Temperature dependent excitonic effects in the optical properties of single-layer MoS$_2$

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Temperature influences the performance of two-dimensional materials in optoelectronic devices. Indeed, the optical characterization of these materials is usually realized at room temperature. Nevertheless, most ab-initio studies are yet performed without including any temperature effect. As a consequence, important features are thus overlooked, such as the relative intensity of the excitonic peaks and their broadening, directly related to the temperature and to the non-radiative exciton relaxation time. We present ab-initio calculations of the optical response of single-layer MoS$_2$, a prototype 2D material, as a function of temperature using density functional theory and many-body perturbation theory. We compute the electron-phonon interaction using the full spinorial wave functions, i.e., fully taking into account effects of spin-orbit interaction. We find that bound excitons (A and B peaks) and resonant excitons (C peak) exhibit different behavior with temperature, displaying different non-radiative linewidths. We conclude that the inhomogeneous broadening of the absorption spectra is mainly due to electron-phonon scattering mechanisms. Our calculations explain the shortcomings of previous (zero-temperature) theoretical spectra and match well with the experimental spectra acquired at room temperature. Moreover, we disentangle the contributions of acoustic and optical phonon modes to the quasi-particles and exciton linewidths. Our model also allows to identify which phonon modes couple to each exciton state, useful for the interpretation of resonant Raman scattering experiments.

I. INTRODUCTION

Ultrathin two-dimensional materials such as graphene and MoS$_2$ are appealing candidates for a new generation of opto-electronic devices such as photoresponisve memories, light-emitting and harvesting devices, or nano-scale transistors. They are also suitable platforms for carrying out research on fundamental physics phenomena like the valley Hall effect, ultrafast charge transfer, valley excitons in two-dimensional materials. Technologically, single-layer MoS$_2$ is relevant due to a direct optical gap at 1.8 eV and a high electron mobility.

The optical response of MoS$_2$ is dominated by strongly bound excitons. The same holds for the other group VI semiconducting single-layer transition-metal dichalcogenides (TMDs) such MX$_2$ with M = Mo or W and X = S, Se, or Te. This suggests their possible use in opto-electronic devices working at room temperature. Nevertheless, most of the modern first-principles ground and excited state simulations are performed at 0 K and thus omit the role of thermal lattice vibrations on the electronic and optical properties.

In general, temperature has a capital influence on the electronic and optical properties of semiconductors determining their application as optoelectronic devices. It is well known that its drives the band gap renormalization, and induces changes in the position and width of the optical peaks. At the same time, the spectra obtained from other techniques such as angle-resolved photoemission spectroscopy (ARPES) are clearly influenced by the temperature due to the enhanced mixing of electron and phonon states.

The possibility to perform electronic structure calculations based on ab-initio approaches including the electron-phonon (EP) interaction is thus of paramount importance. Even though many years ago Heine, Allen and Cardona (HAC) pointed out that the EP coupling can induce corrections of the electronic levels as large as those induced by the electronic correlation, the number of works based on first-principles simulations addressing this problem is still very limited and mainly dedicated to traditional bulk compounds. The inclusion of EP couplings considerably broadens the scope of first-principles electronic-structure calculations beyond the study of temperature effects. It opens the way to the study of many interesting phenomena such as polaron formation in crystals and transport properties.

As for MoS$_2$, theoretical ab-initio studies including the EP interaction have addressed specific aspects such as phonon-limited mobility, thermal conductivity, electron cooling, or electron transport. Tongay et. al. have performed a theoretical and experimental study of the band gap dependence on temperature for multi-layer MoSe$_2$ and MoS$_2$. They have attributed all temperature effects to lattice renormalization induced by the thermal expansion. They capture correctly the band gap trend only for high temperatures (above 300 K). Below room temperature, the electron-phonon interaction plays a crucial role but it is ignored by Tongay et. al. In Ref. 11 Qiu et. al. have studied temperature effects by includ-
ing the quasi-particle linewidths. However, they ignored the energy renormalization and the accurate calculation of the linewidths across all the Brillouin zone. Here we explore using a fully \textit{ab initio} approach how the EP interaction induces changes in the electronic structure and optical properties of the MoS$_2$ single-layer. This also enables us to address photoluminescence,\textsuperscript{26} ARPES,\textsuperscript{17,27} and resonant Raman scattering experiments.\textsuperscript{28}

Differently from most of the recent works on bulk materials\textsuperscript{29} we do not limit our study to the band gap renormalization but we extend our investigation to the full band structure, with special attention to the electron states of interest for opto-electronic applications. Starting from previous studies which established the existence of several kind of excitonic states in this low-dimensional material,\textsuperscript{10,11} whose behavior we characterize as a function of the temperature. We calculate the shift of the binding energy and the non-radiative linewidths of excited states.

