Electronic Polaron in Strongly-correlated Transition Metal Halides

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Formation of polarons has been customarily attributed to electron-phonon coupling in solids. Herein, we present a theory of electronic polarons, in which spontaneous carrier localization occurs solely because of electron-electron interaction. Through a combination of first-principles calculation and scanning tunneling spectroscopy we demonstrate the existence of electronic polarons in strongly correlated two-dimensional transition metal halides, such as CrI₂. While lattice relaxation occurs at the polaron, we stress that this is a secondary effect in response to spontaneous carrier localization. This alters our fundamental understanding of small polarons and indicates that electron-phonon coupling may not be a prerequisite for their formation.

Understanding the polaronic characteristics of doped strongly-correlated systems are of both fundamental and practical importance in condensed matter physics. While polaronic effects are typically significant in ionic semiconductors due to the strong electron-phonon coupling and weak dielectric screening, they are increasingly becoming associated with strongly-correlated systems. For instance, high temperature superconductivity in p-doped cuprates is widely explained by the electron-electron correlation effects of preformed hole polarons in the CuO₂ sublayer. In recent years, polaronic physics in two-dimensional (2D) strongly-correlated systems has attracted considerable attention. Compared with their three-dimensional (3D) counterparts, 2D systems have a smaller dispersion that is expected to increase many-body effects. Furthermore, the ease of carrier injection and the accessibility of such states with surface sensitive techniques, such as scanning tunneling microscopy (STM), make 2D systems a promising platform to substantially further the understanding of polarons, either through direct imaging or through observation of their band dispersion.

Traditional polaron theory is based on the spontaneous localization of carriers due to lattice distortions which break the translational symmetry of the lattice. While such a distortion increases the energy of the underlying lattice, it can trap a carrier and lead to the formation of a localized electronic state in the bandgap, lowering the overall system energy. In other words, the conventional mechanism of polaron formation is through electron-phonon coupling where the bare charge is dressed with a lattice distortion, leading to carrier localization and a substantial increase in the effective carrier mass. However, from the viewpoint of modern polarization theory, the modulation of charge density in solids can be, in principle, a purely electronic effect where a spontaneous ordering of electrons breaks the crystal symmetry, without any atomic displacement. Such a possibility is hinted at in the study of the doped Mott insulating phase in the Hubbard model, which reveals the emergence of localized states, even in the absence of any mechanism for electron-phonon coupling. This raises the question of whether polarons can occur, via a purely electronic mechanism, in materials in the absence of any atomic distortion. Such a mechanism would constitute a fundamentally new type of polaron, here dubbed an electronic polaron, in which the electron-phonon coupling need not play any active role. Instead, electron-electron correlation becomes the key for polaron formation, with atomic relaxation being merely a secondary response of the lattice to electronic localization, in which the surrounding ions tend to screen the spontaneously localized carrier.

In this work, we propose a theory of the formation of electronic polarons, in which the underlying physics is due to electron-electron repulsion. By considering the non-linear dependence of the Coulomb repulsion energy on the occupation matrix of d orbitals, we show that highly correlated materials (with large onsite repulsion) naturally lead to the spontaneous localization of carriers. This understanding is verified through first-principles calculations, both at the density functional theory plus Hubbard U (DFT+U) and the hybrid functional level of theory. We find that the family of 2D strongly-correlated transition metal halides, CrI₂, CoCl₂, CoBr₂, NiCl₂, and NiBr₂, are ideal candidates to host electronic polarons. The formation energy of electronic polaron can be as large as −1.18 eV for CrI₂, of which only −0.26 eV is contributed by atomic relaxation. Taking CrI₂ as a prototypical example, we present the details of the electronic structure, which are highly supported by our scanning tunneling spectroscopy (STS) and microscopy (STM) experiments on high-quality CrI₂ single layer grown via molecular beam epitaxy.

