

# Electron–phonon interaction and breakdown of the adiabatic principle in fullerides and $\text{MgB}_2$

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## Abstract

Novel materials and superconductors are often characterized by small electron Fermi energies  $E_F$ . This situation is expected to give rise to an unconventional electron–phonon phenomenology when the energy scale  $E_F$  becomes comparable with other electron–phonon energy scales as the phonon frequencies  $\omega_{\text{ph}}$  or the electron–phonon matrix elements  $g_{\text{el-ph}}$ . In this contribution we show how this scenario is intrinsically related to the violation of two different adiabatic assumptions on which the conventional electron–phonon picture relies, namely the Migdal’s theorem and the Born–Oppenheimer principle. Focusing on this latter, and using  $\text{MgB}_2$  as a textbook example, we show that the Born–Oppenheimer principle can be violated even in quasi-adiabatic systems ( $\omega_{\text{ph}}/E_F \ll 1$ ) when strong lattice fluctuations are present. Unlike the Migdal’s theorem which is related to the ratio  $\omega_{\text{ph}}/E_F$ , we show that these unconventional nonadiabatic effects are ruled by the ratio  $\kappa = g_{\text{el-ph}}/E_F$ , which in  $\text{MgB}_2$   $\kappa = 0.91$ .

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## 1. Introduction

The electron–phonon interaction plays a fundamental role in the transport and in many superconducting and normal state properties of a wide class of materials. However, although the electron–phonon phenomenology is nowadays well known in common systems, a satisfactory understanding of the same issue is lacking in more complex materials, as the high- $T_c$  superconductors, the colossal magneto-resistance manganites and in fullerides, where the electron–phonon phenomenology is much more unconventional and it is strictly correlated with electronic correlation effects. Similar problematics arise in new classes of materials, as the low dimensional electron systems, organic compounds or molecular crystals.

A common trait which is shared by all this wide family of compounds is the extreme smallness of the electronic energy scale, which competes thus with other internal energy scales. In this scenario the conventional metallic properties are quite unstable. From a practical point of view, the electronic energy scale is often parametrized in terms of the Fermi energy  $E_F$ , to be compared with other energy scales like the Hubbard repulsion  $U$ , the phonon frequencies  $\omega_{\text{ph}}$ , the electron–phonon matrix elements  $g_{\mathbf{k},\mathbf{k}'}$ , the impurity scattering rate  $\gamma_{\text{imp}}$ , etc. A nice view about the smallness of the Fermi energies in many unconventional superconductors is given by the so-called Uemura’s plot (Fig. 1) [1] where the critical temperature  $T_c$  for several different compounds is reported as function of  $E_F$ . Fig. 1 clearly shows that Fermi energies in these exotic superconductors are from one to two orders of magnitude smaller than conventional low- $T_c$  materials, as Sn, Al or Zn. This observation has interesting consequences about the expected physical properties. On one hand  $E_F$  is so small to be comparable with the Hubbard repulsion  $U$ , giving rise to strong electronic correlation effects which are

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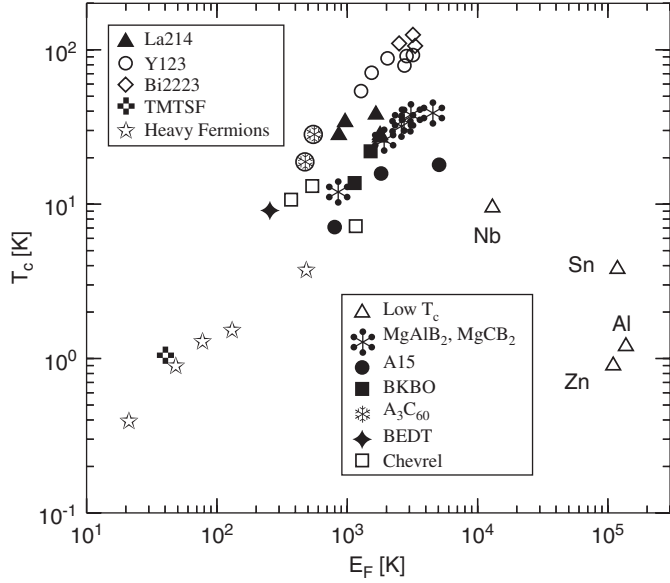


Fig. 1. Re-elaboration of  $T_c$  vs.  $E_F$  plot after Ref. [1] including magnesium diboride alloys.

indeed relevant for almost all these compounds. On the other hand, the same electronic energy scale  $E_F$  become comparable also with typical lattice energy scales, as the phonon frequencies  $\omega_{ph}$ . Just as in the case of the Hubbard repulsion, this scenario is expected to have drastic consequences on the Landau–Fermi liquid picture of the electron–phonon interaction, which is essentially based on the adiabatic limit  $\omega_{ph}/E_F \simeq 0$ . An extreme regime of this breakdown of the Fermi liquid quasi-particle properties is the polaronic one where the local lattice deformations associated with an electron can localize the electron itself leading to a violation of the Bloch-like translational invariance symmetry [2]. For the largest part of these compounds however metallic properties are still observed although with peculiar unconventional features, and an exhaustive comprehension of this anomalous Fermi-liquid phenomenology of the electron–lattice interaction is one of the most interesting challenges in this field.

