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Electronic molecules in solids

F. V. KUSMARTSEV

*Department of Physics, School of Physics and Mathematical Sciences
Loughborough University - LE11 3TU, UK*

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PACS. 73.22.-f – Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals.

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Abstract. – We show that at certain conditions electronic molecules may arise in solids with narrow bands. The behaviour of the electronic molecules is very quantum, their shapes and sizes are not well defined while varying in some limits. In many situations, for example in metal and magnetic oxides, due to the strong Coulomb screening they may have primarily stringed linear form and therefore we have named them electron strings. In general, the form of electronic molecules may be arbitrary and particularly is determined by the structure of an effective electron-electron interaction at short and long distances. We estimate the size and the shape of the electron molecules which may arise in oxide materials. In oxides like cuprates, nickelates and manganites these electron molecules—in particular, electron strings, may be responsible for the creation of the stripe phases.

Metallic and magnetic oxides have been shown to exhibit microscopic electronic phase separation, formation of static and dynamic stripes, colossal magneto-resistance and high-temperature superconductivity. We propose that all of these phenomena may have a natural explanation in the framework of our proposed novel concept of electronic molecules. Here we show that under certain conditions ordinary electrons may form these special electronic molecules, *i.e.* bound configurations within solids. These electronic molecules arise due to a competition between an effective electron-electron attraction mediated by phonons and the usual Coulomb repulsion between electrons. It was Landau [1] who first suggested that an electron in a solid may be surrounded and trapped by a cloud of phonons. This electron-phonon quasi-particle was called a polaron and has been well studied both theoretically and experimentally. A polaron may be viewed as an electronic atom—the electron is the nucleus and the surrounding phonon cloud is analogous to the electron cloud in a normal atom. Up to now, it was generally assumed that individual polarons would repel each other, although a formation of pairs (bi-polarons) and their application has often been discussed [2]. Recently [3, 4], we have shown that in materials with narrow bandwidths there should arise strings—a many-polaron bound state having a linear shape (*i.e.* a linear “molecule”).

Experiments [5] have been performed and support this prediction. Our investigation indicates that the electronic molecules or electronic complexes are drastically different from atomic molecules.

There arise a large variety of different types of electronic molecules. Depending on the type and strength of the electron-phonon and the Coulomb interactions, these molecules may be associated with either a ground or a metastable state. The formation of these electronic molecules can be demonstrated almost in any model. Let us now consider a realistic Hamiltonian which includes the electron-phonon interaction and a long-range Coulomb repulsion:

$$H_{\text{el}} = -t \sum_{\langle ij \rangle} a_i^\dagger a_j + \sum_{\langle ij \rangle} \omega(q) b_q^\dagger b_q + \text{h.c.} + H_{\text{el-ph}} + H_{\text{el-el}}, \quad (1)$$

where the Hamiltonians of electron-phonon and electron-electron interactions are, respectively, defined as

$$H_{\text{el-ph}} = \sum_{iq} n_i g_q [\exp[iqR_i] b_q + \text{h.c.}], \quad H_{\text{el-el}} = \sum_{i < j} \frac{n_i n_j}{\varepsilon_\infty |R_i - R_j|}. \quad (2)$$

Here a_i and b_q are fermionic and bosonic annihilation operators associated with electrons and phonons, respectively, and $n_i = a_i^\dagger a_i$ is a fermionic occupation number operator. The value g_q is a constant of the electron-phonon coupling which depends on the type of phonons and the value $\omega(q)$ is the phonon dispersion.

Using a standard procedure of the shift in the phonon variables as

$$b_q \Rightarrow b_q - \sum_{iq} n_i g_q \exp[iqR_i] / \omega(q), \quad (3)$$

we obtain, instead of a plain Coulomb potential ($\sim 1/(\varepsilon R)$), an effective electron-electron interaction in the form

$$V(R_i - R_j) = \frac{1}{\varepsilon_0 |R_i - R_j|} - \frac{1}{N} \sum_q g_q^2 \cos(q|R_i - R_j|) / \omega(q). \quad (4)$$

