Mobility of 2D materials from first principles in an accurate and automated framework

Thibault Sohier,¹ Davide Campi,¹ Nicola Marzari,¹ and Marco Gibertini¹,²

¹Theory and Simulation of Materials (THEOS), and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
²Department of Quantum Matter Physics, University of Geneva, CH-1211 Geneva, Switzerland

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We present a first-principles approach to compute the transport properties of 2D materials in an accurate and automated framework. We use density-functional perturbation theory in the appropriate bidimensional setup with open-boundary conditions in the third direction. The materials are charged by field-effect via the presence of planar counter-charges. In this approach, we obtain electron-phonon matrix elements in which dimensionality and doping effects are inherently accounted for, without the need for post-processing corrections. The framework shows some unexpected consequences, such as an increase of electron-phonon coupling with doping in transition-metal dichalcogenides. We use symmetries and define pockets of relevant electronic states to limit the number of phonons to compute; the integrodifferential Boltzmann transport equation is then linearized and solved beyond the relaxation-time approximation. We apply the entire protocol to a set of much studied materials with diverse electronic and vibrational band structures: electron-doped MoS₂, WS₂, WSe₂, phosphorene and arsenene, and hole-doped phosphorene. Among these, hole-doped phosphorene is found to have the highest mobility, with a room temperature value around 600 cm²V⁻¹S⁻¹. We identify the factors that affect most the phonon-limited mobilities, providing a broader understanding of the driving forces behind high-mobility in two-dimensional materials.

I. INTRODUCTION

The scientific and engineering community is devoting a major effort towards the identification and fabrication of novel 2D materials¹–¹¹ and their use in electronic devices¹²,¹³. To accelerate the discovery of the best candidates for electronic transport, systematic and accurate methods to compute phonon-limited resistivity and mobility from first principles would be very beneficial. Nevertheless, these quantities are not straightforward to compute and various degrees of approximations are often needed.

A very successful approach relies on the solution of the Boltzmann transport equation¹⁴,¹⁵ (BTE), in which the electron-phonon coupling (EPC) enters the expression for the scattering rates¹⁶,¹⁷ and can be computed from first principles within density-functional perturbation theory (DFPT)¹⁸–²² or with finite-differences schemes²³,²⁴. Although both methods proved to be very successful, DFPT is more efficient in dealing with long-wavelength effects since it does not need large supercells to accommodate the perturbation, and will thus be the method of choice in the following.

Either way, the computation of EPC in 2D materials from first principles presents some challenges. Being ruled by long-range Coulomb interactions, the long-wavelength electron-phonon dynamics are highly dependent on dimensionality. The most obvious example is the Fröhlich interaction in polar materials, which diverges in the long-wavelength limit in 3D while remains finite in 2D²⁵. This fundamentally different behaviour is difficult to capture in standard electronic-structure codes based on plane-wave basis sets because of the spurious interaction with artificial periodic images, which leads to erroneous results when \( q \to 0 \). Thus, special care must be adopted when computing the response of a 2D system to long-wavelength perturbations²⁵–²⁸.

An appropriate treatment of doping is an additional challenge. While field-effect charging is omnipresent in experimental setups, it is usually not included in first-principles simulations. Often, calculations are performed for the neutral case, and the Fermi level is shifted within a frozen-band approximation when integrating the EPC matrix elements to obtain a certain scattering-related quantity. This is approximate because the EPC itself depends on doping, most notably via screening, but also via other mechanisms that will be discussed later. A more realistic description is now possible thanks to a recent development of DFPT for gated 2D materials²⁹, where the doping charge is neutralized by adding planar distributions of counter-charges, mimicking experimental conditions where 2D materials are doped electrostatically through gates.

Another source of challenge is that, in general, a very large number of EPC matrix elements must be computed to obtain a fine enough sampling of the electron-phonon dynamics over the Brillouin zone, which is computationally very expensive. To boost efficiency, one may use Wannier interpolations³⁰–³⁵ to obtain inexpensively the EPC over a dense mesh. However, interpolations work seamlessly only with short-range interactions. Long-range effects, such as Fröhlich or piezo-electric coupling, need to be modeled and treated separately; this has been solved for three-dimensional systems³⁶,³⁷ while in 2D, Fröhlich coupling has been modeled²⁵ and efficient ways to interpolate the phonon dispersions have been put forward²⁸, but a thorough description of EPC interpolation is still missing. Nonetheless, the absence of interpolation techniques might not be, in the long run, a major constraint. Indeed, the reduced dimensionality entails
one less dimension to sample, with a drastic reduction of electronic states and phonons to consider. Thus, it can be argued that for 2D materials, one should focus on addressing dimensionality and charging first, rather than interpolation.

Here, we thus choose a direct approach and compute all EPC matrix elements from DFPT in the appropriate boundary and charging conditions\textsuperscript{29}. The use of symmetries and energy selection rules, in addition to the momenta being restricted to two dimensions, makes the process computationally feasible.

For the solution to the Boltzmann transport equation for electrons and holes, different approaches involving various degrees of approximation have been put forward. In the case of metals, Allen derived an approximate solution\textsuperscript{15} by suitably modifying Eliashberg theory\textsuperscript{16} to transport. This approach has been successfully applied in the early efforts to compute mobilities from first principles\textsuperscript{21,38} and it is now customary in many available transport codes such as EPW\textsuperscript{35}. In the general case, including semiconductors, the major challenge is that the integrodifferential BTE does not have a closed-form solution. Most approaches use then some form of the relaxation-time approximation\textsuperscript{24,39–48} to make it closed.

Still, the errors associated with the various approximate solutions to the BTE in the literature are often difficult to quantify. An iterative scheme to solve the inelastic part of the BTE\textsuperscript{49–51} has been proposed recently, while a very efficient preconditioned conjugate-gradient approach has been reported in Ref.\textsuperscript{52} following a recipe introduced in the context of the phonon Boltzmann equation for thermal transport\textsuperscript{53–55}. Ref.\textsuperscript{51} also offers an interesting comparison of the different methods to solve the BTE and shows a broad agreement for MoS\textsubscript{2}, but this might not be the case for all materials. A full numerical solution to the BTE beyond the relaxation-time approximation was introduced in Ref.\textsuperscript{56} for graphene. Here, we propose its generalization to any 2D material.