In the framework of DFT, the DFT+U method has been widely used to study the properties of correlated electrons and provides a quantitative approach which puts electron-electron and electron-phonon inter-
actions on equal footing. In the DFT+U method, the total energy is written as

\[ E_{\text{total}} = E_{\text{DFT}} + E_U = E_{\text{DFT}}(U) + \sum_i E_U^i, \tag{1} \]

where \( E_{\text{DFT}} \) is the total density functional theory energy with exchange-correlation determined at the local or semi-local level and \( E_U^i \) is the on-site Hubbard Coulomb energy correction to each site \( i \) as defined by

\[ E_U^i = \frac{U}{2} \left[ \sum_{m_1} n_{m_1,m_1}^\sigma - \sum_{m_1,m_2} n_{m_1,m_2}^\sigma n_{m_2,m_1}^\sigma \right]. \tag{2} \]

Here \( n_{m_1,m_2}^\sigma \) gives the \( d \) orbital occupation matrix on each site, where \( m_1 \) and \( m_2 \) denote a particular magnetic quantum number of \( d \) orbitals and \( \sigma \) is the spin. As a repulsive interaction, the inclusion of the onsite Hubbard \( U \) term raises the total energy, regardless of whether the considered state is localized (i.e., polaronic) or delocalized.

While in principle both \( E_{\text{DFT}} \) and \( E_U \) are functions of \( U \), the \( E_{\text{DFT}} \) dependence is expected to be much weaker as it is only indirectly dependent through the charge density. In contrast, for a fixed occupation matrix, \( E_U \) linearly increases with the value of \( U \). This is schematically illustrated in Fig. 1(a) where \( E_{\text{DFT}} \) of a system in which the free carrier is localized (red horizontal line) or delocalized (blue horizontal line) are shown in this limiting case, i.e., with no dependence on \( U \). Although there is no \( U \) dependence, \( E_{\text{DFT}} \) of the localized state is higher due to the increased Hartree energy. On the other hand, \( E_U \) has a quadratic dependence on the occupation matrix \( n_{m_1,m_2}^\sigma \), thus the distinct charge distributions of localized and delocalized states lead to different values of \( \sum_{m_1,m_2} n_{m_1,m_2}^\sigma n_{m_2,m_1}^\sigma \). Therefore, despite both having linear dependence on \( U \), their slopes could dramatically differ from each other. The key point is that \( E_U \) will always be smaller for a localized state than a delocalized one. This can be seen by considering an electronic state distributed uniformly among \( N \) atomic sites by doping one electron into the system, in which case we have

\[ E_U = \frac{U}{2} \left( \frac{1}{N} - \frac{1}{N^2} \right) \times N = \frac{U}{2} \left( 1 - \frac{1}{N} \right). \tag{3} \]

A strongly localized state refers to \( N = 1 \) and delocalized state refers to \( N = \infty \), so that the former always has a lower \( E_U \) than the latter.

An electronic polaron forms if the system containing a doped electron in a localized state is lower in energy than if that electron had trivally occupied the delocalized conduction band minimum (CBM). Thus, only the energy difference of the localized state with respect to the delocalized state is important here. From the previous considerations, one can see that the energy difference in \( E_{\text{DFT}} \) (\( \delta E_{\text{DFT}} = E_{\text{DFT}}^{\text{localized}} - E_{\text{DFT}}^{\text{delocalized}} \)) is almost independent of \( U \), while the difference in \( E_U \) (\( \delta E_U = E_U^{\text{localized}} - E_U^{\text{delocalized}} \)) decreases linearly with \( U \), as shown in Fig. 1(b). Therefore, as systems become more strongly-correlated, with a corresponding increase in the on-site Coulomb repulsion, at some point the magnitude of \( \delta E_U \) must become larger than the energy required to localize the electron (\( \delta E_{\text{DFT}} \)), leading to the spontaneous formation of an electronic polaron. To find systems which may exhibit the underlying physics outlined above and validate the general understanding, we examine electronic polaron formation and the electronic structure of highly-correlated 2D transition metal halides\cite{15, 16} using first-principles calculations.

DFT+U calculations were performed by VASP\cite{17} code with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional\cite{18}. Hybrid functional HSE06 approach\cite{19, 20}, which is believed to provide more physical treatment of many-body effect\cite{21, 22}, was employed to improve the results of band gap. Unless otherwise stated, we used a supercell of size \( 5 \times 5 \times 1 \) to simulate the polaron. \( U \) values were determined by fitting the calculated band gap to experiment for \( \text{CrI}_2 \) and by fitting to HSE06 result where experiment was unavailable. In the remaining part of the paper, unless otherwise indicated, we used \( U = 10.4, 6.9, 7.0, 8.0 \) and 8.0 eV for \( \text{CrI}_2, \text{CoCl}_2, \text{CoBr}_2, \text{NiCl}_2 \) and \( \text{NiBr}_2 \), respectively.

