Electric field – velocity relation for strongly coupled Fröhlich polaron in emerging 2D materials

Ramji Singh1, Mitra Dutta1,2 and Michael A Stroscio1,2,3
1 Department of Electrical & Computer Engineering, University of Illinois at Chicago, 1020 SEO, 851 S. Morgan St. Chicago, IL 60607, United States of America
2 Department of Physics, University of Illinois at Chicago, United States of America
3 Department of Bioengineering, University of Illinois at Chicago, United States of America
E-mail: rsingh54@uic.edu
Keywords: Fröhlich polaron, LO phonon, 2D material

Abstract
In this paper we evaluate the electric field—velocity relation for strong electron—LO phonon coupled 2D materials namely HfS₂, HfSe₂, ZrS₂ and ZrSe₂ by applying Thornber—Feynman (TF) formalism applied to the case of the 2D Fröhlich polaron. We demonstrate that the generally-accepted Fermi’s Golden Rule based approach breaks down for these strongly coupled materials. We predict ZrSe₂ has highest mobility of 449 cm²/V-s at room temperature followed by HfSe₂ with 240 cm²/V-s whereas other materials have below 100 cm²/V-s.

Introduction
Graphene’s zero band gap is a major limitation in its application to electronic devices despite its zero effective mass and high mobility (~10⁴ cm²/V·s) [1, 2]. Accordingly, there has been extensive research on potential two dimensional alternatives, including, TMDc (Transition Metal Dichalcogenides). These TMDc are of the form MX₂ where M is a transition metal and X is a chalcogen, namely, S, Se or Te. Previous studies on carrier transport have been done on monolayer group IV chalcogenides for M = Mo, W and have concluded that carrier—longitudinal acoustic (LA) phonon scattering is the dominant mechanism limiting mobility at room temperature between the range 180–800 cm²/V·sec [3–5].

On the other hand, group IV chalcogenides with M = Hf and Zr have been predicted to have high carrier mobility at room temperature [6, 7]. These high predicted mobility values in materials with finite bandgap, as opposed to other 2D materials such a graphene which has a zero bandgap, make these materials applicable in devices requiring high mobility and opens the way to optical inputs and outputs. Of course, high values of mobility make it possible to realize devices with reduced switching times based on the time required for the carrier to travel from between contacts. The finite bandgaps open the way to optoelectronic applications and the ability to fabricate structures with different 2D materials in van der Waals-bonded successive layers opens the way to multiple wavelength optoelectronic devices.

It should be noted that, the carrier—longitudinal optical (LO) phonon coupling will become the dominant scattering mechanism at room temperature and above if the carrier—LO phonon coupling increases, which is defined by the dimensionless Fröhlich coupling constant α [8, 9]:

\[
\alpha = \frac{e^2}{\hbar} \left( \frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_0} \right) \left( \frac{m_p}{2h \omega_{LO}} \right)^{1/2}
\]  (1)

where, \(m_p\) is the effective electron mass in the conduction band, \(\varepsilon_{\infty}\) and \(\varepsilon_0\) are the (in-plane) high frequency and static dielectric constant and \(\hbar \omega_{LO}\) is the zone-center LO phonon energy, and \(e\) is the electronic charge. Previous studies [3, 5, 10] on MoX₂ (X ≡ S, Se and Te) and WX₂ (X ≡ S, Se and Te) have studied the electron—LO phonon interaction within the purview of Fermi’s Golden Rule (FGR) which is based on first order perturbation theory. The electron coupling to LO phonons in MoX₂ and WX₂ may be modeled using the Fermi Golden Rule since the Fröhlich coupling constant \(\alpha\) is small compared to unity: for MoX₂ (X ≡ S, Se and Te), 0.0048, 0.03
and 0.07, respectively, and for WSe₂, 0.0157. On the other hand, the values of $\alpha$ for HF₆X₃ (X = S and Se) are 0.7875 and 0.5879, and for ZrX₂ (X = S and Se), 0.8495 and 0.6471 which indicate that the electrons couple more strongly to LO phonons in these materials. For such materials with strong coupling as indicated by high $\alpha$, the FGR model breaks down which assumes that collisions of electrons with LO phonons are independent; that is, they are sufficiently separated in time so that there is no quantum interference between the collisions and a further assumption is that the electron interacts with only one phonon at a time. As an example, it was first noted in the context of 3D materials [11] that, for the materials with LO phonon energy in the range 50–100 meV the mean free time between collisions (based on perturbative treatment) becomes as small as 2 x $10^{-15}$ sec which is further reduced at high temperatures where phonon absorption becomes significant. Consequently, in our previous work on 3D wurtzite [12] and cubic materials [13] we investigated the energy loss per unit distance (electric field) versus electron velocity in high alpha materials in the purview of non-perturbative path integral formalism by Thornber and Feynman (TF) [11] and the FGR model and found that the FGR model underestimates the energy lost by the electron as a result of the Fröhlich interaction, as it neglects the situation of many phonons interacting with the electron simultaneously and the quantum interferences between the emitted phonons in successive collisions; in such situations the scattering events cannot be separated in time. The correction factors for the energy loss for the FGR was about an order of magnitude and higher for materials with $\alpha$ in the range 0.21–0.93 for wurtzite and 0.1–0.7 for cubic materials. In this paper we apply Thornber—Feynman path integral formalism for HF₆X₃ (X = S, Se) and ZrX₂ (X = S, Se) and determine the electric field versus velocity relation and also determine other transport parameters such as peak velocity, peak electric field, mobility and effective polaron mass.