Relatively few 2D materials have been theoretically investigated up to now. Graphene has been studied extensively\textsuperscript{24,40,41,43,44,56–69}, showing excellent agreement\textsuperscript{44} with experiments and a detailed understanding of the main processes limiting mobility\textsuperscript{41}, including the effects of dimensionality and charging by field-effect\textsuperscript{29,69}. MoS\textsubscript{2}, another prototypical 2D material, has also been studied in several works\textsuperscript{24,42,43,49–51}, as well as phosphorene\textsuperscript{45–48,70,71}, arsenene\textsuperscript{72–74}, silicene\textsuperscript{24}, and other TMDs\textsuperscript{42}. On the other hand the effects of periodic images and dimensionality are explicitly treated only in some of the first-principles efforts\textsuperscript{24,49,50}. Charging is most often treated as a rigid shift of the Fermi energy in the computation of the transport properties, but not included in the computation of the matrix elements themselves. Consequently, the influence of doping on the EPC is generally neglected. In some instances, electronic screening is accounted for analytically\textsuperscript{40,50,59} but this necessarily entails the use of models and approximations (not obvious in 2D). Also, as will be shown here, screening is not the only effect of doping on EPC matrix elements. Last, computational accuracy is often limited by the very expensive nature of the Brillouin zone (BZ) integrals. For all these reasons, a full treatment of doping and periodicity is necessary, together with an efficient and automatic implementation of all BZ sums.

All these points are addressed in this paper, that is structured as follows. In the first section, we describe the formal framework of the BTE and identify the quantities needed to solve it. In the second section, we present the workflow of first-principles calculations used to compute the physical quantities associated with phonon-limited transport. Then we discuss the results of this workflow applied to a set of known prototypical materials, i.e., three electron-doped TMDs in their 2H form (MoS\textsubscript{2}, WS\textsubscript{2}, WSe\textsubscript{2}), as well as electron-doped arsenene, and both hole- and electron-doped phosphorene.

II. BOLTZMANN TRANSPORT EQUATION

In this first section, we review the framework of the Boltzmann transport equation for electrons in an effort to settle the context and introduce the various quantities used in the rest of the paper. Similar derivations can be found in the literature, e.g. in Ref.\textsuperscript{14,75,76}. We consider any 2D material to be in the $x - y$ plane with an applied electric field in the same plane, in the $-\mathbf{u}_E$ direction. The electric field favors states with wavevectors $\mathbf{k}$ in the opposite direction, $\mathbf{u}_E$, thus taking the electronic distribution $f$ out of its equilibrium Fermi-Dirac ground-state $f^0$. Phonon scattering acts to bring the system back towards its unperturbed equilibrium state; then, a steady-state regime is reached and a net electric current $\mathbf{j}$ emerges. The conductivity, or the inverse of the resistivity, is then defined as\textsuperscript{14,75,76}:

$$\sigma = \frac{1}{\rho} = \sum_\alpha \frac{2e}{|E|} \int_{k \in \alpha} \frac{d\mathbf{k}}{(2\pi)^2} f(\mathbf{k}) v(\mathbf{k}) \cdot \mathbf{u}_E \quad (1)$$

where the factor 2 accounts for spin degeneracy, $e > 0$ is the Coulomb charge, $E$ the electric field, $\alpha$ is an index representing the different valleys in the Brillouin zone, $f(\mathbf{k})$ is the steady-state occupation function, and $v(\mathbf{k})$ the velocity of the electronic state. Here, rather than integrating over all the Brillouin zone, we limit ourselves to the relevant electron or hole pockets that are occupied by temperature or doping. In semi-conductors, those pockets form valleys which we will further define later, and wavevectors $\mathbf{k}$ are taken from these valleys. Mobilities can then be obtained from the Drude model $\mu = \sigma/n$, where $n$ is the electron density (replace with hole density $\rho$ in case of hole doping). The central quantity to obtain is thus the occupation distribution $f(\mathbf{k})$. Assuming this to be spatially uniform and time-independent (steady-state), the Boltzmann transport equation states that the change of the occupation distribution driven by the ele-
tric field must be compensated by scattering\textsuperscript{14,75,76}:

\[-\frac{eE}{\hbar} \cdot \frac{\partial f}{\partial k} = \left( \frac{\partial f}{\partial t} \right)_{\text{scatt}}(k)\]

(2)

The collision integral (right-hand side) can be found using Fermi’s golden rule:

\[
\left( \frac{\partial f}{\partial t} \right)_{\text{scatt}}(k) = \sum_{k'} P_{kk'} f(k') (1 - f(k))
- P_{kk'} f(k) (1 - f(k')) ,
\]

(3)

where \(P_{kk'}\) is the scattering probability from state \(k\) to state \(k'\); \(P_{kk'}\) should include in general all relevant scattering processes. Here, we sum over all electron-phonon scattering probabilities associated to the phonons modes of the system, i.e. \(P_{kk'} = \sum_{\nu} P_{kk',\nu}\), where \(P_{kk',\nu}\) is the sum of phonon emission and absorption terms\textsuperscript{16} for phonon mode \(\nu\) of momentum \(q = k' - k\):

\[
P_{kk'+q,\nu} = \frac{2\pi}{\hbar} \frac{1}{N} |g_{kk'+q,\nu}|^2 \{ n_{q,\nu} \delta(\varepsilon_{k+q} - \varepsilon_k - \hbar\omega_{q,\nu}) \}
+ \{ (n_{q,\nu} + 1) \delta(\varepsilon_{k+q} - \varepsilon_k + \hbar\omega_{q,\nu}) \}.
\]

(4)

In the expression above, \(g_{kk'+q,\nu}\) is the electron-phonon coupling (EPC) matrix element and \(n_{q,\nu}\) is the phonon occupation, which we assume to be the equilibrium Bose-Einstein distribution. The \(\delta\) functions stem from the energy selection rules involved in the scattering. They imply the necessity of evaluating the EPC on very fine momentum grids, making the calculations challenging. Phonon scattering as described in Eq. 4 involves three quasi-particles: an initial electronic state, a final electronic state, and a phonon. The EPC matrix element connecting the initial and final states can be computed within DFPT\textsuperscript{17,22} and reads:

\[
g_{kk+q,\nu} = \sum_{a,i} e_{q,\nu}^{a,i} \sqrt{\frac{\hbar}{2M_a\omega_{q,\nu}}} |k + q| \frac{\partial V_{\text{KS}}(r)}{\partial u_{a,i}(q)} |k|
\]

(5)

where \(a\) is an atomic index, \(i\) a cartesian index, \(e_{q,\nu}^{a,i}\) is the phonon eigenvector, \(M_a\) is the mass of atom \(a\), \(|k|,|k+q|\) are the initial and final electronic states, and \(\frac{\partial V_{\text{KS}}(r)}{\partial u_{a,i}(q)}\) is the derivative of the Kohn-Sham potential with respect to a periodic displacement of atom \(a\) in direction \(i\).