It is worth to underline that in our approach we use the full spinorial nature of the wave functions through all ground and excited state calculations. This is quite important because it is well known that spin-orbit coupling determines the valley polarization dynamics and is fundamental to understand the optical properties of all TMDs.

\section{II. THE THEORETICAL APPROACH}

Our calculations start with density-functional theory (DFT) to obtain a first estimate of the electronic bands. We use density-functional perturbation theory (DFPT) to calculate the phonon modes and the electron-phonon coupling matrix elements. With the latter we calculate the change of the electronic bands due to the lattice vibrations.\textsuperscript{30} Afterwards, we solve the temperature dependent Bethe-Salpeter equation.\textsuperscript{31} We thus explore the change in the optical spectra, and in the exciton energies and linewidths when temperature increases.

The ground state properties of single-layer MoS$_2$, eigenvalues and wave functions, are calculated with the QUANTUM ESPRESSO code\textsuperscript{32} within the local density approximation (LDA) for the exchange-correlation potential. We use DFPT to obtain the phonon modes as well as the first and second order electron-phonon matrix elements.\textsuperscript{33} As mentioned in the introduction the spin-orbit interaction is essential to correctly describe excitons in MoS$_2$, for this reason also the electron-phonon matrix elements are calculated taking into account the full spinor wave functions.

We study the temperature effects on the electronic states and on the excitons by merging DFT/DFPT with many-body perturbation theory. Within this framework, two self-energy diagrams, which correspond to the lowest non-vanishing terms of a perturbative treatment, have to be evaluated. The Fan self-energy,\textsuperscript{33} related to first order terms

\begin{equation}
\Sigma_{\text{Fan}}^{\text{Fan}}(\omega, T) = i \sum_{n', \lambda} \frac{g_{n'k}^{\lambda}}{N_q} \times \left[ N_q(T) + 1 - f_{n'k-q} \right] \left[ \omega - \varepsilon_{n'k-q} - \omega_{\lambda} - i0^+ \right] \times \left[ N_q(T) + f_{n'k-q} \right] \left[ \omega - \varepsilon_{n'k-q} + \omega_{\lambda} - i0^+ \right],
\end{equation}

where $\varepsilon_{n,k}$ are the LDA eigenvalues, $\omega_{\lambda}$ the phonon frequencies, $f_{n,k}$ and $N_q(T)$ are the Fermi and Bose distribution functions of electrons and phonons, respectively. The self-energy associated to an electron state $(n,k)$ is the sum over all the electron states $n'$ and phonon modes $\lambda$, where $N_q$ is the number of $q$ vectors in the Brillouin zone. Conservation of momentum is explicitly enforced. The first order electron-phonon matrix elements $g_{n'k}^{\lambda}$ represents the amplitude for the scattering process $|n,k\rangle \rightarrow |n', k-q \rangle \otimes |\lambda\rangle$,\textsuperscript{30} We have a similar expression for the Debye-Waller (DW) self-energy, related to the second order terms,

\begin{equation}
\Sigma_{\text{DW}}^{\text{DW}}(T) = \frac{1}{N_q} \sum_{\lambda} \Lambda_{n'k}^{\lambda} - \Lambda_{nk}^{\lambda} (2N_q(T) + 1),
\end{equation}

where $\Lambda_{n'k}^{\lambda}$, instead, represents the amplitude for the second-order electron-phonon scattering process $|n,k\rangle \rightarrow |n', k-q - q'\rangle \otimes |\lambda\rangle \otimes |\lambda'\rangle$.\textsuperscript{30} In both self-energy terms, temperature enters via the phonon population. In polar semiconductors the electron-phonon interaction strength becomes larger when including the Fröhlich polar-coupling term.\textsuperscript{34} Nonetheless, the LO-TO splitting in MoS$_2$ is rather small, 3 cm$^{-1}$, and we do not expect significant changes in single-layer.