The same expression may be also obtained with the use of the Lang-Firsov transformation [6]. Depending on the type of the electron-phonon interaction, the form of this effective potential $V(R_i - R_j)$ may be different although some characteristic features remain the same. Without breaking generality, we consider now the specific case of an electron interacting with Jahn-Teller phonons or with Jahn-Teller lattice distortions (see, for details, refs. [7, 8]). Then, with the use of the formula for the effective potential $V(R_i - R_j)$ we obtain the potential for the interpolaron interaction $U(R) = V(R)$, presented in fig. 1. Now we consider the limit of the very narrow electron bandwidth $t \Rightarrow 0$, when the polaron band collapses and, therefore, the kinetic energy of polarons may be neglected. Such a case allows an exact analytic treatment. Then the electronic molecules are formed on crystal lattice sites and are the result of an interpolaron interaction $U(R)$ only, which consists of a short-range (intersite) effective attraction (producing the deep minimum in fig. 1) and a long-range electron-electron Coulomb repulsion: $U(R \geq \sqrt{2}) = \frac{h\sqrt{2}}{R}$, where the distance R is measured in units of the lattice spacing a . The strength of the Coulomb repulsion depends on the screening due to lattice polarisation and is characterised by the height of the Coulomb peak, $h = \frac{e^2}{\varepsilon \cdot a\sqrt{2}}$ (see fig. 1), where ε is a static dielectric constant of the solid. The depth of the minimum, d , depends on the strength of electron-phonon coupling; the stronger the electron-phonon interaction the deeper the minimum. For strong coupling of electrons with Jahn-Teller phonons or with local lattice distortions the polarons are small (the size of a single atom) but have very large masses.

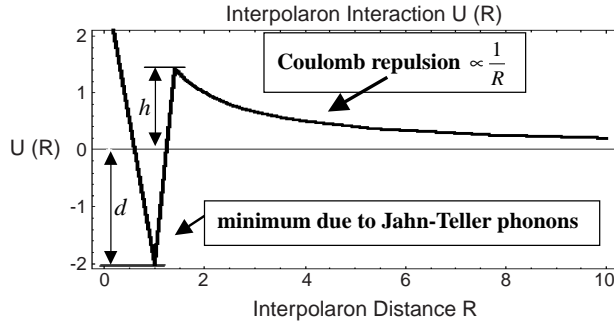


Fig. 1 – The potential of the interpolaron interaction in oxide materials, which consists of a short-range attraction (producing the sharp deep minimum) associated with the Jahn-Teller electron-phonon interaction and a long-range Coulomb repulsion (producing the peak and the shallow slope from the right side of the peak). The depth of the minimum equals d . The minimum is located at $R = 1$. The height of the Coulomb peak equals $h = \frac{e^2}{\epsilon \cdot a \sqrt{2}}$. The peak is located at $R = \sqrt{2}$. All distances are measured in units of the one lattice spacing a .

These heavy polarons would then fall into the deep minimum of the potential $U(R)$ (see fig. 1) and become localised. In this way the polarons may form an electronic molecule.

The variety of the different types of electronic molecules strongly depends on the depth of the minimum d and the height of the Coulomb peak h (see fig. 1). With the decrease of the ratio, h/d , it is energetically more favourable for polarons to create large molecules. Due to a multi-valley many-body energy landscape (as in complex biological systems) these molecules can have different shapes coexisting with each other. Their shape may also change due to quantum fluctuations. For very weak Coulomb repulsion (very small peak height in comparison with the depth of the minimum, $h \ll d$) these multi-electron molecules will transform into droplets, analogous to those introduced originally into the physics of magnetic semiconductors by Nagaev [9]. With increasing Coulomb interaction the number of electrons in a molecule decreases. For very strong Coulomb repulsion or for the very large ratio, $h/d \gg 1$, only bipolarons might exist. For any electronic molecule to exist the bottom of the minimum must be below the reference level, $d = 0$, *i.e.* we must have $d > 0$. If the minimum lies above the reference level (*i.e.* $d < 0$), then individual polarons would repel each other and no electronic molecules could be formed. In this case the free polarons will create a novel polaronic Fermi or non-Fermi liquid.

To illustrate the main principles involved in the formation of electronic molecules, let us consider a square crystal lattice with polarons located on these lattice sites. Then, conditions for the formation of these molecules are completely defined by the parameters of the potential of the interpolaron interaction $U(R)$: d and h . Any multi-electron molecule can be considered in terms of the interaction of all possible pairs of electrons, which make up the molecule. Each pair is interacting via a potential $U(R)$. Due to the very non-monotonic behaviour of the function $U(R)$ the energy contribution from each pair into the binding energy may be positive or negative. This contribution depends on the distance between the particles in a given pair. If this pair of particles are localised on neighbouring sites, *i.e.* located in the minimum of $U(R)$, they gain energy equal to the value d . If the distance between two given particles in the electronic complex is larger than the lattice spacing a , then these two particles repel each other and the contribution from this pair into the binding energy of the multi-electron molecule is negative. That is, due to such repulsion the binding energy of the chosen