We adopt a perturbation approach at first order in electric field and write:

\[
f(k) = f^0(k) + f^1(k)
\]

(6)

where \(f^0(k)\) is the Fermi-Dirac function and \(f^1(k)\) is the linear perturbation proportional to the electric field. By replacing the occupation distribution of Eq. 6 in Eq. 11, and keeping only first-order terms in electric fields while using the detailed balance condition \(P_{kk'} f^0(k')(1 - f^0(k'))\), we get\textsuperscript{75,76}:

\[
-\frac{e|E|}{\hbar} \frac{\partial f^0}{\partial \varepsilon} \hbar v(k) \cdot u_E = \sum_{k'} P_{kk'} f^0(k') \left( 1 - f^0(k') \right) 
\times \left\{ f^1(k') \frac{f^0(k)}{f^0(k')^2} - f^1(k) \right\}
\]

(7)

We now need to solve the above equation to find \(f^1(k)\). It is convenient to make the following general ansatz

\[
f^1(k) = e|E| u_E \cdot F(k) \frac{\partial f^0}{\partial \varepsilon}
\]

(8)

where \(F(k)\) is a vectorial quantity with units of length that can be understood as a mean free displacement\textsuperscript{51}. In the following the only approximation we make is to assume that this mean free displacement is along the band velocity, that is we write:

\[
F(k) = v(k)\tau(k)
\]

(9)

where \(\tau(k)\) is unknown and has the dimension of time. We will call it scattering time, although it is not the scattering time as often understood in the context of the relaxation-time approximation. Now, putting the ansatz Eq. 8 and 9 in Eq. 7, we get:

\[
\frac{\partial f^0}{\partial \varepsilon} v(k) \cdot u_E = \sum_{k'} P_{kk'} \frac{1 - f^0(k')}{1 - f^0(k)} \times \left\{ \frac{\partial f^0}{\partial \varepsilon} v(k) \cdot u_E \tau(k) - \frac{\partial f^0}{\partial \varepsilon} v(k') \cdot u_E \tau(k') \frac{f^0(k') (1 - f^0(k))}{f^0(k) (1 - f^0(k'))} \right\}
\]

(10)

Knowing that \(\frac{\partial f^0(k)}{\partial \varepsilon} = -\frac{f^0(k)(1 - f^0(k))}{kT}\), we can further simplify to get what we will refer to as the linearized Boltzmann transport equation (BTE):

\[
(1 - f^0(k)) v(k) \cdot u_E = \sum_{k'} P_{kk'} (1 - f^0(k')) \times \left\{ v(k) \cdot u_E \tau(k) - v(k') \cdot u_E \tau(k') \right\}
\]

(11)

where we keep the term \((1 - f^0(k)) v(k)\) on the left-hand side to avoid having it on the right-hand side as a denominator, which would bring some numerical instability in the process of solving the equation numerically. Putting back the distribution Eq. 6 in the expression for the conductivity Eq. 1 we get:

\[
\sigma = \frac{1}{\rho} = \sum_{\alpha} \int_{k \in \alpha} \left( \frac{2\pi}{\hbar} \right)^2 \langle v(k) \cdot u_E \rangle^2 \tau(k) \frac{\partial f^0}{\partial \varepsilon}
\]

(12)

A very minimal set of approximations have been made to get to Eq. 11 and 12 (linear order in electric field, steady state, equilibrium phonon distribution, mean free
displacement along band velocity). We will compute the conductivity at this level of approximation. This goes beyond the relaxation time approximation, which would correspond to neglecting the second term in brackets on the right-hand side of Eq. 11, and differs from the approaches in Refs. 51 and 52 only in the assumption of Eq. 9. Our approach to solve the BTE (Eq. 11) will be to discretize over electronic states and solve a linear system, equivalent to inverting a matrix. The general formulation of this “matrix inversion” solution is described in the following.

III. WORKFLOW / CALCULATIONS

In this section we describe the computational workflow developed to calculate the transport properties of 2D materials. Electron-doped WS$_2$ ($n = 5 \times 10^{13}$ cm$^{-2}$) is used as a case study; this is a relatively complex system due to its multi-valley nature. As illustrated in Fig. 1a), the process can be separated into the two following steps:

- EPC: We compute the linear response of the system with respect to a set of phonon momenta $Q$ (defined in the following section, along with all other momenta sets). The resulting EPC matrix elements $g_{k,k'}^{Q}$ are then projected on a set $I$ of relevant initial states $k \in I$ and interpolated on a set $F$ of final states $k' \in F$. The initial states are where we want to evaluate the scattering time. Final states are all the states accessible from the initial states via phonon scattering.

- Transport: The matrix elements are then used to compute the scattering probabilities $P_{kk'}$ and solve the BTE, which yields the scattering time for each initial state in $I$. The scattering time is then interpolated for all states in $F$, as shown in Fig. 1c). The integration of the scattering times gives the transport quantities, like the temperature-dependent mobilities and resistivities shown in Fig. 1d).

In the following we first detail and justify the sampling choices for the momentum sets $I$, $F$ and $Q$. Then we describe each of the two steps outlined above.

A. Sampling

Phonon scattering involves three quasiparticles: an initial electronic state, a final electronic state and a phonon. We use a different momentum sampling over the Brillouin zone (BZ) for each of those quasiparticles, according to their use in the workflow and the cost of the associated calculations.

Only a subset of the electronic states are relevant for transport: we see from the expression of conductivity (Eq. 12) that one needs to find the dependency of the perturbed distribution only for electronic states for which $\frac{\partial f_0}{\partial \varepsilon}$ is significantly different from zero: this represents a set of electronic states with energies in a range of a few $kT$ around the Fermi level. Furthermore, we see in the collision integral that the scattering time at $k$ depends on the scattering time of possible final states at $k'$. This means that the energy range where we need to evaluate $\tau(k)$ must be extended by the maximum phonon energy $\hbar\omega_{\text{max}}$ above and below. Such constraints define pockets or valleys in the BZ, and in WS$_2$ we keep all electronic states up to an energy 0.24 eV above the bottom of the conduction band. Panel c) of Fig. 1 shows these valleys in the Brillouin zone for WS$_2$. We distinguish two kinds of valleys: two K-valleys around the high-symmetry points K and K', and 6 valleys around the Q points, situated approximately halfway between $\Gamma$ and K.

We define a fine grid $F$ on the pockets, see Fig. 2, on which quantities related to the band structure, i.e. energies and velocities are computed. A fine grid is needed to evaluate the velocities (as gradients of the energies) properly and to converge the integrals in Eq. 11 and Eq. 12.