An usual starting point in literature to discuss these issues is by writing down the electron–phonon interaction which in the most general for reads [3]:

$$H = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}} + \sum_{\mathbf{q}} \omega_{\mathbf{q}} c_{\mathbf{q}}^{\dagger} c_{\mathbf{q}} + \sum_{\mathbf{k}, \mathbf{q}} g_{\mathbf{k}, \mathbf{q}} c_{\mathbf{k}+\mathbf{q}}^{\dagger} c_{\mathbf{k}} (a_{\mathbf{q}} + a_{-\mathbf{q}}^{\dagger}), \quad (1)$$

where  $\varepsilon_{\mathbf{k}}$  is the electronic band dispersion,  $g_{\mathbf{k}, \mathbf{q}}$  is the electron–phonon matrix element and  $\omega_{\mathbf{q}}$  are the phonon frequencies. Here for simplicity we have disregarded the electron spin degree of freedom which does not play any role in the following. For practical purpose, these quantities are usually taken from first-principle calculations based on the local density approximation (LDA). In particular,  $\varepsilon_{\mathbf{k}}$  is evaluated at the lattice equilibrium,  $g_{\mathbf{k}, \mathbf{q}}$  is

extracted by the linear response theory or by the electron deformation potential for vanishing small lattice displacements, and  $\omega_{\mathbf{q}}$  is obtained by the linear response theory itself or by frozen-phonon calculation where the lattice displacements are treated as classical variables. The physical properties of the electron–phonon interaction are also usually discussed in terms of two dimensionless parameters, the electron–phonon coupling constant  $\lambda = \sum_{\mathbf{q}} 2N(0) \langle |g_{\mathbf{k}, \mathbf{q}}|^2 \rangle_{FS} / \omega_{\mathbf{q}}$  (where  $N(0)$  is the electron density of states at the Fermi level and  $\langle \dots \rangle_{FS}$  indicate an average of the electron momentum  $\mathbf{k}$  over the Fermi surface) and the “adiabatic” parameter  $\omega_{\mathbf{q}}^{\max} / E_F$ .

In this contribution we would like to review the physical implications related to the smallness of the Fermi energy scale  $E_F$  with respect to the electron–phonon energy scales  $g_{el-ph}$  and  $\omega_{ph}$ . In particular we identify two distinct classes of problematics. The most debated in literature is the “many-body” problem, that is to say, assuming we are able to write down an effective Hamiltonian like Eq. (1), how to define a theoretical scheme capable to evaluate physical properties from the knowledge of the Hamiltonian. As a matter of fact, Eq. (1) still contains indeed the full many-body complexity of the electron–phonon interaction and it cannot be solved exactly. A huge simplification arises in the adiabatic limit  $\omega_{ph}/E_F \ll 1$ , which is relevant for many conventional metals where  $\omega_{ph}/E_F \sim 10^3 - 10^{-4}$ . In this limit the mean-field-like Eliashberg theory was shown to be essentially exact in virtue of the so-called Migdal’s theorem [4] which permits to neglect higher-order vertex processes. This simplification however clearly does not apply in small Fermi energy systems where the Fermi energy  $E_F$  is of the same order of the phonon frequency scale  $\omega_{ph}$ , so that the full many-body problem is needed to be faced.

The second class of problematics is the possibility itself to write down an effective electron–phonon Hamiltonian like Eq. (1). Eq. (1) relies indeed on the assumption that: (i) it is possible to identify single-particle excitations for both the decoupled electronic and lattice degrees of freedom [first two terms in Eq. (1)]; (ii) the electron–lattice interaction appears in this basis as virtual transitions between these single-particle excitations [third term in Eq. (1)]. These constraints are naturally fulfilled within the context of the “adiabatic” Born–Oppenheimer approximation. As we are going to see, however the validity of these assumptions becomes questionable when the electronic energy scales are comparable with the electron–phonon energy scale  $g_{el-ph}$ .

## 2. The Born–Oppenheimer scheme

In order to underline the implicit assumptions on which our knowledge of the conventional electron–phonon phenomenology is based, and to clarify the different origin of these two kinds of violation, it is worth to review in simple terms in this section the practical derivation of Eq. (1) from the Born–Oppenheimer principle. To this aim we follow essentially the derivation of Refs. [3,5]. In

particular we shall distinguish between a “Born–Oppenheimer” *scheme*, which permits to define a complete basis set in the electron–lattice Hilbert space, and the adiabatic “Born–Oppenheimer” *approximation*, which reduces the full electron–lattice Hamiltonian into an (approximate) diagonal form.

Let us thus do a step back with respect to Eq. (1) and consider the general electron–lattice Hamiltonian:

$$H = H^{\text{cl}}(\mathbf{r}, \mathbf{u}) - \frac{\hbar^2 \nabla_{\mathbf{u}}^2}{2M}, \quad (2)$$

$$H^{\text{cl}}(\mathbf{r}, \mathbf{u}) = -\frac{\hbar^2 \nabla_{\mathbf{r}}^2}{2m} + V^{\text{el-ion}}(\mathbf{r}, \mathbf{u}) + V^{\text{ion}}(\mathbf{u}), \quad (3)$$

where  $\mathbf{r}$  are electronic coordinates,  $m$  the electron mass and  $\mathbf{u}$  and  $M$  are, respectively, the ion displacement from the lattice equilibrium and the reduced mass associated to a particular vibrational mode. In this notation the Hamiltonian term  $H^{\text{cl}}$  represents the classical Hamiltonian counterpart for the lattice degrees of freedom where the lattice motion is neglected, and it reduces to the whole lattice Hamiltonian in the limit case where the lattice degrees of freedom are treated in a classical way ( $M \rightarrow \infty$ ).