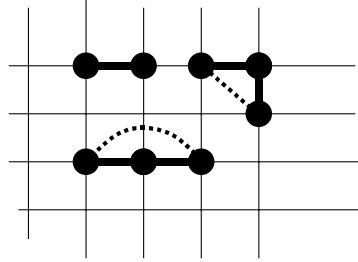


Fig. 2 – Possible shapes of two- and three-electron molecules on a square lattice. The bi-polaron has the dumb-bell shape. The lowest-energy state of the three-electron molecule is the string. The bold solid lines indicate an inter-polaron attraction. The dashed lines indicate a Coulomb repulsion, which gives a negative contribution into the binding energy of electronic molecules.

multi-electron molecule decreases by an amount of $\sim ch$. The constant c is associated with all virtual pairs in the molecule where the distance between electrons is larger than the lattice spacing a , *i.e.* the electrons creating a virtual pair should not be located on neighboring sites. The value of the constant c is equal to the sum of the inverse distances taken for all such virtual pairs in the molecule. In this simplest model there is a very general expression for the binding energy per particle of any multi-electron molecule. For an electronic molecule consisting of n particles this expression has the following form:

$$E_b = (md - ch\sqrt{2})/n, \quad (5)$$

where m is a number of pairs of adjacent electrons, where the two electrons in the pair are located on neighbouring sites in this n -electron molecule and $c = 1/x_1 + 1/x_2 + \dots$ is the sum of inverse distances $x_i > 1$ (measured in units of a) for all pairs for which the electrons in each pair are farther away from each other than a single lattice spacing a .

Let us consider examples of simplest electronic molecules on the square lattice. If there are only two particles located on neighbouring sites, then they are localised in the deep minimum of $U(R)$ and, therefore, are bound into a two-electron molecule (a bi-polaron) with binding energy per particle $E_b = d/2 \equiv -U(1)/2$ (see fig. 2). Here the parameter values are $m = 1$, $c = 0$ and $n = 2$. A three-electron molecule may also exist. The three-particle molecule may be considered as three pairs. Two of these pairs can be located on neighbouring sites. The size of the third pair is always larger than the lattice spacing a . Therefore, due to Coulomb repulsion $U(R > \sqrt{2})$, the contribution to the binding energy of this three-electron molecule arising from this third pair is always negative. The binding energy per particle is maximal if the distance between these two particles is the largest possible value (provided that the inter-particle distance in other pairs of the three-electron molecule is equal to the lattice spacing a). There is only one such configuration and this is the linear molecule (the string configuration [3, 4], see fig. 2). The binding energy per particle of such a string is equal to $E_b = (2d - h/\sqrt{2})/3$. This is consistent with eq. (5) when the parameter values are $m = 2$, $c = 1/2$ and $n = 3$. From a comparison of this binding energy with the binding energy of the bi-polaron one may find that the bi-polaron has a lower binding energy per particle than the 3-electron string if $d < h\sqrt{2}$.

Four polarons may create a four-electron molecule whose optimal shape depends on the relation between the height of the Coulomb peak h and the depth of the phonon minimum d . Using eq. (5) one may readily estimate the binding energy for the square electronic molecule

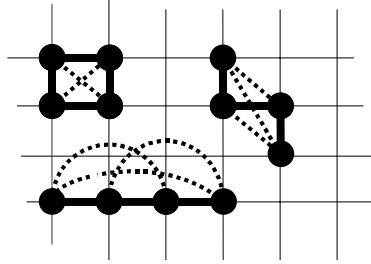


Fig. 3 – Possible shapes of a four-electron molecule on a square lattice: the optimal shape is the square. The bold solid lines indicate an inter-polaron attraction. The dashed lines indicate a Coulomb repulsion, which gives a negative contribution into the molecule binding energy.

(see fig. 2) as $E_{\text{square}} = (4d - 2h)/4$, for the “zig-zag” molecules as $E_{\text{zig-zag}} = (3d - (2 + \sqrt{2}/\sqrt{5})h)/4$ and finally for the string molecule as $E_{\text{string}} = (3d - 4\sqrt{2}h/3)/4$. From these estimations it is clear that the “zig-zag” molecule always has a binding energy smaller than the square molecule and also smaller than the string molecule. The string and the square molecules are associated with the local minima, which are separated by a barrier associated with other shapes of the molecule like the “zig-zag” and “corner” shapes. Therefore these electronic molecules, the string and the square, may coexist with each other. In a ground state the molecule has a square shape if $d > (2 - 4\sqrt{2}/3)h$. A comparison of the binding energy of the square electronic molecule with the binding energy of a bi-polaron shows that the square molecule has a lower binding energy than a bi-polaron if $d > h$.