To compute the eigenenergies on a fine grid, the ground-state electronic density is first computed on a relatively coarse grid ($32 \times 32 \times 1$); then, non self-consistent calculations are performed on a finer grid. Since the second step is relatively inexpensive, one can afford very fine sampling. We always define the grid such that the distance between two consecutive k-points is 0.01 Å$^{-1}$ (or as close as possible to this value using a Monkhorst-Pack mesh). For example, in WS$_2$, this corresponds to 226×226 k-points. The scattering times are interpolated on this grid and integrated to get the conductivity, resistivity, or mobility, as shown in Fig. 1c-d). In this work, more focused on accurate linear response, band structures are computed within DFT. However, the same approach could use bands computed at a higher level of theory, such as hybrid functionals, many-body perturbation theory (e.g. GW associated to a Wannier interpolation technique$^{34}$), or applying a correction to the fundamental band-gap obtained from an evaluation of the derivative discontinuity as in GLLBsc functionals$^{77,78}$, or even bands fitted on experiments$^{79,80}$.

As written in Eq. 11, the BTE gives the value of $\tau(k)$ at an initial state $k$ as a function of $\tau(k')$ at all possible final states $k'$ linked to initial states by a phonon-scattering event. As will be explained in Sec. III C, the sampling of initial and final states needs not be the same, and we simply need a map from the final states to their closest symmetry-equivalent initial state. The set of final states ultimately defines the set of scattering events we account for, represented by the scattering probability $P_{kk'}$. These quantities have low symmetry since they combine the initial and final states with the phonon that links them. Thus, the final states of the BTE need to cover the full extent of the valleys. Furthermore, one needs to account for the sharp variations of $P_{kk'}$ due to the energy selection rules in Eq. 4. We thus use the fine sampling of the pockets $F$ for the final states in the
FIG. 1. a) Schematic description of the first-principles workflow for electronic transport b) Interpolated electron-phonon couplings $g_{k,k'}$ for electron-doped WS$_2$. The initial state $k$ considered here is indicated by a white star; the other points are the possible final states in the finely sampled pockets, where the color of the point indicates the strength of the electron-phonon coupling matrix element. The index of the phonon mode indicated at the top of each subplot refers to a purely energetic ordering of the phonon modes associated with each transition. This implies that crossings in phonon dispersions may lead to discontinuities in the plots. This explains the set of seemingly out-of-place EPC matrix elements in the K’ valley for modes 5 and 6, and in lesser measure in the Q valleys for modes 2 and 3. c) Scattering times interpolated on the fine grid of electronic states $\mathcal{F}$, shown using a color scale for each electronic state in the valleys of WS$_2$. d) Temperature-dependent resistivity and mobility of electron-doped WS$_2$ ($n = 5 \times 10^{13}$ cm$^{-2}$).
BTE. This simply means that the EPC eventually needs to be interpolated on this grid. The set of momenta \( \mathcal{I} \) is where we want to compute to scattering times by solving the BTE, and it is convenient to note that the scattering times \( \tau(\mathbf{k}) \) have the symmetry of the electronic eigenenergies \( \varepsilon_\mathbf{k} \). This is not obvious because the computation of the resistivity involves the electric field and phonons which break the symmetries of the band structure. The integrand in Eq. 12, for example, has the symmetry of the band structure plus the electric field. This quantity and the aforementioned \( P_{\mathbf{k}\mathbf{k}'} \) have thus lower symmetry than the electronic states. On the other hand, the form of the ansatz for the perturbed distribution (Eqs. 8 and 9) is such that the effect of the electric field is separated out and \( \tau(\mathbf{k}) \) essentially represents the dependency of the perturbed distribution on the electronic states only. Further analysis of the BTE (Eq. 11) shows that \( \tau(\mathbf{k}) \) depends on a sum over all possible final states. While each term of the sum might not have the symmetries of the band structure \( (P_{\mathbf{k}\mathbf{k}'}, \text{e.g., does not}) \), the sum is invariant under the symmetry transformations associated with the BZ. So, since \( \tau(\mathbf{k}) \) has the symmetry of the band structure, the initial states \( \mathcal{I} \) are sampled from an irreducible representation of the valleys. This sampling should be chosen fine enough to capture the variations of the scattering time; however, the size of \( \mathcal{I} \) defines the size of the linear system to solve for the BTE and it is a factor in the total number of EPC matrix elements to compute. Those calculations have a non-negligible computational cost, and using the irreducible states in the fine grid of the pockets would be unnecessarily expensive. As shown in Fig. 2, we use a coarser grid: for all materials in this work we found that a grid with a \( k \)-points spacing approximatively 2.6 times larger than the fine grid \( \mathcal{F} \) leads to a converged solution to the Boltzmann transport equation at a reasonable computational cost. For example, in WS\(_2\), this leads to 126 irreducible initial states, while using the fine pockets grid would have led to more than 800 initial states.

The electronic wave functions in Eq. 5 can be easily recomputed from the ground-state charge density, while the rest is associated with a given phonon perturbation, and is the bottleneck in terms of computational cost (in particular the calculation of \( \partial \varepsilon_{\mathbf{k}\alpha}(\mathbf{r}) / \partial u_{\alpha\beta}(\mathbf{q}) \)). There are methods\(^{32,33,35,36} \) to interpolate the perturbation \( \partial \varepsilon_{\mathbf{k}\alpha}(\mathbf{r}) / \partial u_{\alpha\beta}(\mathbf{q}) \) to the Kohn-Sham potential, but the spirit of the current approach is to compute this quantity directly in DFPT. We will, however, take full advantage of symmetries and use a reasonable sampling of phonon momenta. Each scattering event from an initial to a final states defines a phonon momentum \( \mathbf{q} = \mathbf{k}_f - \mathbf{k}_i \), where \( \mathbf{k}_f \) spans the pockets \( \{ \alpha \} \), and \( \mathbf{k}_i \) spans the irreducible states in the pockets. We use the same support as for \( \mathcal{I} \) and \( \mathcal{F} \), but define a coarser grid, as shown in Fig. 2. We then obtain the set of phonons momenta \( \mathcal{Q} \), where we actually compute the linear response to the phonon perturbation, by the following process: first, we find all possible \( \mathbf{q} \) vectors connecting all final states and initial states in the coarse grid. For these, there are many duplicates, since a single momentum can link several pairs of initial and final states, and so we remove those duplicates. The \( \mathbf{q} \) points are then reduced by symmetry. Indeed, from one \( \mathbf{q} \)-point, the linear response code (as implemented in Quantum ESPRESSO) allows, as a post-process, the computation of \( \partial \varepsilon_{\mathbf{k}\alpha}(\mathbf{r}) / \partial u_{\alpha\beta}(\mathbf{q}) \) for all \( \mathbf{q} \) points in the set \( \mathcal{Q}^* \) defined as all \( \mathbf{q}^* = S(\mathbf{q}) \) where \( S \) is a symmetry operation of the crystal. The symmetry reduction is done with a tolerance of about the grid step, since the momenta in \( \mathcal{Q}^* \) do not always fall exactly on the grid. The number of phonons to compute thus depends on the initial grid chosen for the electronic states in a non-straightforward way. We go through the above process several times until we reach a number of phonons that is largely sufficient to capture the variations of EPC while staying reasonable in terms of computational cost. For example, in WS\(_2\), this results in 200 \( \mathbf{q} \)-points where to compute the linear response \( \partial \varepsilon_{\mathbf{k}\alpha}(\mathbf{r}) / \partial u_{\alpha\beta}(\mathbf{q}) \). For materials with less valleys (such as phosphorene studied in Section IV), less than 100 phonons are needed.