We want to introduce now a suitable basis for the electronic and lattice degrees of freedom wherein the Hamiltonian (3) can be written in a matricial form. In the spirit of the “Born–Oppenheimer” *scheme* we can thus solve the purely electronic quantum problem

$$H^{\text{cl}}(\mathbf{r}, [u])\varphi_n(\mathbf{r}, [u]) = \varepsilon_n^{\text{cl}}[u]\varphi_n(\mathbf{r}, [u]), \quad (4)$$

where  $[u]$  indicates a parametrical (not quantum) dependence on the lattice variables. For each  $u$  the eigenfunctions  $\varphi_n(\mathbf{r}, [u])$  represent a complete, orthonormal basis for the electronic Hilbert space. We can thus write down the electronic matrix structure  $H_{nm}$  of the full Hamiltonian (3) as [5]:

$$H_{nm} = \varepsilon_n^{\text{cl}}[u]\delta_{nm} + \Delta H_{nm}[u], \quad (5)$$

$$\Delta H_{nm}[u] = - \int d\mathbf{r} \varphi_n^*(\mathbf{r}, [u]) \frac{\hbar^2 \nabla_{\mathbf{u}}^2}{2M} \varphi_m(\mathbf{r}, [u]). \quad (6)$$

Since  $\varphi_n(\mathbf{r}, [u])$  is an eigenfunction of  $H^{\text{cl}}$ , it is clear that  $H_{nm}^{\text{cl}}$  will be diagonal and the only non diagonal elements of  $H_{nm}$  will come from  $\langle \varphi_n([u]) | \hbar^2 \nabla_{\mathbf{u}}^2 / 2M | \varphi_m([u]) \rangle$  (note that this term will give rise also to *diagonal* elements).

So far we have just written our original electron–lattice problem in a different electronic Hilbert space, but we have not introduced any approximation, and the solution of Eqs. (4)–(5) will in principle provide an exact solution. In particular the eigenstates  $\Psi^\mu(\mathbf{r}; \mathbf{u})$  of the full Hamiltonian (2),

$$H\Psi^\mu(\mathbf{r}; \mathbf{u}) = E^\mu\Psi^\mu(\mathbf{r}; \mathbf{u}), \quad (7)$$

can be written in general way in the form

$$\Psi^\mu(\mathbf{r}; \mathbf{u}) = \sum_n \chi_n^\mu(u)\varphi_n(\mathbf{r}; [u]), \quad (8)$$

where the coefficients  $\chi_n^\mu(u)$  fulfill the relations:

$$E^\mu \chi_n^\mu(u) = \varepsilon_n^{\text{cl}}[u]\chi_n^\mu(u) - \frac{\hbar^2 \nabla_u^2 \chi_n^\mu(u)}{2M} - \sum_m A_{n,m}[u] \frac{\hbar \nabla_u \chi_m^\mu(u)}{\sqrt{2M}} - \sum_m B_{n,m}[u]\chi_m^\mu(u), \quad (9)$$

where

$$A_{n,m}[u] = \int d\mathbf{r} \varphi_n^*(\mathbf{r}, [u]) \frac{\hbar \nabla_u}{\sqrt{2M}} \varphi_m(\mathbf{r}, [u]), \quad (10)$$

and

$$B_{n,m}[u] = \int d\mathbf{r} \varphi_n^*(\mathbf{r}, [u]) \frac{\hbar^2 \nabla_u^2}{2M} \varphi_m(\mathbf{r}, [u]). \quad (11)$$

Eqs. (9)–(11) define a set of coupled Schrödinger-like equations for the lattice coordinates. Note however that  $\chi_n^\mu(u)$  are *not* eigenfunctions of the lattice problem (9)–(11) since they are coupled with  $\chi_m^\mu(u)$  ( $m \neq n$ ) through the terms  $A_{nm}$  and  $B_{nm}$ . We can however introduce a complete basis  $\phi_{\alpha,n}(\mathbf{u})$  even for the lattice degrees of freedom solving the reduced problem defined as

$$E_{\alpha,n}\phi_{\alpha,n}(\mathbf{u}) = \varepsilon_n^{\text{cl}}[u]\phi_{\alpha,n}(\mathbf{u}) - \frac{\hbar^2 \nabla_{\mathbf{u}}^2 \phi_{\alpha,n}(\mathbf{u})}{2M}. \quad (12)$$

The functions  $\phi_{\alpha,n}(\mathbf{u})\varphi_n(\mathbf{r}, [u])$  define now a complete basis in the whole electron–lattice Hilbert space, so that the total eigenfunction can be written as

$$\Psi^\mu(\mathbf{r}; \mathbf{u}) = \sum_{\alpha,n} \gamma_{\alpha,n}^\mu \phi_{\alpha,n}(\mathbf{u})\varphi_n(\mathbf{r}; [u]), \quad (13)$$

where the coefficients  $\gamma_{\alpha,n}^\mu$  fulfill the matricial relation [5]

$$E^\mu \gamma_{\alpha,n}^\mu = E_{\alpha,n}\gamma_{\alpha,n}^\mu - \sum_{\alpha',m} a_{\alpha,n;\alpha',m} \gamma_{\alpha',m}^\mu - \sum_{\alpha',m} b_{\alpha,n;\alpha',m} \gamma_{\alpha',m}^\mu, \quad (14)$$

and where

$$a_{\alpha,n;\alpha',m} = \int du A_{n,m}[u] [\phi_{\alpha',m}^\mu(u)]^* \left[ \frac{\hbar \nabla_u \phi_{\alpha,n}^\mu(u)}{\sqrt{2M}} \right], \quad (15)$$

$$b_{\alpha,n;\alpha',m} = \int du B_{n,m}[u] [\phi_{\alpha',m}^\mu(u)]^* \phi_{\alpha,n}^\mu(u). \quad (16)$$