The fully interacting electron propagator (accounting for the electron-phonon interaction) is

\begin{equation}
G_{nk}(\omega, T) = (\omega - \varepsilon_{nk} - \Sigma_{nk}^{\text{Fan}}(\omega, T) - \Sigma_{nk}^{\text{DW}}(T))^{-1}.
\end{equation}

The complex poles of this equation define the electronic excitations of the interacting system. If the quasi-particle approximation (QPA) is valid, and assuming a smooth frequency dependence, the electron-phonon self-energy can be expanded up to the first order around the bare energies ($\varepsilon_{nk}$). In this case the temperature dependent quasi-particle energies are defined as,\textsuperscript{35}

\begin{equation}
E_{nk}(T) = \varepsilon_{nk} + Z_{nk}(T) \left[ \Sigma_{nk}^{\text{Fan}}(\varepsilon_{nk}, T) + \Sigma_{nk}^{\text{DW}}(T) \right].
\end{equation}

It is clear that the quasi-particle energies depend on temperature and are complex numbers, where the real parts are the quasi-particle energies and the imaginary parts, $\Gamma_{nk}(T)$, correspond to the quasi-particle widths. The renormalization factor $Z_{nk}$ represents the quasi-particle charge. Therefore the QPA makes sense when
III. TEMPERATURE DEPENDENT ELECTRONIC STRUCTURE OF SINGLE-LAYER MOS$_2$

The calculation of the electronic structure of MoS$_2$ has been done in a plane-wave basis using norm-conserving pseudopotentials and a kinetic energy cutoff of 80 Ry and a k-grid of $12 \times 12 \times 1$. On top of self-consistent DFT simulations, electron-phonon matrix elements are obtained by DFPT in the local-density approximation. From the explicit expressions of the self-energy terms (Eqs. (1) and (2)), it becomes clear that a careful convergence over the number of bands $n'$ and the number of transferred phonon momenta $q$ to evaluate the integral over the Brillouin zone, is required. From our study we have found that, the spectral functions of MoS$_2$ converge using a set of 400 randomly distributed $q$ points and 36 bands (18 occupied bands - we do not take into account Mo-semicore electrons - and 18 empty bands). The calculations are converged with respect to number of $q$-points and bands. We have checked this on the profile of the spectral function which is a more stringent test than checking the eigenvalue correction. We have used a Lorentzian broadening of 60 meV. Recent works on diamond and silicon required a much larger number of bands and $q$-points to reach convergence.\textsuperscript{36} The rapid convergence with the number of $q$-points we have found here is mainly due to the two-dimensional nature of the material under investigation.

Figure 1 shows the spectral function of single-layer MoS$_2$ for temperature 0 K (left panel) and 300 K (right panel). An animated representation of the band structures for temperature ranging from 0 to 1000 K in step of 100 K can be found in the Supplementary Informations. Dotted black lines represent the LDA band structure (without electron-phonon interaction). We have marked with squares some important points in the band structures, which will be discussed in more detail below. The bands are no longer a line and they acquire a broadening. This broadening is directly related to the linewidths of each quasiparticle state. Considering that lifetimes are inversely proportional to linewidths, narrow lines are related to long lifetimes, i.e., stable states. On the opposite, broader states have a stronger interaction with phonons and they have more non-radiative recombination paths, meaning a shorter lifetime.

We identify very narrow line shapes at the band edges like the valence band states at $K$ and $\Gamma$ points. In the conduction band we find narrow line shapes at $K$ and at the minimum between $K$ and $\Gamma$. Temperature tends to reduce the quasi-particle energy but it does not change significantly the spectral function, it only moves the maximum to lower energies. The increase of temperature results in a shrinking of the gap. Even at 0 K the gap is diminished by 75 meV (with respect to its value calculated without electron-phonon coupling). This is an effect of the zero-point vibrations of the atoms.

The spectral functions of quasi-particle states far from the band edges have a different aspect. Close to crossings, the bands become blurred, making it difficult to distinguish individual bands. For instance, the conduction band around $\Gamma$ and the crossing close to $M$ have a noticeable broadening, even at 0 K. The $M$ point shows also broader bands than the $\Gamma$ and the $K$ point. The increasing of temperature blurs even more the reminiscence of the LDA band dispersion. In areas close to $\Gamma$, the band index becomes almost obsolete and we observe a wide spectral range.\textsuperscript{37} It is worth to note that quasi-particle states are not necessarily broadened peaks centered at the renormalized electron energy. They can also be mixed states which can have a structure very different from the superposition of the electron and hole density of states. We also expect important consequences on the optical properties. Excitons from states in these range of energies (like the resonant or van-Hove exciton\textsuperscript{10,11}) should be affected by the increasing of temperature much more than those coming from band edges.