In Fig 3 we show both the set of irreducible phonon momenta \( \mathcal{Q} \) and the relevant phonon momenta in \( \mathcal{Q}^* \) that lead to final states in the BZ for at least one of the initial states.
B. Phonons and EPC calculations

Phonons are computed using the recent implementation of DFPT, and all relevant phonons (in red light blue) that can be obtained from the latter by symmetry transformations. To help visualizing the corresponding pairs of initial and final electronic states, the dashed lines correspond to a BZ centered either the high-symmetry K point (green) or the bottom of the Q valley (orange) at the origin, the Q valley being approximately halfway between Γ and Q.

C. Transport

Suppose sampling $\mathcal{I}$ yields $N_i$ irreducible initial states, while sampling $\mathcal{F}$ yields $N_f$ final states. Writing the BTE for the $N_i$ irreducible states yields $N_i$ equations and $N_f$ unknown variables $\tau(\mathbf{k}')$. To solve the corresponding system, we first need to fold it back on the irreducible states, using the fact that $\tau(\mathbf{k}') \approx \tau(\mathbf{k}')$ where $\mathbf{k}' \in \mathcal{I}$ is the symmetry equivalent of $\mathbf{k}' \in \mathcal{F}$:

$$
\left(1 - f^0(\mathbf{k})\right) \mathbf{v}(\mathbf{k}) \cdot \mathbf{u}_E = 
\sum_{\mathbf{k}'} P_{kk'} \left(1 - f^0(\mathbf{k}')\right) \mathbf{v}(\mathbf{k}) \cdot \mathbf{u}_E \times \tau(\mathbf{k}) 
- \sum_{\mathbf{k}'} \left(\sum_{\mathbf{k}''} P_{kk''} (1 - f^0(\mathbf{k}'')) \times \mathbf{v}(\mathbf{k}'') \cdot \mathbf{u}_E\right) \tau(\mathbf{k}').
$$

Considering all the $\mathbf{k} \in \mathcal{I}$ leads to $N_i$ equations for $N_i$ unknown variables. The size of the system to solve thus depends on the sampling of the initial states.

To arrive at the final form of the BTE, we address the fact that its solution $\tau(\mathbf{k})$ is ill-defined when $\mathbf{v}(\mathbf{k}) \cdot \mathbf{u}_E$ approaches zero. Indeed, considering $\mathbf{v}(\mathbf{k}) \cdot \mathbf{u}_E = 0$, any $\tau(\mathbf{k})$ satisfies the above equation. In practice, this brings numerical noise. This situation can happen: i) if $\mathbf{v}(\mathbf{k}) \approx 0$, which is relatively rare in practice (e.g. only when $\mathbf{k}$ is very close to the extremum of a valley); ii) if $\mathbf{v}(\mathbf{k}) \perp \mathbf{u}_E$, where $\mathbf{u}_E$ is the direction of the electric field. Situation i) can be treated approximately, without much consequences on the transport results (indeed, states with zero velocity do not contribute to the transport), and we compute the scattering time using the closed form of the BTE shown in App. B. In situation ii), we do need a consistent evaluation of $\tau(\mathbf{k})$. Indeed, even though $\mathbf{k} \in \mathcal{I}$ does not contribute to the conductivity because its velocity is perpendicular to the field, this is not necessarily true for all $\mathbf{k} \in \mathcal{F}$ that are equivalent to $\mathbf{k}$ according to the symmetries of the BZ. We use the following technique: since $\tau(\mathbf{k})$ has the symmetry of the band structure, it does not depend on the direction.
of the electric field. In other words, any choice for the
direction of the electric field gives the same τ's. Thus, we
are free to use any direction for the electric field to solve
the BTE, and we can choose different directions for each
of the \( N_f \) equations corresponding to the \( N_f \) \( \mathbf{k} \) points.
For each \( \mathbf{k} \), we choose the direction \( \mathbf{u}_k = \frac{\mathbf{k}}{|\mathbf{k}|} \), where \( \mathbf{k} \) is
\( \mathbf{k} \) taken from the extremum of its valley, since \( \mathbf{v}(\mathbf{k}) \perp \mathbf{u}_k \)
virtually never happens.

We then have a well-behaved set of \( N_f \) equations with
\( N_f \) unknowns. Written as a matrix-vector product, it
reads:

\[
\forall \mathbf{k} \in \mathcal{I}, \quad F_k = \sum_{k'} S_{k,k'} \tau_{k'},
\]

(14)

where

\[
F_k = \left( 1 - f^0(\mathbf{k}) \right) \mathbf{v}(\mathbf{k}) \cdot \mathbf{u}_k
\]

(15)

\[
S_{k,k'} = \left( \sum_{k''} P_{kk''} \left( 1 - f^0(\mathbf{k}'') \right) \mathbf{v}(\mathbf{k}) \cdot \mathbf{u}_k \right) \delta_{k,k'}
- \left( \sum_{k''=k} P_{kk''} \left( 1 - f^0(\mathbf{k}') \right) \times \mathbf{v}(\mathbf{k}') \cdot \mathbf{u}_k \right)
\]

(16)

Solving the BTE gives us the values of \( \tau \) on the \( \mathcal{I} \)
grid. It is then rotated according to the symmetries of the
band structure, and interpolated linearly on the fine
grid of the pockets \( \mathcal{F} \). Note that once we have the angular
and energy dependent \( \tau(\mathbf{k}) \), which does not depend
on the electric field in itself, we can compute the conduction integral for an arbitrary direction of the electric
field, thus probing any diagonal element of the conductivity tensor. The \( \delta \) functions in Eq. 4 are replaced by
Gaussians, and a convergence test is performed on the
associated smearing.