We would like to stress that so far no kind of approximation has been introduced. We have just applied the Born–Oppenheimer scheme to define a useful basis for the Hilbert space where the electron–lattice problem is written in matricial form. Solving the coupled electron–lattice quantum problem is however still a formidable task for two main reasons: (i) the evaluation of each matrix element requires solving an electron problem (Eq. (4)) for *any* lattice distortion; (ii) even assuming that all the matrix elements are known, the  $a$  and  $b$  matrices are highly non-diagonal and, in the absence of a *theory* which permits to restrict on some subset or to find some recursion formula, the practical solution of the electron–lattice problem is inaccessible.

### 3. The Born–Oppenheimer approximation

As mentioned before, Eq. (14) is just an exact matricial representation for the whole electron–phonon problem and it does not contain any degree of approximation. As we are going to see however this basis is a suitable starting point since it permits to introduce in a very straightforward way the Born–Oppenheimer *approximation*. In this approximation we assume that lattice distortions affect very weakly the electronic wave-functions  $\varphi_n$  [3] so that  $\nabla_u \varphi_n(\mathbf{r}; [u]) \sim 0$  and  $\nabla_n^2 \varphi_n(\mathbf{r}; [u]) \sim 0$ . Within this approximation the matrices  $A_{n,m}[u]$ ,  $B_{n,m}[u]$  (and hence  $a_{\alpha,n;\alpha',m}, b_{\alpha,n;\alpha',m}$ ) are negligible and Eq. (14) reduces to a simple diagonal problem where the total wave-function  $\Psi^\mu(\mathbf{r}; \mathbf{u})$  factorizes in the Born–Oppenheimer product of electron and lattice wave-functions:

$$\Psi^\mu(\mathbf{r}; \mathbf{u}) = \phi_{\alpha,n}(\mathbf{u}) \varphi_n(\mathbf{r}; [u]). \quad (17)$$

Under the same assumption we can in addition in good approximation replace  $\varphi_n(\mathbf{r}; [u])$  with the one evaluated at the lattice equilibrium  $\varphi_n(\mathbf{r}; [u]) \rightarrow \varphi_n^0(\mathbf{r}) \equiv \varphi_n(\mathbf{r}; [u=0])$ . The lattice and electron degrees of freedom are now completely disentangled and we can express the original electron–lattice problem in terms of a non-interacting electron–phonon Hamiltonian,  $H^{\text{BO}} = H^{\text{el}} + H^{\text{ph}}$ . Note that the above described scheme of approximation is precisely what is done in LDA calculations for crystal systems, where the ground state and excited electron-wave-functions  $\varphi_n^0(\mathbf{r})$  are just given by the proper Slater’s determinants of the single-particle Bloch-like state  $c_{\mathbf{k}}^\dagger$  with energies  $\varepsilon_{\mathbf{k}}$ . In similar way ground state and excited lattice wave-functions are given by the symmetric product of single lattice excitations  $a_{\mathbf{q}}^\dagger$  with frequency  $\omega_{\mathbf{q}}$  obtained by the solution of the dynamical matrix, so that

$$H^{\text{BO}} = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} c_{\mathbf{k}}^\dagger c_{\mathbf{k}} + \omega_{\text{ph}} \sum_{\mathbf{q}} a_{\mathbf{q}}^\dagger a_{\mathbf{q}}. \quad (18)$$

Summarizing the main results of this section, we can say that: (i) the Born–Oppenheimer approximation permits to neglect all the off-diagonal elements in the matricial form of the electron–lattice Hamiltonian (14); (ii) the same assumptions on which the Born–Oppenheimer approximation relies [ $\varphi_n(\mathbf{r}; [u])$  weakly dependent on the lattice variables  $u$ ] permits also to express the total wave-function in terms of single electron and lattice excitations. In other words, in the Born–Oppenheimer approximation we are able to identify the disentangled electron and lattice excitations appearing in Eq. (18) (point (ii)) and we are able to define a compelling *theory* to deal with their many-body interaction (the simplest one: they *do not interact!*) (point (i)).