Figures 2(a) and (b) depict the atomic structure of the 1-T phase for transition metal halides, where transition metal atoms coordinate with six halogen atoms, in a distorted octahedral geometry. Figures 2(c)-(f) show the DFT+U results, \( \delta E_U \) and \( \delta E_{\text{DFT}} \), for \( \text{CrI}_2, \text{CoCl}_2 \) and \( \text{NiCl}_2 \), respectively. From Fig. 2(c), we see that for real materials, both \( \delta E_U \) and \( \delta E_{\text{DFT}} \) depend on \( U \), unlike the idealized case in Fig. 1(b). However, \( \delta E_{\text{DFT}} \) has a weak dependence, while \( \delta E_U \) has a strong dependence and it eventually becomes a linear function of \( U \). As such, \( \delta E_U \) dominates the total energy difference at large \( U \). There is a critical value of \( U \), at which the
ground state changes from a delocalized state to a polaronic state. Similar results are obtained for CoCl$_2$ and NiCl$_2$ [see Figs. 2(e) and (f)]. Since $U$ is a property of the transition metal element, replacing halogen atoms has negligible effect. With regard to the $U$ dependence of $\delta E_{DFT}$ in Fig. 2(c), we note that, despite that overall the delocalized nature of the CBM state and the localized nature of the polaronic state are preserved in the calculation, details such as $d-p$ hybridization can still change with $U$ and modify the charge distribution. The extent of this effect is illustrated in Fig. 2(d), where we perform a non-self-consistent (nsc) calculation in which the charge density is fixed. Indeed, the basic features in Fig. 1(b) are fully restored. Note that throughout the calculations, the translational symmetry of the crystal is fixed, thus the driving force for the polaron formation is purely electronic, as a result of the competition between $\delta E_{DFT}$ and $\delta E_U$.

Table I shows the spontaneous localization energy ($E_L$), defined as the energy difference between the localized and delocalized states, and the atomic relaxation energy ($E_R$), defined as the energy difference between a fully relaxed and a structurally-unrelaxed electronic polaron. In all cases, $E_L$ is negative at the DFT+U level, implying a spontaneous localization of the electron at the CBM without the involvement of phonons. While not depicted in the table, we note that $E_R$ for the electronic polaron is quite insensitive to the value of $U$, indicating that the atomic relaxation is simply a response to the electron localization. Table I also shows the HSE06 results for Cr- and Co-based systems, which qualitatively agree with the results of DFT+U. For Ni-based systems, however, $E_L > 0$, indicating the electron does not spontaneously localize without atomic relaxation. Despite this, the polaron formation energy ($E_P = E_L + E_R$) is still negative ($-49$ meV and $-113$ meV for NiCl$_2$ and NiBr$_2$, respectively). Regardless, even though pure electronic polaron may be quenched in Ni-based systems, the energy reduction due to $\delta E_L$ is present and is always in favor of the localized state. This can be easily seen for NiCl$_2$ and NiBr$_2$ by performing a calculation without the $U$ term. In both cases, polarons cannot be stabilized by electron-phonon coupling. Hence, electron-electron correlations could be a general driving force, although may not be the only one, to the formation of polaronic states.

Recently, we have achieved the growth of high-quality CrI$_2$ single layer on graphene covered SiC(0001) substrate via molecular beam epitaxy. Here we examine the validity of our first-principles calculations via STM/STS measurements, for which the technical details have been given in a previous publication. From the STM topography in Figs. 3(a) and (b), CrI$_2$ single layer shows a considerable density of intrinsic defect-like (DL) states. These states appear as depression spots at a positive bias of $3.0$ V, corresponding to the energy of conduction bands, and protrusion dimers at a negative bias of $-3.0$ V, corresponding to the energy of valence bands. Differential conductance spectrum of defect-free area has an insulating gap of $\sim 3.3$ eV, while the spectrum of a typical DL state indicates two prominent in-gap states separated by $\sim 0.5$ eV [Fig. 3(c)]. In Fig. 3(d), we compare the calculated $dI/dV$ spectrum of polaron with the measured differential conductance spectrum of a typical DL state. Here the polaron is calculated with fully relaxed lattice structure, i.e., both electron-electron correlation and electron-phonon coupling are included. The features of in-gap states are properly captured by our