**Theory**

An electron in any polar material interacts strongly with the neighboring lattice causing it to distort, as a result the electron is surrounded with a cloud of phonons, a state referred to as ‘polaron’. This distorted lattice state moves along with the electron in the lattice [14, 15]. The electron in the lattice experiences apparent effective mass and undergoes change in its eigen energy states. In [14] Feynman modelled the electron interaction with LO phonon in the purview of Fröhlich model where the LO phonon perturbation Hamiltonian is given as:

$$H = \sum_{q} \left( C_{q} a_{q} e^{iq\cdot r} + C_{q}^{\dagger} a_{q}^{\dagger} e^{-iq\cdot r} \right)$$  \hspace{1cm} (2)

where,

$$C_{q} = \left( -i\frac{\hbar \omega_{LO}}{q} \right) \left( \frac{\hbar}{2m_{b} \omega_{LO}} \right)^{\frac{1}{2}} \left( \frac{4\alpha}{V} \right)^{\frac{1}{2}}$$

In the above equation, $q$ is the LO phonon wave vector, the Fröhlich coupling constant is denoted by $\alpha$, $m_{b}$ is the electron effective mass, $a_{q}^\dagger$ and $a_{q}$ are the phonon creation and annihilation operators, and $V$ is the volume of the material. The phonon creation and annihilation operators are defined by

$$a_{q}^\dagger |N_{q}\rangle = \sqrt{n_{q} + 1} |N_{q} + 1\rangle$$

$$a_{q} |N_{q}\rangle = \sqrt{n_{q}} |N_{q} - 1\rangle$$

where $|N_{q}\rangle$ is a state of $N_{q}$ phonons and where the phonon occupation number is

$$n_{q} = \frac{1}{\exp(h\omega_{n}/k_{B}T) - 1}$$

The LO phonon frequency $\omega_{LO}$ is assumed to be dispersion less and taken as the zone center frequency. Feynman applied the path integral method to eliminate the lattice coordinates to find the upper bound on the ground state eigen energy of the polaron (see Equations (31) and (33) in [14]). For the present 2D case we use the 2D scaled Hamiltonian of equation (2) [16], such that:

$$C_{q} = \frac{C}{\sqrt{A\pi}} = -i\hbar \omega \left( \frac{\sqrt{2} \pi \alpha}{Aq} \right)^{\frac{1}{4}} \left( \frac{\hbar}{m_{b} \omega} \right)^{\frac{1}{4}}$$  \hspace{1cm} (3)

where, $q$ and $r$ are 2D vectors and $A$ is the area of the material. The ground state energy of this 2D Fröhlich polaron is obtained by minimizing the following expression with respect to the variational parameters $r$ and $w$ [16, 17]:

---

This text is a part of a scientific paper discussing the interaction of electrons with lattice vibrations in polar materials, focusing on the Fröhlich interaction and its implications on electron transport properties. The theoretical framework involves the use of quantum mechanics and path integral methods to model electron-phonon interactions, leading to expressions for the electron effective mass and other transport parameters. The results are compared with experimental data and previous theoretical models to highlight the significance of the interaction in various materials.
Further, the mass of polaron becomes:

\[
m^* = \frac{m_0}{m_b} \frac{v_0^2}{w_0^2}
\]

where, \(v_0\) and \(w_0\) are obtained after minimizing \(G\) in equation (4). We plot variation of \(v_0\) and \(w_0\) as a function of \(\alpha\) in figure 1(a) and variation of ratio of polaron mass to effective mass of electron, \(m^*/m_b\) in figure 1(b).