This extremely rigorous application of the Born–Oppenheimer approximation is of course quite problematic since it neglects the physical electron–phonon scattering arising from virtual states. The same Born–Oppenheimer approximation provides however also the way to include these effects. The simplest way to see it is to evaluate the first correction beyond the Born–Oppenheimer approximation by considering a finite gradient term  $\varphi_n'(\mathbf{r}) =$

$[\nabla_u \varphi_n(\mathbf{r}; [u])]_{u=0} \neq 0$  [5]. The matrix  $A$  in Eq. (10) contains now off-diagonal elements which, in the spirit of the Born–Oppenheimer, can be evaluated at the lattice equilibrium,  $A_{nm}[u] \simeq A_{nm}[u=0]$ , and which represent the electron–phonon scattering matrix elements  $g_{\mathbf{k},\mathbf{q}}$  appearing in Eq. (1). We would like to stress that these terms, as discussed above, are expected to vanish in the Born–Oppenheimer adiabatic limit when the lattice dynamics is much slower than the electron one (for instance, they scale as  $1/\sqrt{M}$ ). This argument does not rule out however the possibility that *virtual* transitions can have a sizable impact on the electron and lattice properties. This is indeed the case as it is shown already by second order perturbation theory analysis [3], where the energy correction  $\Delta E_N^{(2)}$ ,

$$\begin{aligned} \Delta E_N^{(2)} &= \sum_{M \neq N} \frac{|\langle N | H^{\text{el-ph}} | M \rangle|^2}{E_N - E_M} \\ &\simeq \sum_{\mathbf{k},\mathbf{q}} \frac{|g_{\mathbf{k},\mathbf{q}}|^2}{\omega_{\mathbf{q}}}, \end{aligned} \quad (19)$$

does not vanish in the adiabatic limit. Here  $|N\rangle$  and  $|M\rangle$  represent electron + phonon disentangled eigenstates of Eq. (18) with electron momenta  $\mathbf{k}$  close to the Fermi surface and  $H^{\text{el-ph}}$  is the third term of Eq. (1) arising from the first order corrections to the Born–Oppenheimer approximation.

Virtual transitions, as shown in Eq. (19), give rise to a renormalization of the electron and phonon properties as well as to finite lifetimes for the Born–Oppenheimer eigenstates. As discussed above, these effects survive in the adiabatic limit and they are mainly governed by the electron–phonon coupling constant  $\lambda$ . For strongly-intermediate coupled systems all the higher order terms are however also important. This means that, starting from the Born–Oppenheimer assumption, we are indeed able in principle to identify in the adiabatic limit the first order corrections beyond the Born–Oppenheimer approximation [off-diagonal elements of matrix (14)], but a resummation series of infinite terms is required to evaluate electron–phonon physical properties.

This latter inconvenient was solved by Migdal in the late 1950s [4] showing that only “rainbow” virtual transitions occur in the strictly adiabatic limit, where electron and phonon excitations are reabsorbed in the same order as they are emitted (see Fig. 2). Similar arguments select also only “ladder” terms in the two-particle channel [6]. This simplification, known as Migdal’s theorem, provides thus a useful scheme which, starting from the knowledge of the single-particle electron and phonon excitations evaluated within the Born–Oppenheimer approximation (Eq. (1)), defines a closed self-consistent theory for the electron–phonon many-body problem [3,6,7].

### 4. Breakdown of the adiabatic hypothesis in fullerenes and $\text{MgB}_2$

In the previous sections we have discussed in detail how the Born–Oppenheimer approximation is employed to

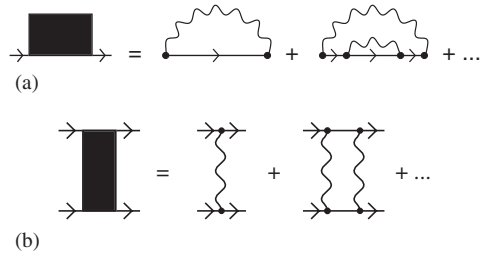


Fig. 2. Diagrammatic representation of the electron–phonon scattering within the Migdal’s theorem: (a) one-particle self-energy diagrams; (b) two-particle (Cooper channel) interaction.

derive a well-defined theoretical scheme on which the conventional (Migdal–Eliashberg) picture of the electron–phonon interaction is based. We identified two different logical steps. The first one is the actual application of the Born–Oppenheimer approximation which permits to define one-particle electron and phonon excitations as well as their scattering matrix elements. Upon this assumption we are able to write down the standard electron–phonon Hamiltonian (1) and to evaluate the electronic band structure  $\varepsilon_{\mathbf{k}}$ , the phonon dispersion  $\omega_{\mathbf{q}}$  and the electron–phonon matrix elements  $g_{\mathbf{k},\mathbf{q}}$ . These quantities are often extracted by LDA calculations which are indeed based on the Born–Oppenheimer principle. The Hamiltonian (1) defines now the quantum many-body electron–phonon problem which is in principle unsolvable. The second logical step is thus to introduce some kind of theory to provide a solvable close set of equations. This task is achieved by the Migdal’s theorem which restricts the electron–phonon scattering processes to a sub-class which can be evaluated in a self-consistent way. It is important to underline that, although it is also based on the adiabatic limit  $\omega_{\text{ph}}/E_{\text{F}}$ , the range of validity of the Migdal’s theorem is not necessarily the same of the Born–Oppenheimer approximation. In better words, as we are going to discuss in more details, the breakdown of Migdal’s theorem ( $\omega_{\text{ph}}/E_{\text{F}} \neq 0$ ) is unavoidably associated with a violation of the Born–Oppenheimer assumption, but different sources for the violation of the Born–Oppenheimer approximation, not associated with a sizable  $\omega_{\text{ph}}/E_{\text{F}}$ , are also possible, in particular in the presence of strong zero point motion lattice fluctuations. In this latter case new kinds of nonadiabatic effects are triggered on by the comparison between the energy scales  $g_{\text{el-ph}}$  and  $E_{\text{F}}$ , so that the ruling parameter for these effects is  $g_{\text{el-ph}}/E_{\text{F}}$ .