| system | functional | $E_L$  | $E_R$  |
|--------|------------|-------|-------|
| CrI$_2$ | DFT+U      | -0.924 | -0.256 |
|        | HSE06      | -0.153 | -0.357 |
| CoCl$_2$ | DFT+U      | -0.531 | -0.263 |
|        | HSE06      | -0.067 | -0.223 |
| CoBr$_2$ | DFT+U      | -0.676 | -0.188 |
|        | HSE06      | -0.148 | -0.162 |
| NiCl$_2$ | DFT+U      | -0.411 | -0.329 |
| NiBr$_2$ | DFT+U      | -0.447 | -0.307 |

FIG. 2: (Color online) (a) Top and (b) side views of atomic structure of the 1-T phase. (c), (e), and (f) are self-consistent DFT+U results for CrI$_2$, CoCl$_2$, and NiCl$_2$, respectively. (d) is a non-self-consistent result of CrI$_2$ in which the electron density is fixed to the one calculated by $U = 10.4$ eV.
FIG. 3: (Color online) (a, b) The STM topography of DL states in CrI$_2$ single layer at positive (a) ($V_s = 1.6$ V, $I_t = 50$ pA) and negative (b) ($V_s = -3.0$ V, $I_t = 100$ pA) sample bias. An isolated DL state is denoted by yellow square. (c) Differential conductance spectra (set point condition: $V_s = 0.8$ V, $I_t = 3$ pA) measured on defect-free area (black) and a typical DL state (red). The blue arrows mark two in-gap states. (d) Comparison between experiment and theory for CrI$_2$. Red circles and blue curve denote, respectively, the measured differential conductance spectrum of DL state and calculated $dI/dV$ spectrum of polaron. Insert shows the simulated STM topography of polaron at positive (top) and negative (bottom) bias.

calculation, despite their splitting is slightly underestimated as 0.4 eV. Our calculation of local density of states shows that the in-gap states come from the $e_g$ orbitals of central Cr atom, and these states already exist before any lattice relaxation. [See Supplemental Material for details]. The insert of Fig. 3(d) shows the calculated STM topography of polaron at positive (top) and negative (bottom) bias. The polaron displays depressions at positive bias and dimer protrusions at negative bias, which agree nicely with the results of DL states. These agreements strongly indicates the DL states are of polaronic nature, which not only demonstrate the existence of localized polarons in CrI$_2$, but also indicates that the essential physics of the electronic polaron is well captured in the DFT+U method.

The identification of the DL states as polaronic in nature is further bolstered by our ability to directly manipulate them with the STM tip. Indeed, a DL state can be moved by the tip when we locate the tip close to it and gradually increase the sample bias voltage to above 3.5 V [Figs. 4(a) and (b)]. We can also controllably create a DL state with the tip by gradually increasing the sample bias voltage to above 3.5 V at a defect-free area [Figs. 4(c) and (d)]. Moreover, the DL state can be eliminated by positioning the tip above it and adding a large enough negative bias voltage $\sim -3.5$ V [Figs. 4(e) and (f)]. This ability to reversibly create and destroy the DL state strongly suggest that the defect is not associated with nonstoichiometry, but instead has an electronic origin possibly coupled with a local lattice distortion. These observations, along with the agreement of the simulated STM/STS of the electronic polaron with experiment, provide strong evidence that the observed DL state is indeed the predicted electronic polaron.

In summary, we propose a new form of polaron, an electronic polaron, in strongly correlated materials. By first-principles calculations combined with STM/STS experiments, we present evidence for their existence in transition metal halides, particularly in monolayer CrI$_2$ due to its strongly correlated nature. The underlying physics for the formation of the electronic polaron lies in the strong on-site Coulomb repulsion, which leads to a non-linear dependence on the spatial distribution of $d$ electrons, manifested in their occupation matrix. We also note that this electron localization is a barrierless process, and the formed polarons can be controllably manipulated via STM tip. Furthermore, atomic relaxation is not required to stabilize the polaron (in startling contrast to conventional theory), but instead it releases internal strain associated with the carrier localization. As electronic polaron formation becomes increasingly stable with respect to Coulomb repulsion, they are expected to be a general feature of highly correlated materials greatly altering their carrier mobility, ionization energy,
and transport properties.

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