Figure 2 represents the spectral function of the quasi-particle states marked with squares in Fig. 1. We have selected three temperatures, 0 (dotted), 300 (dashed) and 1000 (solid) K. The arrow indicates the LDA energy. Even though 1000 K is a very high temperature for common experiments, it can help us conceptually to discuss the nature of the electron-phonon interaction. Panels (a) and (b) of Fig. 2 show the conduction and valence band extrema at $K$. We observe a shift of the peaks with a slight broadening, but always conserving the Lorentzian shape. Regarding the spin-orbit interaction, there is no electron-phonon mediated spin mixing, neither of the conduction nor of the valence band states at $K$.\textsuperscript{38} Our calculation rules out the possibility of intervalley scattering from the point $K$ to $K'$ at the VBM. For the conduction band states, the electron-phonon interaction conserves the spin degeneracy. However, the valence band states are splitted due to the spin-orbit interaction. Comparison with MoS$_2$ ARPES data collected at 80 K is a delicate issue.\textsuperscript{17} Experimental broadening is not exclusively related to electron-phonon decay. Nevertheless, the measured spin-orbit splitting of 145 meV agrees very well with our calculation of 135 meV.

Fig.2 (c) shows the spectral function of the state in the local minimum between $K$ and $\Gamma$. This spectral function has a similar behavior as the cases (a) and (b) but its asymmetry is stronger. This result is compatible with the exposition of Ref. 39, in which transitions are possible.
We have found a signature of a potential breakdown of the quasi-particle approximation for some states above the band gap. Figure 2 (d) shows a drastic change of the spectral function due to temperature effects. We have chosen a band close to $\Gamma$, relevant for describing the exciton $C$. The shape even at 300 K becomes asymmetric and when we reach 1000 K a secondary peak emerges. Notice that the high energy peak is separated from the low energy one by an energy far larger than any phonon in MoS$_2$. This latter peak appears at higher energy of the LDA energy, contrary to the others spectral functions. This is a proof of the many-body character of the new state and of the breakdown of the quasi-particle approximation. The new states cannot be interpreted any more as an independent sum of electrons and phonon replica. The energy separation between the shoulder and the lower peak is bigger than any phonon frequency. Following Ref. 41, the electron is fragmented in several entangled electron-phonon states, as a result of virtual transitions not bound to respect the energy conservation. This explains the appearance of these structures in a wide energy range. 

We follow the analysis of the temperature dependent electronic structure by investigating the band gap renormalization. We have seen that at 0 K the band gap of single-layer MoS$_2$ shrinks. The reason is the uncertainty principle and this is known as the zero-point motion renormalization (ZPR) effect. At 0 K, atoms cannot be at rest and have zero velocity, there is a minimum quantum of energy which supplies the vibration which makes possible the electron-phonon interaction. Table I shows the ZPR for several semiconductors, calculated in previous works. Single-layer MoS$_2$ exhibits a smaller ZPR effect, especially in comparison with Diamond. The wave function of the conduction and valence band state at $K$ are mostly concentrated around the molybdenum atoms.

The large mass of molybdenum reduces the phonon amplitude with the consequence of a smaller correction.

In order to shed light on which phonon modes contribute to the electron-phonon interaction it is useful to calculate the Eliashbergh functions.

$$g^2 F(\omega) = \sum_{\lambda,q} \left[ \frac{\sum_{n'} |q^\lambda_{nn'k}|^2 N_{N-1}^{N-1}}{\varepsilon_{n'k} - \varepsilon_{n'k'}} \right] \delta(\omega - \omega_{q\lambda})$$

$$- \sum_{\lambda,q} \left[ \frac{\sum_{n'} q^{\lambda}_{nn'k} N_{N-1}^{N-1}}{\varepsilon_{n'k} - \varepsilon_{n'k'}} \right] \delta(\omega - \omega_{q\lambda}).$$ (5)
We have analyzed the Eliashberg functions at different $k$ momentum from many electron and hole states of different electron and hole states of different electron momentum $k$ and we are just examining a few states. We have analyzed the Eliashberg functions at different $k$ points (around $K$ and $\Gamma$) observing a small energy shifts but not drastic changes under small changes of $k$. From this result we can affirm that the identification of Ref. 28 correspond to the excitons A and C. A definitive proof of this statement would consist in calculating the Raman tensor (in resonant conditions) but this is out of the scope of our work.\textsuperscript{43}

IV. FINITE TEMPERATURE EXCITONIC EFFECTS ON THE OPTICAL ABSORPTION

As mentioned in the introduction it is well known that temperature not only affects the energies but also the widths of the peaks in the optical spectra of materials. Up to now a systematic study of the behaviour of the absorption spectrum of MoS$_2$ (both as single-layer or bulk) on temperature is still missing. Only the low energy A exciton has been measured in photoluminescence at different temperature.\textsuperscript{44} Measurements of the absorption (reflectance) spectra of MoS$_2$ are usually done at room temperature.