From the materials science point of view, the nonadiabatic effects related to  $\omega_{\text{ph}}/E_{\text{F}}$  are most relevant in fullerene compounds [8], where  $\omega_{\text{ph}} \sim 0.2$  eV and  $E_{\text{F}} \sim 0.25$  eV ( $\omega_{\text{ph}}/E_{\text{F}} \sim 0.8$ ) [9], while the nonadiabatic effects associated with the lattice quantum fluctuations are nicely pointed out in  $\text{MgB}_2$  where  $g_{E_{2g}} \sim 0.41$  eV and  $E_{\text{F}} \sim 0.45$  eV ( $g_{E_{2g}}/E_{\text{F}} \sim 0.9$ ), but  $\omega_{\text{ph}}/E_{\text{F}} \sim 0.1 - 0.2$  [10]. The consequences of the breakdown of the adiabatic hypothesis related to  $\omega_{\text{ph}}/E_{\text{F}}$  in fullerenes and in cuprates, have been investigated in details in Refs. [11–18], while the relevance

of the lattice fluctuations with respect to the violation of the Born–Oppenheimer principle has been pointed out only recently in Ref. [10]. We address the reader to the above references for more details. In the last part of this contribution on the other hand we would like to spent some more words in order to clarify the physical conditions under which these kinds of nonadiabatic breakdown occur. On this point the specific case of  $\text{MgB}_2$ , in comparison with the fullerene case, will be useful.

Let us thus assume for the moment the Born–Oppenheimer approximation to be valid and let us give a look at the electronic band structure of  $\text{MgB}_2$  reported in Fig. 3 as obtained by LDA calculations for the undistorted lattice structure [19–21]. It contains a set of three-dimensional highly dispersive  $\pi$  bands and two almost bidimensional  $\sigma$  bands which cut the Fermi level quite close to the top. We can distinguish a Fermi energy for the  $\pi$  bands,  $E_{\text{F}}^{\pi}$ , of the order of some eVs, similar to many simple metals, and a Fermi energy  $E_{\text{F}}^{\sigma}$  for the  $\alpha$  band sub-structure, which is mainly given by the distance between the Fermi level and the top of the  $\sigma$  bands,  $E_{\text{F}}^{\sigma} \sim 0.4 - 0.6$  eV. LDA calculations show in addition that the  $\pi$  bands are weakly coupled with the phonons whereas the electron–phonon interaction is dominated by the coupling between the  $\sigma$  bands and the  $\mathbf{q} \approx 0$  phonon modes of the optical  $E_{2g}$  branch [20–24]. The main effect of these lattice modes is to split the degeneracy of the two  $\alpha$  bands at the  $\Gamma$  point. The electron–phonon properties can be described thus in good approximation by the simple reduced Hamiltonian [25]:

$$H = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}} \pm I_{E_{2g}} \sum_{\mathbf{k}} c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}} u - \frac{\hbar^2 \nabla_{\mathbf{u}}^2}{2M_{E_{2g}}} + V(u), \quad (20)$$

where  $c_{\mathbf{k}}^{\dagger}$  represents single-particle excitations in the two degenerate  $\sigma$  states,  $u$  is the lattice displacement of the  $E_{2g}$  phonon mode with lattice potential  $V(u)$ , and  $I_{E_{2g}}$  is the deformation potential of this phonon mode relative to the  $\sigma$  bands. The sign  $\pm$  takes into account the Jahn–Teller splitting of the bands, shifting one band upwards and the other one downwards. Comparing the phonon frequency for the  $E_{2g}$  mode  $\omega_{E_{2g}} \sim 70 - 75$  meV (taking into account the anharmonic hardening) and the Fermi energy for the  $\sigma$

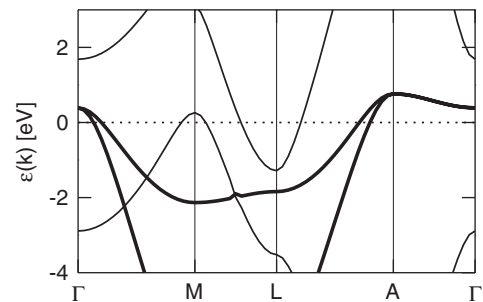


Fig. 3. Band structure of  $\text{MgB}_2$  for the undistorted lattice. Tiny lines are the  $\pi$  band while thick lines represent the almost two-dimensional  $\sigma$ -bands. The horizontal dotted line is the Fermi level.