From figures 1(a) and (b), it is evident that in weak coupling limit \(v_0 \rightarrow w_0\) and \(m^* \rightarrow m_b\). It is to be noted that there exists a definite scaling relation between 3D and 2D polaron properties which has been derived in [18] and is reproduced below:

\[
m_{2D}(\alpha) = \frac{m_{3D}}{m_b} \frac{\frac{3\pi}{4} \alpha}{m_b}
\]

(5.1)

\[
Z_{2D}(\alpha; \omega) = Z_{3D} \left( \frac{\frac{3\pi}{4} \alpha}{\omega} \right)
\]

(5.2)

\[
\mu_{2D}(\alpha) = \mu_{3D} \left( \frac{\frac{3\pi}{4} \alpha}{\omega} \right)
\]

(5.3)

It can be seen from equation (5.1) and in figure 1(b) dotted line that for the same value of \(\alpha\) the 2D polaron is heavier as compared to a 3D polaron. Since the mass of electron is heavier in a 2D material as compared to a 3D material due to polaronic effects, the threshold velocity is reached in 2D materials at a lower value than for 3D materials. The field-velocity curves are shifted to lower velocities in the 2D cases. Further, equations (5.2) and (5.3) suggest that the apparent impedance experienced by the polaron and its mobility in 2D can be computed from the 3D expression as in [11, 15] with the substitution \(\alpha \rightarrow \frac{3\pi}{4} \alpha\).

Electric field—velocity relation

In [11], motivated by finding the peak energy loss of the electron to the lattice due to interaction with LO phonon, Thornber—Feynman approached the entire problem by finding the expectation value of the steady—state velocity obtained by the electron when subjected to a one—dimensional electric field \(E\). The general expression (expressed in Feynman units \(\hbar = m_b = \omega_q = 1\)) which preserves the physics of the problem is given below:
\[ E = \int_{-\infty}^{\infty} d\xi \sum_{q} |C_{q}|^2 \frac{\cos(\omega_{q}\xi)}{\sin\left(\frac{1}{2}\beta\omega_{q}\right)} e^{-\beta v(\xi+\frac{i\beta}{2})} e^{-k^2 K_{q}(\xi)} \]  

(6)

where, \( \beta = 1/k_{B}T \) in Feynman units (\( \beta = \hbar\omega_{LO}/k_{B}T \) in SI units), \( v \) is the steady state velocity of electron and \( K_{q}(\xi) \) is a an expression which depends on impedance of the electron and oscillator distribution, \( K_{q}(\xi) = D(\xi + i\beta/2) / 2 \) [11, 15] is given as below:

\[ K_{q}(\xi) = \frac{1}{2} \frac{w_{q}^2}{v_{q}} \left[ \frac{v_{q}^2 - w_{q}^2}{w_{q}^2 v_{q}} \right] \times \frac{\cos\left(\frac{1}{2}\beta v_{q}\right) - \cos\left(v_{0} v_{q}\right)}{\sinh\left(\frac{1}{2}\beta v_{q}\right)} + \frac{\xi^2}{4} + \frac{\beta}{4} \]

In the above expression of \( K_{q}(\xi) \), the \( v_{0} \) and \( w_{0} \) are as given in figure 1(a). In the Feynman model it is assumed that the phonon model of the lattice consists of a single frequency. It should be noted that \( E \) in equation (6) represents \( eE, \) and the equation (6) should be interpreted as electric field necessary to balance the loss of energy by the electron to the lattice as a result of LO phonon interaction while maintaining a steady state velocity \( v. \)

We need to scale equation (6) for the 2D case, we start by expanding \( \cos(v_{0} v_{q}) \) to the second power in the expression of \( K_{q}(\xi), \) such that \( \cos(v_{0} v_{q}) \approx 1 - \frac{v_{0}^2 v_{q}^2}{2}, \) consequently we can write (the simplification is shown in appendix A):

\[ K_{q}(\xi) = \frac{B_{0}}{2}\beta + \frac{A_{0}\xi^2}{2\beta} \]

where,

\[ A_{0} = \left[ \frac{v_{q}^2 - w_{q}^2}{v_{q}} \right] \times \left[ \frac{v_{0}\beta}{2\sinh\left(\frac{1}{2}\beta v_{q}\right)} - 1 \right] + 1 \]

\[ B_{0} = \frac{\beta w_{q}^2}{v_{q}^2} \left[ \frac{v_{q}^2 - w_{q}^2}{w_{q}^2 v_{q}} \right] \times \tanh\left(\frac{1}{4}\beta v_{q}\right) + \frac{\beta}{4} \]