IV. RESULTS

We have applied our approach to a set of 6 different
cases: 5 electron-doped materials (WS\(_2\), MoS\(_2\), WSe\(_2\),
arssene, and phosphorene), as well as hole-doped phosphorene. These are common 2D systems often praised
for their potential for transport applications. Also, this
set leads to an interesting diversity of band structures,
in terms of valleys, their symmetries and their energetic accessibility. Let us stress that we are working here in
the framework of DFT, rather than higher levels of theory,
and without spin-orbit coupling (SOC). Both approximations can of course affect the bands of the materials
studied here. For SOC, we expect the variations to be relatively small for electron-doped arsenene and phosphorene\(^{70}\). The case of TMDs is a more delicate one: the relative positions of the K and Q valleys seems to be sensitive to many aspects of the calculations, like the inclusion of SOC\(^{86}\), choice of pseudo potentials, lattice parameters, level of theory\(^{87}\) (DFT versus GW) or doping\(^{88}\). Thus, while we will be able to compare between the three TMDs and discuss qualitative trends, we
do not claim to be quantitative with respect to experiments. That being said, the methodological approach
presented in this work is very flexible. One can combine the electron-phonon coupling matrix elements found in
DFPT with the band structure found by any mean; e.g.,
one can use a band structure computed at the highest
level of theory, and/or correct it to better fit experiments,
before inserting it in the workflow. Regarding SOC, it
can be easily included in the band structure calculations
and EPC calculations; further development is planned to
include it in the solution to the BTE.

As previously mentioned, first-principles calculations are performed with the Quantum ESPRESSO distribution\(^{81,82}\) including a 2D Coulomb cutoff and the possibility to charge the material with gates\(^9\), and using the SSSP Accuracy library\(^{88–91}\). Structures are taken from the database described in Ref. 11. To build this
database, structural relaxations were performed in the neutral material, using the SSSP library as well and a k-
point sampling corresponding to a spacing of 0.2 Å\(^{-1}\) in
each direction. We use a symmetric double-gate setup
to charge the materials with a density of \( 5 \times 10^{13} \) cm\(^{-2}\)
electrons or holes for all systems except for electron-
doped phosphorene, where we choose a lower density of
\( 5/3 \times 10^{13} \) cm\(^{-2}\) to avoid raising the Fermi level too high
in the conduction band, where additional valleys appear.
Each gate carries half the opposite charge of the material,
such that the electric field has equal norm but opposite
direction on each side of the material. We could also have
used a single-gate setup, with an electric field only on one
side, but no large difference is expected since the impact
of the electric field setup should come mainly from its
effect on spin-orbit coupling, which is not included here.
Barrier potentials are added to avoid leakage of electrons
towards the gates. These also lead to a hardening
of the ZA phonons in the long-wavelength limit, with
a non-zero frequency at Γ around 10 – 15 cm\(^{-1}\) for
the materials considered. Ground state and linear-response
calculations on the charged materials are performed with
a \( 32 \times 32 \times 1 \) k-point grid and 0.02 Ry Methfessel-Paxton
smearing to sample the Fermi surface. Note that we are working at relatively high doping, such that the Fermi
surface is large enough to be sampled correctly. Non self-consistent calculations are performed to obtain
the band structure on the fine grid \( \mathcal{F} \).

The interpolated EPC matrix elements for electron-doped WS2 are shown in Fig. 1; for electron-doped arssene in Fig. 4; and for hole-doped phosphorene in Fig. 5. Equivalent plots for electron-doped MoS2 and WSe2 are in App. A; they are very similar to WS2. The angular
dependencies of the EPC are non-trivial: the EPC can undergo some rather sharp variations, most often for intervalley transitions via acoustic modes. For intervalley transitions, we observe overall smoother variations if we
ignore the discontinuities coming from phonon crossings.
However, intervalley scattering is activated or not de-
pending on the valleys and the mode in rather non-trivial ways. These plots also serve to give a visual confirmation that we use sufficient sampling to capture the variations of the EPC. One important aspect to keep in mind when interpreting these plots and the transport properties of the system is that energy and momentum conservation conditions drastically reduce the final states effectively relevant for a given initial state.

The BTE is solved in all these systems, giving the mobilities shown in Fig. 6. These cover three orders of magnitude, and the hole side of phosphorene shows mobilities ten times larger than the rest, almost reaching $10^3 \text{ cm}^2/\text{Vs}$ at room temperature. For comparison, electron-doped graphene has mobilities of the order of $10^4$ to $10^5 \text{ cm}^2/\text{Vs}$ depending on the density. Table I summarizes our findings, focusing on room-temperature results, and compares them with some values available in the literature. Below, we identify the general trends and discuss three important factors in the prediction of transport properties in 2D materials. Finally, we argue that those three factors might account for a large part of the discrepancies observed in Table I.

A. Intervally scattering

The ranking of the above materials in terms of mobility reflects the importance of intervalley scattering. This is clearly demonstrated by considering the three TMDs: these have essentially the same type of electronic and phonon band structures, as well as similar EPC matrix elements. Yet, we obtain an order of magnitude variation in the mobilities. This stems from the position of the Q valley: indeed, as the Q valley approaches the Fermi level, it offers an additional scattering channel for the electrons. As shown in Fig. 7, the scattering time gets shorter (more scattering) at energies close to the bottom of the Q valleys. The largest contributions to the resistivity of TMDs ($\approx 80\%$) comes from the scattering with the LA and TA modes: LA at $\Gamma$ (intravalley scattering) and M (K$\leftrightarrow$Q scattering) and TA at K (K$\leftrightarrow$K’ scattering). This is not obvious from the plots of the electron-phonon matrix elements, because the dispersions of the three acoustic modes cross each other between $\Gamma$ and K, and between $\Gamma$ and Q. However, looking at the phonon displacements, it is quite clear that in-plane acoustic modes are associated with the regions of strong electron-phonon coupling in the first three sub-plots of Fig. 1b, and in Figs. 10, 12 and 11 of the Appendix.

The multi-valley nature of a material does not necessarily deteriorate the mobility in itself. The presence of multiple valleys increases both the accessible phase space for scattered states and the density of states, and the corresponding effects on the mobility cancel each other. Rather, it is the existence of a strong EPC between the valleys that increases scattering and lowers the mobility. For the small subset studied here, all multi-valley materials showcase strong intervalley EPC. It may be argued, in general, that intervalley EPC is often strong compared to intravalley EPC. This could first be explained by the fact that intervalley EPC is not bound to vanish at long wavelengths, contrary to the coupling to acoustic phonons. Second, it involves larger phonon momenta and the EPC tends to be less screened, since the dielectric function goes to 1 in the short-wavelength limit.