bands  $E_F^\sigma \sim 0.4\text{--}0.6\text{ eV}$  we estimate an adiabatic parameter  $\omega_{\text{ph}}/E_F \sim 0.1\text{--}0.2$ , which suggests that, at this level of investigation, nonadiabatic effects arising from the breakdown of the Migdal's theorem are indeed present [26] but they probably do not play a primary role. In common metals the same parameter rules also the validity of the Born–Oppenheimer approximation since it compares the typical energies of the lattice dynamics with the electronic one. It is important to stress however that in this kind of analysis we are comparing a phonon energy  $\omega_{\text{ph}}$ , taken from the quantum solution of the Schrödinger lattice problem with the electron energies evaluated *in the absence* of lattice dynamics, namely in the frozen crystal structure  $u = 0$ . In terms of the Born–Oppenheimer language, this means that the condition  $\omega_{\text{ph}}/E_F \ll 1$ , where  $E_F$  is evaluated from the electron band structure *in the absence* of lattice distortion  $u = 0$ , ensures the validity of the Born–Oppenheimer condition  $\nabla_u \varphi(\mathbf{r}, [u]) \sim 0$  *only in neighborhood* of  $u = 0$ , namely  $\nabla_u \varphi(\mathbf{r}, [u])|_{u=0} \sim 0$ ,  $\nabla_u^2 \varphi(\mathbf{r}, [u])|_{u=0} \sim 0$ . One could however question how much this limit is representative of a full quantum treatment of the lattice degrees of freedom. In particular from that Eqs. (15)–(16) we note that the enforcement of the Born–Oppenheimer assumption requires the matrices  $A_{n,m}[u]$ ,  $B_{n,m}[u]$  (and hence  $\nabla_u \varphi(\mathbf{r}, [u])$ ,  $\nabla_u^2 \varphi(\mathbf{r}, [u])$ ) to be negligible in the *whole*  $u$  space weighted, respectively, by  $\phi^*(u)\nabla_u \phi(u)$  and  $\phi^*(u)\phi(u)$ .

We are now in the position to investigate this point in the specific case of  $\text{MgB}_2$ . We employ the Born–Oppenheimer framework underlying the LDA calculations to check its internal consistency. As discussed above, the case of  $\text{MgB}_2$  is quite simple since the  $\sigma$ -band electrons are linearly coupled with only one single ( $E_{2g}$ ) lattice mode. We evaluate the effective lattice potential  $\varepsilon_0^{\text{cl}}[u]$  appearing in Eq. (12) for these lattice vibrations, by means of frozen phonon calculations [10,25] (Fig. 4a) and we solve numerically the Schrodinger equation (12) to obtain the ground state lattice wave-function  $\phi_{0,0}(u)$  [10]. The corresponding probability distribution function  $P(u) = |\phi_{0,0}(u)|^2$  is also shown in Fig. 4a. It represents the physical range of the lattice vibrations associated with the  $E_{2g}$  mode. In the classical limit it is just a  $\delta$ -function  $P(u) = \delta(u)$ . The spatial  $u$ -extension of  $\phi_{0,0}(u)$  is thus related with the zero point motion lattice fluctuations and it gives the relevant range of  $u$  wherein the electron wave-function and its derivatives need to be evaluated. An appropriate quantity to estimate the amplitude of the lattice quantum fluctuations is the root mean square (rms) of the lattice displacement,

$$\langle u^2 \rangle^{1/2} = \left[ \int du u^2 P(u) \right]^{1/2}, \quad (21)$$

which, in the case of the  $E_{2g}$  mode and taking into account also anharmonic effects,  $\langle u^2 \rangle^{1/2} = 0.034 \text{ \AA}$ .

In order to check the validity of the Born–Oppenheimer assumption in  $\text{MgB}_2$  we plot in Fig. 4b (dashed lines) the electronic band structure obtained by LDA techniques in