(7)

Now, substituting for \( K_{q}(\xi) \) from equation (7) in equation (6), we get (the simplification is shown in appendix B):

\[ E = \frac{\alpha}{4\sinh\left(\frac{1}{2}\beta\right)} \sqrt{\frac{\beta}{\pi}} \frac{1}{A_{0}} \int_{0}^{2\pi} d\phi \cos(\phi) \int_{0}^{\infty} dk \frac{q}{|q|} \exp\left(-\frac{\beta q^2}{8A_{0}} \left[ \frac{4B_{0}}{\beta^2} - A_{0} \right] \right) \]

\[ \times \left( e^{-\frac{\beta}{2}} \exp\left(-\frac{\beta}{2} \frac{\cos(\phi)v}{\sqrt{A_{0}}} - \frac{q^2}{2} + \frac{1}{4} \right) \right) e^{\frac{\beta}{2} \exp\left(-\frac{\beta}{2} \frac{\cos(\phi)v}{\sqrt{A_{0}}} - \frac{q^2}{2} + \frac{1}{4} \right) \right) \]

(8)

The expression in equation (8) is the final expression for the energy lost per unit distance (eE), in Feynman units, for an electron interacting with LO phonons in a 2D polar medium with a steady state velocity \( v. \)

Now, we derive the Fermi’s golden rule based model to compare it with the above expression obtained in the purview of non-perturbative treatment. The scattering rate of phonons for an electron for a transition from a state \( |k\rangle \) to \( |k'\rangle \) is given as:

\[ \frac{1}{\tau_{ee}} = \frac{2\pi}{\hbar} |M_{q}|^2 \delta(E(k') - E(k) \pm \hbar\omega_{LO}) \]

(9a)

where, the upper ‘+’ sign in the parenthesis indicates emission and the lower ‘−’ for absorption respectively. \( M_{q} \) is the electron—phonon coupling matrix element defined by [9]:

\[ M_{q} = \begin{cases} \{k', \quad N_{q} + \frac{1}{2} \pm \frac{1}{2} \} & k, \quad N_{q} + \frac{1}{2} \pm \frac{1}{2} \end{cases} \]

(9b)

In equation (9b), \( N_{q} = 1 / (\exp(\frac{\hbar\omega_{LO}}{k_{B}T}) - 1) \) is the phonon occupation number. It is to be noted that during emission of phonons the electron—phonon state changes from \( |k, N_{q}\rangle \) to \( |k', N_{q} + 1\rangle \) and during absorption it changes from \( |k, N_{q}\rangle \) to \( |k', N_{q} - 1\rangle \). We consider the electrons to be strictly two dimensional, so the wavefunction can be written as:

\[ |k\rangle = \frac{e^{ik_{x}r}}{\sqrt{A}} \]

(10)
Evaluating the equation $(9a)$, we get:

$$\frac{1}{\tau_{\text{em}}} = \alpha \omega_{\text{LO}} \sqrt{\frac{\hbar \omega_{\text{LO}}}{\varepsilon} \left( N_q + \frac{1}{2} \pm \frac{1}{2} \right) \int_{q_{\text{min}}}^{q_{\text{max}}} dq \frac{1}{q} \sqrt{1 - \frac{\hbar^2}{2m_b} \left( \varepsilon \pm \frac{m \omega_{\text{LO}}}{q^2} \right)^2} }$$  

(11)

where, $\varepsilon = \frac{hq}{2m_{\text{el}}}$ is the kinetic energy of the electron in the conduction band and $q_{\text{min}}$ and $q_{\text{max}}$ are the limits determined for emission and absorption as follows:

Emission:

$$q_{\text{min}} = \frac{\sqrt{2m_b}}{h} \left( \sqrt{\varepsilon} - \sqrt{\varepsilon - \hbar \omega_{\text{LO}}} \right)$$

$$q_{\text{max}} = \frac{\sqrt{2m_b}}{h} \left( \sqrt{\varepsilon} + \sqrt{\varepsilon - \hbar \omega_{\text{LO}}} \right)$$  