B. Symmetries of the valleys

Effective masses are among the most influential features to consider when studying mobilities, and anisotropic effective masses can be very beneficial. Indeed, small effective masses have the benefit of bringing large carrier velocities while large effective masses have the benefit of bringing high carrier densities. Thus, one might combine those benefits having a small effective mass in the transport direction and a large one in the perpendicular direction. This contributes to phosphorene’s good transport performance. In fact, phosphorene is the only material in the present study showing significant transport anisotropy. The transport properties of TMDs are isotropic because the bottom of the K and Q valleys are roughly isotropic. In the case of arsenene, each single valley is quite anisotropic, but when summing up the six equivalent valleys the angular dependency of the transport averages out and vanishes$^{73}$. Fig. 8 shows the mobility of P (h), As (e) and WS$_2$ (e) as a function of the direction of the electric field. The mobility of phosphorene is highly directional, while all others are isotropic.

C. Doping effects on electron-phonon interactions

The effects of doping on electron-phonon scattering are many. The first one is to move the Fermi surface within the electronic landscape. This leads to variations of the density of states and determines whether certain valleys are accessible via phonon scattering or not. As we saw in TMDs, the activation of intervalley scattering can have drastic consequences on transport. Those effects come from the energy selection rules of Eq. 4. Doping also has consequences on the strength of EPC matrix elements themselves (Eq. 5). A well-known and important effect is the additional screening coming from the electrons added in the conduction band or holes in the valence band. In our computational framework, this is inherently accounted for since we compute the linear-response of the charged system. Any EPC related to a periodic variation of the effective scalar potential in which the electrons move will be screened. This includes: i) a variation of the charge state via a variation of the area of the unit cell, as induced by longitudinal acoustic phonons; ii) any EPC related to dipole or Born effective charges, like Fröhlich or piezo-electric EPC, in which phonons interact with electrons via the generation
FIG. 4. Interpolated $g_{kk'}$ for electron-doped arsenene. The initial state considered is indicated by a white star. The rest of the points are the possible final states in the finely sampled pockets and the color of the point indicates the strength of the electron-phonon coupling matrix element. The index of the phonon mode indicated at the top of each subplot refers to a purely energetic ordering of the phonon modes associated with each transition.

FIG. 5. Interpolated $g_{kk'}$ for hole-doped phosphorene. The initial state considered is indicated by a white star. The rest of the points are the possible final states in the finely sampled pockets and the color of the point indicates the strength of the electron-phonon coupling matrix element. The index of the phonon mode indicated at the top of each subplot refers to a purely energetic ordering of the phonon modes associated with each transition.
Doping also affects EPC beyond screening: as the occupations of the valleys vary, certain orbitals/bands in the material get populated or depleted, which can directly change the amplitude of the coupling. This happens in TMDs, as shown in Fig. 9 in which we computed intravalley scattering for several doping levels. In particular, we compute the average of the long-wavelength coupling $\langle g^2 \rangle$ along a fixed iso-energetic line at $\varepsilon = E$, by taking a few initial states on the iso-energetic section of each the K and Q valleys, and six phonon momenta with a fixed small norm. Linear-response calculations are then performed for each doping to capture non-trivial dependencies of the EPC matrix elements. We average on the phonon momenta and on the initial states to get $\langle g^2 \rangle$ for each valley $\alpha = K, Q$. We sum the contributions from acoustic and optical phonon modes separately. Fig. 9 shows that as doping increases in WS$_2$, the intravalley coupling in K increases while it decreases in Q. The couplings to both acoustic and optical phonons show variations of 50 \textendash{} 60%. Similar trends where observed in the literature\cite{105}, but this kind of effect is poorly understood and difficult to predict, highlighting the importance of explicitly including doping in the linear-response calculations.

Last, we note that the way doping is induced can be important. An example is the gate-induced coupling to flexural phonons in graphene\cite{29,69}, related to a broken mirror symmetry with respect to the graphene plane. However, we do not expect such effects to be significant for the subset of materials studied here.

D. Comparison with literature

Due to the diversity of the techniques employed, both at the BTE and EPC level, discrepancies between different first-principles results can have many different explanations. However, comparison with the literature points to the three factors discussed above being quite relevant. Indeed, intravalley scattering, doping and anisotropy, which we identified to be essential in determining the transport properties of 2D materials, also turn out to be the least well treated. Many models include intravalley coupling only (e.g. "deformation potential" models), thus neglecting intervalley transitions. Furthermore, given the complexity of EPC in multivalley materials, most analytical models of EPC with fitted parameters from first-principles are incomplete. It is no coincidence that works employing such approaches show the greatest differences with the current results, often largely overestimating mobility, like the results on TMDs reported in Ref. 93, on arsenene in Ref. 73, or phosphorene in Ref. 70. When intravalley scattering is accounted for, it can still be a source of discrepancy depending on the relative positions of the valleys. This is the case for TMDs, in which the position of the Q valley with respect to the bottom of the K valley is difficult to determine, as mentioned before, from first-principles. For example, the energy separation between the two extrema in MoS$_2$ ranges between 70\cite{92} and 260 meV\cite{49,51} with the latter results closer to our calculations. This difference brings a large intervalley contribution for MoS$_2$ in Ref. 92 that we don’t observe, and that we find instead in the W-based TMDs. The relative energy separation of the K and Q valley affects also our ranking in terms of electron mobility among the TMDs, with MoS$_2$ performing better than WS$_2$, contrary to the findings in Ref. 42. In Ref. 42 the energy separation between K and Q is 80 meV in MoS$_2$ and 67 meV in WS$_2$ resulting in a similar intervalley scattering between the two materials and a better mobility for WS$_2$ on the basis of its lighter effective mass. In our case instead the K-Q energy separation shows a larger variation, from 250 meV in MoS$_2$ to only 150 meV in WS$_2$ resulting in an increased intervally scattering that undermines the advantage of a lighter effective mass.

In all the cases references mentioned in Table I, first-principles calculations are done in neutral materials. Doping is sometimes entirely ignored or included only a posteriori as a shift of the Fermi level in the computation of transport properties. In some instances, analytical models of screening are used, but those are not well established in 2D materials. In any case, we have seen that the effect of doping goes beyond shifting the Fermi level and electronic screening. Thus, performing
TABLE I. Room-temperature mobilities of the 6 systems considered (at the DFT/DFPT level without SOC). Mobilities are given in cm$^2$/Vs, doping densities are indicated in parentheses, in units of 10$^{13}$ cm$^{-2}$. Question marks for densities of experimental works indicate that the information was not provided. For theoretical works, "-" means that the mobility was derived from a density-independent model. Note that SOC is not included in any of those works. Results on phosphorene are reported in both the armchair (ac) and zig-zag (zz) directions.