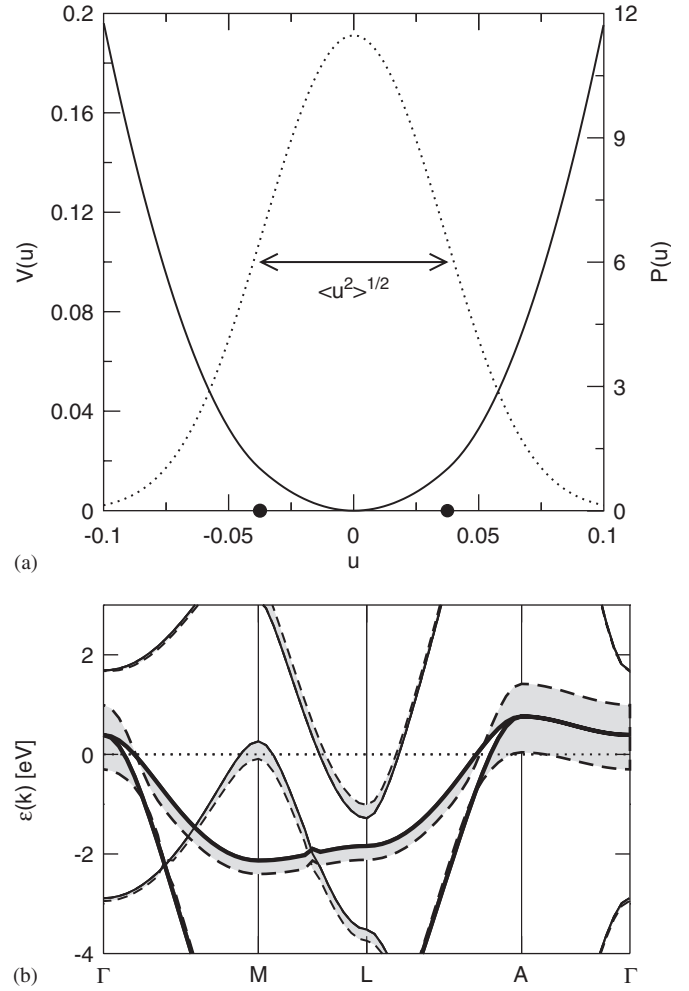


Fig. 4. (a) Frozen phonon potential  $V(u)$  for the  $E_{2g}$  mode in  $\text{MgB}_2$  (solid line, left side scale), and probability distribution function  $P(u) = |\psi_{0,0}(u)|^2$  (dotted line, right side scale),  $u$  is in units of  $\text{\AA}$ ,  $V(u)$  in units of eV and  $P(u)$  in units of  $\text{\AA}^{-1}$ . The filled circles on the  $u$ -axis mark the lattice distortion for which the Fermi energy of one  $\sigma$  band is zero,  $E_F^\sigma = 0$ . (b) Effects of the zero point lattice motion associated with the  $E_{2g}$  phonon mode on the electronic structure. The solid lines represent the electronic structure of undistorted  $\text{MgB}_2$  (bold lines are the  $\sigma$ -bands). The dashed lines show the band structure evaluate at the  $u = 0.034 \text{ \AA}$ , corresponding to the rms value of the lattice fluctuations.

the distorted crystal structure with  $u = \pm \langle u^2 \rangle^{1/2}$  [10]. The important thing here to be noted is that the physical range of the quantum lattice fluctuations has huge effects on the electronic structure. This means that the simple check of the validity of the Born–Oppenheimer principle close to  $u = 0$  is *not* representative of the physical range of lattice fluctuations. More precisely, while the Born–Oppenheimer assumption can be expected to be fulfilled around  $u = 0$ , it is drastically questioned at  $u = \pm \langle u^2 \rangle^{1/2}$  where the Fermi energy of the  $\sigma$ -bands is almost vanishing and  $E_F/\omega_{E_{2g}} \ll 1$ .

This analysis points out that unconventional nonadiabatic effects can arise even in “quasi adiabatic” systems [ $\omega_{\text{ph}}/E_F(u=0) \ll 1$ ] as far as lattice fluctuations are strong enough to probe lattice configurations where  $E_F(u) \sim 0$ . We have shown in Fig. 4b that this is the case in  $\text{MgB}_2$  where

the changes of the electronic structure  $\Delta\epsilon_{\mathbf{k}}$  induced by the lattice fluctuations associated with the zero point motion are of the same order of the Fermi energy of the  $\sigma$  bands. The Hamiltonian model (20) permits to quantify in a simple way these effects, namely  $\Delta\epsilon_{\mathbf{k}} = I_{E_{2g}} \langle u^2 \rangle^{1/2} \simeq 0.41 \text{ eV}$ , where the value  $I_{E_{2g}} = 12 \text{ eV}/\text{\AA}$  is provided by LDA calculations [25] and  $\langle u^2 \rangle^{1/2} = 0.034 \text{ \AA}$  obtained by the lattice Schrödinger equation [10]. Note that  $I_{E_{2g}} \langle u^2 \rangle^{1/2}$  is nothing else than the energy-dimensional electron–phonon matrix element appearing in Eq. (1) for the  $E_{2g}$  phonon mode.

In a general way we can thus define, from Eq. (1), an independent dimensionless parameter  $\kappa = g_{\text{el-ph}}/E_F$ , different from  $\omega_{\text{ph}}/E_F$ . Just as  $\omega_{\text{ph}}/E_F \sim 1$  rules the appearing of nonadiabatic effects due to the breakdown of the Migdal’s theorem, the condition  $\kappa \sim 1$  implies the breakdown of the Born–Oppenheimer approximation due to the presence of strong lattice fluctuations. The large value of  $\kappa \simeq 0.91$  in  $\text{MgB}_2$  points out the inconsistency in this compound of the Born–Oppenheimer principle and of the theoretical approaches based on it.

## 5. Conclusion

In summary, in this contribution we have investigated the possible onset of unconventional electron–phonon phenomenology in small Fermi energy materials, as full-erides and  $\text{MgB}_2$ , where the Fermi energy  $E_F$  can be of the same order of the phonon frequencies  $\omega_{\text{ph}}$  or of the electron–phonon matrix elements  $g_{\text{el-ph}}$ . A detailed derivation of the Born–Oppenheimer approximation has permitted to point out two possible sources of breakdown of the conventional electron–phonon theory. The first one assumes the validity of the Born–Oppenheimer approximation, which permits to define disentangled electron and phonon one-particle excitations, and it is related to the breakdown of the Migdal’s theorem for  $\omega_{\text{ph}} \sim E_F$ . The second one is more subtle and it is associated with the violation of the Born–Oppenheimer principle even in “quasi-adiabatic” system ( $\omega_{\text{ph}}/E_F \ll 1$ ) in the presence of strong lattice fluctuations. In this scenario the electron band structure evaluated in the undistorted case  $u = 0$  is no more representative, quantum lattice fluctuations make the system to probe highly nonadiabatic configurations, and the Born–Oppenheimer constraints  $\nabla_u \varphi(\mathbf{r}, [u]) \sim 0, \nabla_u^2 \varphi(\mathbf{r}, [u]) \sim 0$ , are broken down in a relevant range of the lattice space.

As a final consideration we have to notice however that, while the investigation of the breakdown of the Migdal’s theorem has led to the definition of a nonadiabatic theory of the electron–phonon interaction in the  $\omega_{\text{ph}}/E_F \sim 1$  regime [11–18], a similar self-consistent theory is nowadays

still lacking for what concerns the violation of the Born–Oppenheimer principle driven by  $g_{\text{el-ph}}/E_F$ . In our opinion this is one of the most challenging lines of research in this field and we hope the present work would contribute to trigger on further investigation on this subject.

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