(12)

Absorption:

$$q_{\text{min}} = \frac{\sqrt{2m_b}}{h} \left( -\sqrt{\varepsilon} + \sqrt{\varepsilon + \hbar \omega_{\text{LO}}} \right)$$

$$q_{\text{max}} = \frac{\sqrt{2m_b}}{h} \left( \sqrt{\varepsilon} + \sqrt{\varepsilon + \hbar \omega_{\text{LO}}} \right)$$  

(13)

From equation (11) it follows that an electron looses an energy $\hbar \omega_{\text{LO}}$ when it travels a distance $\tau \varepsilon$ and similarly it gains $\hbar \omega_{\text{LO}}$ when it travels $\tau \varepsilon$ so the net loss in energy per unit distance in the FGR regime is given by [19]:

$$E = \frac{\hbar \omega_{\text{LO}}}{\nu} \left( \frac{1}{\tau \varepsilon} - \frac{1}{\tau a} \right)$$  

(14)

Also, from equation (12) it is clear that the condition for emission is $\varepsilon > \hbar \omega_{\text{LO}}$ because the limits must be a real positive number which represents the phonon wave vector. So, the FGR predicts that no loss of energy takes place unless the electron energy is greater than or equal to the LO phonon energy.

**Results and discussion**

We first plot in figure 2 the phonon emission and absorption rates in FGR regime as obtained in equation (11), we observe that for all the four materials the phonon emission rate is ~2.1–3.7 times higher than the phonon absorption rate at room temperature (actual values tabulated in table 1), unlike 3D materials where the emission...
rate is about an order of magnitude or higher [9]. Thus, the phonon absorption rate cannot be neglected here at room temperature and have been duly accounted for in equation (14) to model energy loss per unit distance. From figure 2 and table 1, we see that the mean time between the emission ranges from $\sim 0.9 \times 10^{-14}$ to $1.7 \times 10^{-14}$ sec whereas, the FGR is valid only when the electron phonon interaction time scale $\tau > \frac{2}{\omega_L}$ [9, 12] which lies in the range $\sim 3.9 \times 10^{-14} - 6.9 \times 10^{-14}$ sec. It is evident that the mean time between phonon emissions is even smaller than the minimum interaction time required for the validity of the FGR.

Now we plot thornber—Feynman curves as obtained in equation (8) after converting from Feynman units and compare them with FGR curves as obtained in equation (11). We see that the TF curves exhibit a monotonically increasing relation between $\Delta E$ and velocity until a threshold velocity $v_{th}$ when the electron phonon interaction time scale $t \geq \frac{2}{\omega_L}$ [9, 12] which corresponds to peak energy loss, say $E_{th}$. This region with increasing slope is the stable region as any increase in the velocity (due to fluctuation) causes energy loss to the lattice to increase and hence the velocity decreases until the total energy is balanced by the energy gained from the electric field, alternatively, if the velocity decreases then the loss to the lattice is reduced below what the electron gains energy from the external field due to this net gain of energy the velocity increases until the loss to lattice is balanced by the gain from the field. Similarly, the region with negative slope in the TF curve is the unstable region as any increase in the velocity is accompanied by a decrease in the energy loss to the lattice consequently the electron gains a net energy and continues to accelerate indefinitely unless there are some other scattering mechanisms with higher thresholds. The region of negative slope and the associated unstable region have been discussed previously in the literature for different material systems [19]. While a discussion of these effects goes beyond the scope of this paper, it is worthy of note that previous works on Si and Ge devices indicate that electron runaway and negative differential mobility in two-dimensional electron gas in elementary semiconductors can lead to oscillations similar to those of the Gunn effect as discussed in [19], and previous works on GaN and AlN lead to runaway effects in the nitrides [as discussed in [19]].