| Material (e or h doped) | Present result $\mu(n)$ | Other first-principles results $\mu(n)$ | Experimental $\mu(n)$ |
|-------------------------|--------------------------|----------------------------------------|----------------------|
| MoS$_2$ (e)             | 136 (5)                  | 265 (5)$^{10}$, 150 (-)$^{9}$, 130 (-)$^{10}$, 320 (0.01)$^{39}$, 410(0.01-340(1)$^{19}$, 340 (-)$^{93}$ | 217 (0.46)$^{72}$, 150 (0.7)$^{44}$, 81 (0.7)$^{96}$, 63 |
| WS$_2$ (e)              | 61 (5)                   | 320 (-)$^{42}$, 1103 (-)$^{93}$        | 44 (10?$)^{47}$, 44 (?)$^{96}$, 45 (0.6)$^{89}$, 25-83 |
| WSe$_2$ (e)             | 23 (5)                   | 30 (-)$^{42}$, 705 (-)$^{93}$          | 7 (?)$^{102}$, 30 (1-1.5?)$^{103}$ |
| As (e)                  | 41 (5)                   | 21 (-)$^{71}$, 1700 (-)$^{73}$         | -                    |
| P (h-ac)                | 634 (5)                  | 640-700 (-)$^{10}$, 460 (-)$^{38}$, 292 (5)$^{96}$, 170 (-)$^{71}$, 19 (-)$^{48}$ | |
| P (h-zz)                | 47 (5)                   | 10000-26000 (-)$^{10}$, 90 (-)$^{38}$, 157 (5)$^{96}$, 35 (-)$^{71}$, 3 (-)$^{48}$ | |
| P (e-ac)                | 302 (5/3)                | 1100-1140 (-)$^{10}$, 210 (-)$^{38}$, 738 (5)$^{96}$, 430 (5)$^{47}$, 170 (-)$^{71}$, 20 (-)$^{48}$ | |
| P (e-zz)                | 33 (5/3)                 | 80 (-)$^{71}$, 40 (-)$^{71}$, 114 (5)$^{96}$, 80 (5)$^{97}$, 50 (-)$^{71}$, 10 (-)$^{48}$ | |

FIG. 7. Scattering times in MoS$_2$, WS$_2$, and WSe$_2$ (from left to right). The color scale is the same for all subplots. The scattering rate $(\hbar/\tau)$ clearly increases for states with energy high enough for the Q valley to be accessible. The Fermi levels are: -2.83, -2.46, and -2.13 eV, respectively.
FIG. 8. Angle-dependent mobilities at room temperature for hole-doped and electron-doped phosphorene, and electron-doped arsenene and WS$_2$. The angle corresponding to the transport direction refers to the direction of the in-plane electric field driving the current with respect to the $x$ direction indicated in the plots of EPC. For phosphorene, 0 ($\pi$/2) corresponds to the zig-zag (armchair) direction. While phosphorene shows highly anisotropic transport. Small variations of the order of $10^{-2}$ cm$^2$/Vs can be observed in WS$_2$. In arsenene, very small variations of $10^{-7}$ cm$^2$/Vs, below numerical accuracy, confirm the isotropic transport properties expected from theory$^{73}$.

V. CONCLUSIONS

We have developed an automated procedure to determine the transport properties of 2D materials from first-principles. We aim for the highest accuracy achievable within the framework of density-functional perturbation theory, with as few assumptions and simplifications as possible. The method includes several strengths and improvements with respect to existing approaches. Electron-phonon coupling matrix elements are directly computed from density functional-perturbation theory in the correct dimensionality framework and with the correct electrostatics of field-effect doping. The linearized Boltzmann transport equation is solved numerically in full, without the use of the relaxation-time approximation or any other closed-form expressions for the scattering time. The implementation of this entire transport workflow within the AiiDA infrastructure provides great flexibility to improve or adapt the method to different applications, as well as the data storage and provenance necessary to build and disseminate databases. Here, we studied in detail a small test set of 6 systems (electron-doped MoS$_2$, WS$_2$, WSe$_2$, arsenene and phosphorene as well as hole-doped phosphorene) presenting different characteristics. Our results point out the crucial role of intervalley scattering, band anisotropy and doping to the transport properties of 2D materials, in turn under-scoring the importance of an accurate treatment of these aspects in first-principles simulations. Hole-doped phosphorene is found to yield the highest mobility, thanks to its mono-valley and anisotropic nature. Electron-doped arsenene shows a lower mobility than could be expected, due to the importance of intervalley scattering.
transport properties of electron-doped TMDs are found to be very sensitive to the relative positions of the K and Q valleys: these quantities are still subject of study at the highest levels of theory and experimentally. While this work is based on DFT band structures, more accurate predictions would be reached by including spin-orbit interactions, GW corrections and by fitting at least the most important features of the valleys to experimental data.

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Appendix A: additional EPC plots:

Here we show additional plots for the EPC matrix elements of MoS$_2$, WS$_2$, WSe$_2$ and phosphorene.

Appendix B: Closed Form of BTE

Re-writing Eq. 11 as

$$1 = \sum_{k'} P_{kk'} \frac{1 - f^0(k')}{1 - f^0(k)} \times \left\{ \tau(k) - \tau(k') \frac{v(k') \cdot u_E}{v(k) \cdot u_E} \right\},$$

(B1)

we see that a closed form can be obtained by assuming \( \tau(k) \approx \tau(k') \):

$$\frac{1}{\tau(k)} = \sum_{k'} P_{kk'} \frac{1 - f^0(k')}{1 - f^0(k)} \times \left\{ 1 - \frac{v(k') \cdot u_E}{v(k) \cdot u_E} \right\},$$

(B2)

This closed form expression can be further simplified by replacing \( u_E \) with \( v(k) \) to obtain the so-called momentum relaxation-time approximation (mRTA) for the scattering time:

$$\frac{1}{\tau_{mRTA}(k)} = \sum_{k'} P_{kk'} \frac{1 - f^0(k')}{1 - f^0(k)} \times \left\{ 1 - \frac{v(k') \cdot v(k)}{v(k)^2} \right\}$$

(B3)

If the second term in brackets on the right-hand side is neglected, we finally obtain the scattering time within the energy relaxation-time approximation (eRTA):

$$\frac{1}{\tau_{eRTA}(k)} = \sum_{k'} P_{kk'} \frac{1 - f^0(k')}{1 - f^0(k)}$$

(B4)
FIG. 10. Interpolated $g_{kk'}$ for electron-doped MoS$_2$. The initial state considered is indicated by a white star. The rest of the points are the possible final states in the finely sampled pockets and the color of the point indicates the strength of the electron-phonon coupling matrix element. The index of the phonon mode indicated at the top of each subplot refers to a purely energetic ordering of the phonon modes associated with each transition.

FIG. 11. Interpolated $g_{kk'}$ for electron-doped WS$_2$, with the initial state at the bottom of the Q valley.
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FIG. 13. Interpolated $g_{kk'}$ for electron-doped phosphorene, with the initial state at the bottom of the $\Gamma$ valley.
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