When the screening is strong, the Coulomb repulsion is weak, $d \gg h$, the optimal shape is a square. With an increase of the Coulomb repulsion the electronic molecule may form a string shape or it may directly decay into the bi-polaronic molecules. In the framework of the simple model chosen we may estimate the most optimal shape of electronic molecules on the square lattice. Depending on the strength of the electron-phonon interaction and the Coulomb screening (or the ratio d/h) the optimal molecules (*i.e.* having the lowest energy) are the 2-particle or dumb-bell bi-polaron (see the dumb-bell in fig. 2) and the 4-particle molecule having the shape of a square lattice plaquette (see the square in fig. 3). The optimal shape for a many-electron molecule is a droplet having the form of a dense lattice of squares (see, for example, fig. 4).

In general, the form and the number of electrons in electronic molecules may be arbitrary and is largely determined by the overall interaction consisting of the effective (phonon-mediated) electron-electron attraction at short distances and the form of Coulomb repulsion at long distances. The electron screening effects may fundamentally change the shape and the size of these molecules. If there is a Debye screening, then the long-range Coulomb repulsion

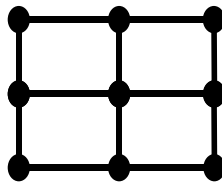


Fig. 4 – We present the typical optimal form of the multielectron complex consisting of 9 electrons on the square lattice.

takes the form $U(R > \sqrt{2}) = \frac{\hbar\sqrt{2}}{R} \exp[-R/R_D]$, where R_D is the Debye radius. In this case the optimal shape may have the form of a string. Moreover, at any finite value of the Debye radius R_D there exists instability resulting in the formation of stripes. This instability arises if the electron-phonon coupling (or the ratio d/h) reaches some critical value. For larger values of the electron-phonon coupling there arise strings which are then ordered into stripes. For example, if the Debye radius is equal to $R_D = 2$, then this instability arises if $d > \hbar\sqrt{2}$. In order for stripes to be formed the electron-phonon interaction must be strong, the dielectric constant ε must be large and the Debye radius must be small. The larger the Debye radius R_D , the stronger the electron-phonon coupling has to be for the formation of electronic stripes.

An effective short-range attraction between particles in $U(R)$ (the deep minimum in fig. 1) may be created not only due to electron-phonon interaction but, for example, due to anti-ferromagnetic exchange interaction. In fact these anti-ferromagnetic correlations were originally proposed as the main mechanism for stripe formation [10,11]. Therefore the electronic molecules may be formed even without the participation of phonons [12] but due to a competition of the attraction associated with the short-range anti-ferromagnetic interaction and long-range Coulomb repulsion.

The concept of electronic molecules yields fundamentally new insights for a wide range of materials, like metallic and magnetic oxides. A creation of such molecules in perovskite manganites will lead to a microscopic phase separation observed recently in $\text{La}_{5/8-y}\text{Pr}_y\text{Ca}_{3/8}\text{MnO}_3$ (see, for details, refs. [13,14]). In this experimental work it was clearly concluded that *the percolative transport through sub-micrometre-scale two-phase mixture* (which may be associated with the described electronic molecules) *is responsible for a colossal magnetoresistance behaviour observed in these manganites*. These molecules may be distributed in a disordered way or ordered into the static charged stripes observed in refs. [13,14]. Thus the phenomenon of the formation of these static charged stripes is related to the ordering of electronic molecules or, precisely speaking, to the stripe instability associated with the formation of electronic molecules.

Due to the fact that electronic masses are smaller than atomic masses the electronic molecules have much smaller masses than atomic molecules and therefore inside the solid they may be very mobile. Also due to their small masses they are very much quantum objects. Therefore, the shape of these electronic molecules fluctuates and changes in time. The existence of these quantum molecules in cuprate oxides, like YBCO, LaCuO and others, may result in the formation of dynamical stripes or the string glass formation discussed intensively in ref. [5] and in other extensive literature during the last decade [15–18]. It is probable that the fluctuation dynamics associated with the quantum nature of electronic molecules gives rise to the mysterious dynamical stripes observed in these materials.

Due to the small electronic masses the vibronic modes of these electronic molecules have higher frequency (much faster) than in usual molecules. These high-frequency vibronic modes of electronic molecules may play an important role in the Cooper pairing mechanism. Due to the high values of the frequency of such modes, as in MgB_2 , the resulting superconducting critical temperature, estimated with the aid of BCS-like theory, could be very high. Thus the electronic molecules may play an important role in the origin of the high-temperature superconductivity observed in cuprates.

Thus, for metallic and magnetic oxides (cuprates, nickelates and manganites), with high values of dielectric constant the screening and the electron-phonon coupling are strong. Therefore these electronic molecules are likely to arise in these materials and may be very important in explaining many of their exotic properties enumerated above, like, for example, a microscopic electronic phase separation and the formation of stripes [13–18].

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