From the theoretical point of view, if electron-phonon interaction is not taken into account, the \textit{ab-initio} optical spectra are restricted to the use of a homogeneous \textit{ad-hoc} broadening. Here, following Ref. 31, we solve the temperature-dependent Bethe-Salpeter equation, where the corresponding excitonic Hamiltonian is:

$$H^F_{ee,hh'} = (E_e + \Delta E_e(T) - E_h - \Delta E_h(T))\delta_{eh,e'h'} + (f_e - f_h)\Xi_{ee'h'h'}.$$  

$E_e$ and $E_h$ stand for electron and hole energies, $f_e$ and $f_h$ are the occupations and $\Xi_{ee'h'h'}$ is the Bethe-Salpeter (BS) kernel.\textsuperscript{31,45} The BS kernel is the sum of the direct and exchange electron-hole scattering. In a temperature independent formulation, we would calculate the energies and the BS kernel from DFT with the corresponding GW corrections to take care of the bandgap underestimation inherent to DFT.\textsuperscript{46} In this work we have used a scissor operator of 0.925 $eV$ and a stretching factor of 1.2 for the conduction and valence bands. These values were obtained by comparison of the DFT-LDA band structure with a GW calculation for single-layer MoS$_2$.\textsuperscript{13,47} In the temperature-dependent approach we use the QP eigenvalues obtained from Eq. 4, which now are complex numbers and depend on temperature. As said above, the finite linewidth is given as the imaginary part of the eigenvalues. The temperature-dependent BS Eq. 6 contains a non-hermitian operator. The excitonic states will thus have a complex energy $E^X(T)$ depending on temperature and the imaginary part represents the non-radiative linewidth of the exciton.\textsuperscript{31} Moreover, temperature not only changes the energy of the excitonic states, adding the imaginary term for the linewidth. In systems with a strong electron-lattice interaction, temperature-dependent excitonic states are a mixture of the excitonic
states from the temperature-independent regime. For instance, in hexagonal boron nitride, temperature changes dramatically the oscillator strength of the excitons and one observes temperature-driven transition from dark to bright exciton.\(^{31}\) Certainly, the temperature effect will also depend on the kind of excitons as we will see below. It is also worth to mention that although at \(T = 0\) K the BS Eq. does not reduce to the frozen-atom approximation due to the zero-point vibrations. We only recover the BS equation within the frozen-atom approximation when the terms \(\Delta E_e(T)\) and \(\Delta E_h(T)\) are explicitly removed.

The dielectric function\(^{31}\) depends explicitly on the temperature

\[
\varepsilon(\omega, T) \propto \sum_X |S_X(T)|^2 \Im \left( \frac{1}{\omega - E_X(T)} \right),
\]

where \(S_X(T)\) is the oscillator strength of each exciton. The broadening of the excitonic peaks is introduced naturally as the imaginary part of the exciton energy, without introducing any damping parameter. It is worth to notice than the linewidth associated with the electron-electron interaction is negligible in the energy range in which we study the optical spectra.

Figure 4 shows the Bethe-Salpeter spectra calculated without electron-phonon interaction (black dashed line), at 0, 100, 200 and 300 K (red, green, magenta, and cyan respectively), and with dots the experimental data at room temperature from Ref. 26. The change on the electronic states due to temperature has a repercussion on the excitons and on the optical spectra. We have calculated the Bethe-Salpeter spectra in a \(30 \times 30 \times 1\) \(k\)-grid, for 4 conduction band states and 2 valence band states. The rest of convergence criteria can be found elsewhere.\(^{10}\)

The temperature correction to the quasi-particle states have been done in the same \(k\)-grid and following the previous convergence criteria with respect to the number of bands and \(q\) points.