We have tabulated the peak energy loss and the threshold velocity for all the materials in table 2. We can see that ZrS$_2$ with Fröhlich coupling constant $\alpha = 0.85$ has maximum energy loss and HfSe$_2$ with $\alpha = 0.59$ has minimum peak energy loss, the peak energy loss should increase with $\alpha$ as it indicates strong interaction with LO phonons. However, we also expect that a higher $\alpha$ will increase the apparent mass as in figure 1(b) this increase causes reduction in the threshold velocity because near the threshold region $\frac{1}{2}m_b \left( \frac{v}{V} \right)^2 \approx \frac{\hbar^2}{2m_b\omega_L}$ [11] and hence as depicted in table 2 we observe that with increasing $\alpha$ the threshold velocity is reduced. However, the ratio of peak energy loss as predicted by TF to FGR peak increases with decrease in $\beta$. We see that for HfS$_2$ with $\beta = 1.28$ has the ratio 2.4 whereas for ZrSe$_2$ which has lowest $\beta = 0.74$ at room temperature of all the four materials has a ratio of 3.5, this is because a lower $\beta$ implies higher phonon occupation number $N_b$ and since the energy loss to lattice in TF formalism duly takes care of interferences between emitted phonons predicts a higher energy loss as compared to TF which treats phonon emissions independent of each other. Finally, we deduce the mobility, $\mu_{TF}$ using the $E(v)$ curves in figure 3 by finding averaging $\frac{dv}{dE(v)}$ in the stable region [13], we have depicted them in table 2. It is seen that ZrSe$_2$ has the highest mobility 449 cm$^2$/V·s of all the materials followed by HfSe$_2$ whose mobility is 240 cm$^2$/V·s.

### Table 1. Comparison of min interaction limit with actual phonon mean free time.

| Material     | $t_{min} = \frac{2}{\omega_L}$ (10$^{-14}$ sec) | Average mean time between phonon emission (×10$^{-14}$ sec) |
|--------------|-----------------------------------------------|--------------------------------------------------|
| HfS$_2$     | 3.97                                          | 0.97                                             |
| HfSe$_2$    | 5.2                                           | 1.6                                              |
| ZrS$_2$     | 4.1                                           | 0.92                                             |
| ZrSe$_2$    | 6.9                                           | 1.7                                              |

### Table 2. Comparison of computed TF and FGR parameters.

| Material     | $E_a$ (KV/cm) | $\nu_a$ (×10$^7$ cm$^{-1}$) | $E_b$ (KV cm$^{-1}$) | $\nu_b$ (×10$^7$ cm$^{-1}$) | $\frac{K_{TF}^2}{K_{FGR}^2}$ | $\beta = \frac{\hbar \nu_b}{kT}$ | $\alpha$ | $\mu_{TF}$ (cm$^2$/V·s) |
|--------------|---------------|-------------------------------|-----------------------|-------------------------------|-----------------------------|---------------------------------|---------|--------------------------|
| HfS$_2$     | 476           | 3.0                           | 196.7                 | 2.2                           | 2.42                        | 1.28                            | 0.7875  | 90.8                     |
| HfSe$_2$    | 246.6         | 4.0                           | 87.7                  | 2.3                           | 2.81                        | 0.98                            | 0.5879  | 240                      |
| ZrS$_2$     | 576.7         | 2.5                           | 231.8                 | 1.93                          | 2.49                        | 1.24                            | 0.8495  | 58.3                     |
| ZrSe$_2$    | 252           | 3.8                           | 72                    | 1.77                          | 3.5                         | 0.74                            | 0.7371  | 449                      |

J. Phys. Commun. 6 (2022) 095009
Figure 3 provides a comparison of the FGR and TF results for a wide range of velocities as predicted by the inherently many-body (multiple phonon) results of the TF path-integral theory. As discussed at length, by Thornber and Feynman in [11], the phonon-carrier interaction for large Frohlich coupling constants—as is the case in the present discussion—results in multiple phonon emission events of the femtosecond time scale and the carrier-phonon interaction becomes an inherently many-phonon interaction. In the case of the FGR description of scattering which describes only the interaction of a single phonon and a single electron, it is necessary for the electron velocity to result in an electron kinetic energy at least equal to the energy of the emitted phonon; thus, the low velocity portions of the FGR curves in figure 3 begin at this threshold velocity for phonon emission. Because of the many-phonon nature of the TF theory the interaction is possible for electron velocities below the threshold velocity as depicted in figure 3. All material parameters used for calculation in this paper is shown in table 3.

### Table 3. Material parameters used in calculation.

| Material  | $\omega_{LO}$ (cm$^{-1}$) | $m_b$  | $\varepsilon_{\infty}$ | $\varepsilon_0$ |
|-----------|------------------------|--------|------------------|----------------|
| HfS$_2$   | 267.6$^a$              | 0.24$^b$ | 10.2$^b$         | 53.6$^b$       |
| HfSe$_2$  | 205$^a$                | 0.18$^b$ | 13.9$^b$         | 83$^b$         |
| ZrS$_2$   | 260.2$^a$              | 0.31$^b$ | 11.2$^b$         | 66.7$^b$       |
| ZrSe$_2$  | 153.7$^a$              | 0.22$^b$ | 15.76$^c$        | 84.59$^c$      |

$^a$ [20].  
$^b$ [21].  
$^c$ [22].

