrac{1}{2}\nabla_r^2 - \frac{\beta}{r} - \frac{\gamma}{z} + V(z) \ , \tag{2}$$

$$h_p = \sum_{\mathbf{q}_\parallel} b^\dagger_{\mathbf{q}_\parallel} b_{\mathbf{q}_\parallel} \ , \tag{3}$$

and

$$h_{e\text{-}p} = \sum_{\mathbf{q}_\parallel} [\xi_{q_\parallel} e^{-i\mathbf{q}_\parallel \cdot \boldsymbol{\rho}} e^{-\mathbf{q}_\parallel z} b^\dagger_{\mathbf{q}_\parallel} + \text{H.c.}] \ , \tag{4}$$

where everything is dimensionless and units are so chosen that $\hbar = m = \omega = 1$, m being the Bloch effective mass of the electron and ω the dispersionless optical-phonon frequency. Here $\mathbf{r}(x,y,z) = (\boldsymbol{\rho}, z)$ refers to the position vector of the electron, β measures the electron-impurity coupling and is given by

$$\beta = \frac{2e^2}{\hbar\omega_s(\epsilon_s + 1)} \left[\frac{\hbar}{m\omega_s}\right]^{-1/2} \ , \tag{5}$$

ϵ_s being the static dielectric constant, γ denotes the strength of the image potential generated by the electron and has the form[9]

$$\gamma = \frac{1}{4\epsilon_\infty} \frac{(\epsilon_\infty - 1)}{(\epsilon_\infty + 1)} \ , \tag{6}$$

ϵ_∞ being the high-frequency dielectric constant, and for $V(z)$ we shall use the form[7]

$$V(z)=0 \quad \text{for } z>0\ ,$$
$$=\infty \quad \text{for } z\le 0\ , \tag{7}$$

which ensures that the electron cannot leak into the material. In (3) and (4), $b^\dagger_{\mathbf{q}_\parallel}$ ($b_{\mathbf{q}_\parallel}$) stands for the creation (annihilation) operator for a dispersionless surface optical phonon of wave vector $\mathbf{q}_\parallel$ [$=(q_x,q_y,0)$] and $\xi_{q_\parallel}$ appearing in (3) is the electron-phonon interaction coefficient given by[9]

$$\xi_{q_\parallel}=i\left[\frac{\sqrt{2}\pi\alpha}{Aq_\parallel}\right]^{1/2}, \tag{8}$$

where α is called the electron-phonon coupling constant and can be written in a dimensionless form as[9]

$$\alpha=e^2\left[\frac{\epsilon_s-1}{\epsilon_s+1}-\frac{\epsilon_\infty-1}{\epsilon_\infty+1}\right]\left[\frac{m}{2\hbar^2\omega}\right]^{1/2}. \tag{9}$$

For the variational calculation of the ground and low-lying excited states of the above system we shall follow the modification of Huybrecht[6] of the Lee, Low, and Pines canonical transformation method.[7] In this method the variational energy of the nth state is given by

$$E_n=\langle\Phi_n(\mathbf{r})|\langle 0|\tilde{H}|0\rangle|\Phi_n(\mathbf{r})\rangle\ , \tag{10}$$

where

$$\tilde{H}=U_2^{-1}U_1^{-1}HU_1U_2 \tag{11}$$

with

$$U_1=\exp\left[-ia\sum_{\mathbf{q}_\parallel}\mathbf{q}_\parallel\cdot\boldsymbol{\rho}b^\dagger_{\mathbf{q}_\parallel}b_{\mathbf{q}_\parallel}\right], \tag{12}$$

$$U_2=\exp\left[\sum_{\mathbf{q}_\parallel}(f_{\mathbf{q}_\parallel}b^\dagger_{\mathbf{q}_\parallel}-f^*_{\mathbf{q}_\parallel}b_{\mathbf{q}_\parallel})\right], \tag{13}$$