First, the A and B excitons are shifted down in energy but the intensity is rather constant. The A peak is slightly narrower than the B peak, in agreement with the experiments. The B excitons is build mainly from the second valence band maximum, which has more non-radiative paths for recombination than the A exciton. The behavior of the C exciton is drastically different to that of A and B excitons. The C exciton comes from transitions close to the \(\Gamma\). In this region of the band structure the electron-phonon interaction alters substantially the electronic states but not the energy. The inten-
sity drops remarkably from the BS spectrum in absence of electron-phonon interaction. It is worth to notice that we have used an homogeneous broadening of 50 meV for the BS spectra without electron-phonon interaction. The increasing of temperature reduces C exciton intensity with a faster pace than in the case of the others excitons and also increases the width. Another effect is the collapse of the multi-peak structure at the LDA spectra in one broad peak. The result is consistent with the spectral functions of Figs. 1 and 2.

In order to see in a clearer way the temperature effects on the exciton energies, Figure 5 shows the exciton energy as function of temperature. The dashed area stands for the width of every excitonic state. The dashed line represents the exciton energy without electron-phonon interaction. All the excitonic states decreases their energy with increasing temperature but not with the same pace. The biggest correction to the energy of the excitons A and B is made by the ZPR, being very similar to both states (75 meV). We can see that the width of these states is almost constant with the increasing of temperature, being only slightly bigger for the B exciton (44 meV vs. 36 meV). In the case of the C excitons we have a surprising behaviour. We expected a larger ZPR correction, proportional to the width. While the width is already large, 88 meV at 0 K and 132 meV at 300 K, the temperature increasing does not imply a strong correction of the excitonic energy, which remains rather constant. From the spectral functions of Figs. 1 and 2(d) we can see that the states close to Γ exhibit a remarkably increasing of the broadening but it seems that more or less centred at the same energy. We have added the photoluminescence results of Ref. 44, representing the full width at half-maximum (FWHM) with the gray dashed area. The energies show a good agreement at low temperatures and diverge slightly starting at 200 K. The main causes of this disagreement is the thermal expansion, not included in our calculations. Regarding the widths, both experimental and theoretical values increase with temperature but the experimental to a larger extend. This suggests the contribution of more processes like the radiative recombination, has larger lifetimes than the carrier-phonon scattering processes described here. From the theoretical results we can infer that the band-gap dependence on temperature is dictated mainly by EP interaction, whereas linewidths are influenced by other processes like radiative recombination or defects scattering.44

The comparison with the experimental data is rather satisfactory. We can explain the broadening of the C peak as the coupling of electron with lattice vibrations. On the another side, the A and B peaks compare also well. The approximation made for modeling the C exciton seems to be valid, at least to give a qualitative explanation of the spectral width. It is worth to note that modelling temperature effects on the optical properties cannot rely only on the thermal expansion,25 especially at temperatures below 200 K, where the thermal expansion is small. Moreover, only by taking into account the electron-phonon interaction we can calculate non-radiative linewidths and interpret some data from photoluminescence spectra such as the FWHM or the broadening of the optical spectra.

V. CONCLUSIONS

We have presented, to our knowledge, the first calculations of temperature effects on the electronic structure and the optical properties of a 2D material in the presence of spin-orbit coupling. For this purpose, we have calculated the electron-phonon matrix elements and the temperature-dependent spectral function using full spinorial wave functions. We have used single-layer MoS2 as a test material and we expect that this work is a good basis for studies in other monolayer TMDs and in multilayer MoS2. The electron-phonon interaction serves also to understand the behaviour of the resonant Raman spectroscopy. The Eliashberg functions evaluate the exciton-phonon coupling and we can identify which excitons will couple to each phonon mode. We have also discovered a different behaviour with temperature for the two kind of excitons existing in MoS2. First, excitons from the band edges (bound excitons A and B) are down-shifted in energy when temperature increases and the small linewidth does not change significantly. In the case of resonant excitons (C exciton) the situation is more complex. Our calculations show that bands far from the bandgap have more non-radiative paths available for decaying, as the electron states occupy a wider energy range. Consequently, the non-radiative linewidth is strongly affected by the increase of temperature. The overall result is an
optical absorption with a characteristic inhomogenous broadening, with a C peak much broader than A and B peaks. Our theoretical spectra agrees well with recent experimental measurements. With this contribution we show the importance of temperature effects, determined by electron-phonon coupling, for a more realistic approach to the optical properties of semiconductor 2D materials.

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By spin mixing we mean that an electron in the VBM and with momentum $K$ and spin up or mostly up can relax into a state at $K$ with spin down or mostly down.