Figure 3 provides a comparison of the FGR and TF results for a wide range of velocities as predicted by the inherently many-body (multiple phonon) results of the TF path-integral theory. As discussed at length, by Thornber and Feynman in [11], the phonon-carrier interaction for large Frohlich coupling constants—as is the case in the present discussion—results in multiple phonon emission events of the femtosecond time scale and the carrier-phonon interaction becomes an inherently many-phonon interaction. In the case of the FGR description of scattering which describes only the interaction of a single phonon and a single electron, it is necessary for the electron velocity to result in an electron kinetic energy at least equal to the energy of the emitted phonon; thus, the low velocity portions of the FGR curves in figure 3 begin at this threshold velocity for phonon emission. Because of the many-phonon nature of the TF theory the interaction is possible for electron velocities below the threshold velocity as depicted in figure 3. All material parameters used for calculation in this paper is shown in table 3.

### Conclusion

In this paper we have evaluated energy lost per unit distance (electric field) versus velocity of electrons for 2D materials with strong carrier - LO phonon interactions within the purview of Thornber—Feynman formalism applied to 2D Frohlich polaron. We demonstrated that Fermi’s Golden Rule based scattering rate cannot be applied to these materials and it underestimates the energy loss by the electron to the lattice. We find the energy loss rates are underestimated by the FGR by about an order of magnitude for the materials considered with the largest carrier—LO phonon coupling constants. Finally, out of all four materials ZrSe$_2$ has the highest mobility $449.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. As discussed in the text, potential applications of such high-mobility finite
bandgap materials include devices with reduced switching times and structures for multiple wavelength optoelectronic applications as reviewed in [23].

**Acknowledgments**

This research has been supported, in part, under AFOSR award FA9550–19–1–0282.

**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

**Appendix A**

Herein, we analyze and evaluate $\hat{K}_{\beta'}(\xi)$ by expanding it to the second power in $\xi$.

Beginning with the discussion following equation (5) and $s$, using, $\cos(x) \approx 1 - \frac{x^2}{2}$, we obtain the following sequence of simplifications:

\[
\hat{K}_{\beta'}(\xi) = -\frac{1}{2} \frac{w_0^2}{\nu_0^2} \left( \frac{v_0^2 - w_0^2}{w_0^2 \nu_0} \right) \times \left( \cosh \left( \frac{1}{2} \beta \nu_0 \right) - 1 + \frac{v_0^2 \xi^2}{2} \right) \sinh \left( \frac{1}{2} \beta \nu_0 \right) + \frac{\xi^2}{\beta} + \frac{\beta}{4} \]

\[
\hat{K}_{\beta'}(\xi) = -\frac{1}{2} \frac{w_0^2}{\nu_0^2} \left( \frac{v_0^2 - w_0^2}{w_0^2 \nu_0} \right) \times \left( \frac{2 \sinh^2 \left( \frac{1}{4} \beta \nu_0 \right)}{2 \sinh \left( \frac{1}{2} \beta \nu_0 \right) \cosh \left( \frac{1}{4} \beta \nu_0 \right)} + \frac{v_0^2 \xi^2 / 2}{\sinh \left( \frac{1}{2} \beta \nu_0 \right)} \right) + \frac{\xi^2}{\beta} + \frac{\beta}{4} \]

\[
\hat{K}_{\beta'}(\xi) = -\frac{1}{2} \frac{w_0^2}{\nu_0^2} \left( \frac{v_0^2 - w_0^2}{w_0^2 \nu_0} \right) \times \left( \tanh \left( \frac{1}{4} \beta \nu_0 \right) + \frac{v_0^2 \xi^2 / 2}{\sinh \left( \frac{1}{2} \beta \nu_0 \right)} \right) + \frac{\xi^2}{\beta} + \frac{\beta}{4} \]

\[
\hat{K}_{\beta'}(\xi) = \frac{1}{2} \frac{\beta w_0^2}{\nu_0^2} \left( \frac{v_0^2 - w_0^2}{w_0^2 \nu_0} \right) \times \tanh \left( \frac{1}{4} \beta \nu_0 \right) + \frac{\beta}{4} \]

\[
+ \frac{\xi^2}{2} \frac{w_0^2}{2 \beta \nu_0^2} \left( \frac{v_0^2 - w_0^2}{w_0^2 \nu_0} \right) \times \frac{v_0^2 \beta}{2 \sinh \left( \frac{1}{2} \beta \nu_0 \right)} + 1 \]