$f_{\mathbf{q}_\parallel}$ and a being variational parameters, $|0\rangle$ is the unperturbed zero-phonon state, and $\Phi_n(\mathbf{r})$ is the electronic function for the nth bound state to be chosen variationally. Choosing $f_{\mathbf{q}_\parallel}$ to be symmetric in $\mathbf{q}_\parallel$, we obtain, after minimizing (10) with respect to $f_{\mathbf{q}_\parallel}$,

$$E_n=\left\langle\Phi_n\left|-\tfrac{1}{2}\nabla_{\mathbf{r}}^2-\frac{\beta}{r}-\frac{\gamma}{r}\right|\right\rangle$$
$$-\sum_{\mathbf{q}_\parallel}|\xi_{q_\parallel}|^2\frac{|\langle\Phi_n|e^{i(1-a)\mathbf{q}_\parallel\cdot\boldsymbol{\rho}-q_\parallel z}|\Phi_n\rangle|^2}{\left[1+\dfrac{a^2q_\parallel^2}{2}\right]}\ . \tag{14}$$

We are interested in the ground ($1s$) and the first two excited states ($2s,2p$) for which we choose hydrogenic wave functions as the trial electronic functions:

$$\Phi_{1s}=2\lambda_1\lambda_2\left[\frac{2\lambda_2}{\pi}\right]^{1/2}e^{-\lambda_1\rho}e^{-\lambda_2|z|}|z|\ , \tag{15}$$

$$\Phi_{2s}=2\left[\frac{18\pi}{16\lambda_3^2}\right]^{-1/2}\left[1-\frac{4\delta}{\lambda_3}+\frac{6\delta^2}{\lambda_3^2}\right]^{-1/2}\lambda_4^{3/2}$$
$$\times\left[1-\frac{4\delta}{3}\rho\right]e^{-(2/3)\lambda_3\rho}e^{-\lambda_4|z|}|z|\ , \tag{16}$$

$$\Phi_{2p}=\left[\frac{4\lambda_5}{3}\right]^2\left[\frac{\lambda_6^3}{3\pi}\right]^{1/2}e^{-(2/3)\lambda_5\rho}e^{-\lambda_6|z|}|z|e^{i\theta}\ , \tag{17}$$

where λ_i's ($i=1,2,\ldots,6$) are variational parameters and δ is so chosen that $\langle\Phi_{1s}|\Phi_{2s}\rangle=0$. Variations with respect to a and λ_i's lead to three coupled integrodifferential equations for each of the three states. These equations cannot be solved analytically and so we performed the minimization numerically. The results are shown graphically in Figs. 1 and 2.

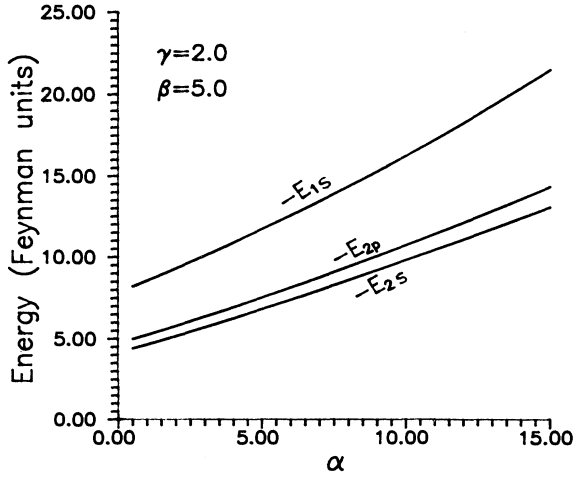

FIG. 1. $1s$, $2s$, and $2p$ state energies [in Feynman units ($\hbar=m=\omega=1$)] versus α for $\beta=5.0$ and $\gamma=2.0$ for an extrinsic bound polaron.

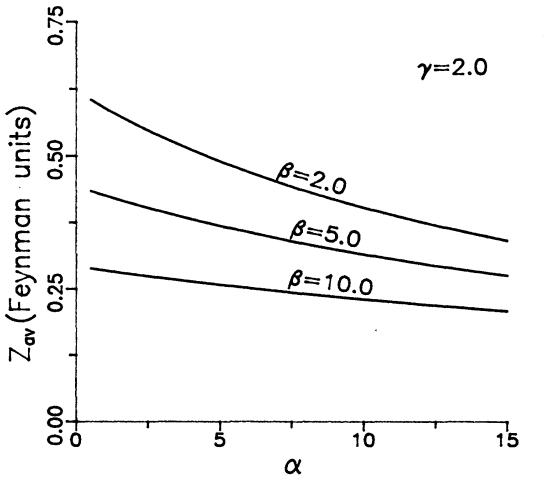

FIG. 2. The average distance of the polaron from the material surface as a function of α for $\beta=2,5,10$ and $\gamma=2$.

TABLE I. $1s$, $2s$, and $2p$ state energies (in meV) of an extrinsic bound polaron for a few polar materials. The values of α, β, γ, and phonon frequency ω are taken from Ref. 8.

Material	α	β	γ	E_{1s}	E_{2s}	E_{2p}
GaAs	0.116	1.01	1.45	−57.28	−44.89	−46.32
CdS	0.98	2.33	1.96	−157.61	−108.30	−114.80
MnO	2.05	1.68	1.13	−186.94	−130.19	−138.02
KCl	9.70	16.83	4.31	−1951.04	−1105.36	−1118.40
Cu_2O	5.07	5.52	4.76	−1396.14	−937.89	−992.29

In Fig. 1 we plot the GS energy (E_{1s}) and the first two excited state (ES) energies (E_{2s},E_{2p}) of the bound polaron as a function of the electron-phonon coupling constant α and for $\beta=5$ and $\gamma=2$. That the binding energies of the polaron do increase with increasing α is clearly evident from the figure. The important feature to note is, however, the lifting of the $2s$-$2p$ degeneracy of the bare impurity atom due to the electron-phonon interaction leading to what is called the phonon-induced Lamb shift. We have also studied the cases for $\beta=2$ and 10 which are, however, not shown here to save space. As expected, the polaronic binding becomes stronger with increasing β. Moreover, the Lamb shift is also large for larger values of β and in general increases with increasing α. We also find that the binding energies are in general an order of magnitude larger for $\gamma=5$ than those for $\gamma=2$. The reason is easy to understand. As γ increases, the extrinsic electron experiences a greater attractive force towards the material and hence will have a tendency to localize closer to the surface. Consequently, the binding energy of the polaron will increase. We find, however, that for $\gamma=5$ and $\beta=2$, the $2s$-$2p$ degeneracy is not lifted at small α. But these levels do split up at intermediate values of α. For $\gamma=5$ and $\beta=5$ the Lamb shift is, however, quite significant even at small α.

The most interesting feature which emerges from the above studies is that the electron-phonon interaction lowers the $2p$ level more than the $2s$ level leading to what may be called a negative Lamb shift in contrast to the usual positive Lamb shift observed in several bulk materials both theoretically and experimentally. It may be mentioned here that a similar reversal in the signature of the Lamb shift has also shown up in our recent calculation on a purely two-dimensional quantum-well polaron.[8]

In Fig. 2 we study the average distance of the polaron from the material surface (z_{av}) as a function of α for $\beta=2,5,10$ and for $\gamma=2$. We have also studied the behavior for $\gamma=5$ (not shown in this paper). We observe that as any one of the three parameters α, β, or γ increases, z_{av} decreases implying more and more binding of the polaron. The variation of z_{av} with α is indeed quite sharp for small values of γ and β.

In Table I we present the $1s$, $2s$, and $2p$ state energies for a few selected polar materials. For the weak-coupling GaAs the Lamb shift is found to be negligibly small while for Cu_2O the shift is quite large and hence should be measurable by optical-absorption experiments. For all the materials we have considered the Lamb shifts are again found to be negative.

In conclusion, we have studied the ground and the first two excited states of an impurity-bound surface optical polaron using a variational method. We have shown that the $2s$-$2p$ degeneracy of an impurity atom adsorbed on the surface of an ionic crystal or a polar semiconductor is lifted by the electron-phonon interaction giving rise to the phonon Lamb shift which may be quite significant if the electron-impurity coupling is large and which increases with increasing electron-phonon interaction strength. We have furthermore shown that the signature of this Lamb shift is opposite to that observed both theoretically and experimentally in the case of a bulk crystal. In our opinion this is an interesting theoretical observation and it should show up in infrared spectroscopic experiments.

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