Letting $B_0 = \frac{\beta w_0^2}{\nu_0^2} \left( \frac{v_0^2 - w_0^2}{w_0^2 \nu_0} \right) \times \tanh \left( \frac{1}{4} \beta \nu_0 \right) + \frac{\beta}{4}$

we obtain,

\[
\hat{K}_{\beta'}(\xi) = B_0 + \frac{\xi^2}{2} \frac{w_0^2}{\nu_0^2} \left( \frac{v_0^2 - w_0^2}{w_0^2 \nu_0} \right) \times \frac{v_0^2 \beta}{2 \sinh \left( \frac{1}{2} \beta \nu_0 \right)} + \frac{w_0^2}{\nu_0^2} \]

Now, writing $\frac{w_0^2}{\nu_0^2} = - \left( \frac{v_0^2 - w_0^2}{v_0^2} \right) + 1$
we find,

\[
\bar{\mathcal{R}}_{\beta'}(\xi) = \frac{B_0}{2\beta} + \frac{\xi^2}{2\beta} \left[ \left( \frac{v_0^2 - w_0^2}{v_0} \right) \times \frac{\beta}{2 \sinh \left( \frac{1}{2} \beta \nu \right)} \right] - \left( \frac{v_0^2 - w_0^2}{v_0} \right) + 1
\]

or,

\[
\bar{\mathcal{R}}_{\beta'}(\xi) = \frac{B_0}{2\beta} + \frac{\xi^2}{2\beta} \left[ \left( \frac{v_0^2 - w_0^2}{v_0} \right) \times \left\{ \frac{v_0 \beta}{2 \sinh \left( \frac{1}{2} \beta \nu \right)} - 1 \right\} + 1 \right]
\]

Letting \( A_0 = \left( \frac{v_0^2 - w_0^2}{v_0} \right) \times \left\{ \frac{v_0 \beta}{2 \sinh \left( \frac{1}{2} \beta \nu \right)} - 1 \right\} + 1 \)

We finally obtain,

\[
\bar{\mathcal{R}}_{\beta'}(\xi) = \frac{B_0}{2\beta} + \frac{A_0 \xi^2}{2\beta}
\]

Appendix B

To obtain equation (8), we begin with equation (6),

\[
E = \int_{-\infty}^{\infty} d\xi \sum_k |C_k|^2 k \cos (\omega_k \xi) \frac{e^{-ikv(\xi+i/2)}}{\sinh \left( \frac{1}{2} \beta \omega_k \right)} e^{-k^2 \bar{\mathcal{R}}_{\beta'}(\xi)}
\]

It is assumed that the applied electric field is in x-direction:

\[
E = \int_{-\infty}^{\infty} d\xi \sum_k |C_k|^2 k \cos (\omega_k \xi) \frac{e^{-ikv(\xi+i/2)}}{\sinh \left( \frac{1}{2} \beta \omega_k \right)} e^{-k^2 \bar{\mathcal{R}}_{\beta'}(\xi)}
\]

Taking the real part of above equation and substituting \( \omega_k = 1 \) (since phonons are assumed to be dispersion less and we work in Feynman units \( \hbar = m_b = \omega \omega = 1 \)) and \( k_x = k \cos (\phi) \)

\[
\sum_k |C_k|^2 = \frac{1}{(2\pi)^2} \int d^2k |C_k|^2 = \frac{1}{(2\pi)^2} \int \sqrt{2} \pi \frac{\alpha}{k} d\phi dk = \frac{\alpha}{2^{3/2} \pi} \int d\phi dk
\]

Substituting, \( \bar{\mathcal{R}}_{\beta'}(\xi) = \frac{B_0}{2\beta} + \frac{A_0 \xi^2}{2\beta} \) and integrating w.r.t \( \xi \) first:

\[
E = \frac{\alpha}{2^{3/2} \pi} \int d\phi dk k \cos (\phi) e^{k v \cos (\phi) / 2} e^{-k^2 B_0 / 2\beta} \int_{-\infty}^{\infty} d\xi (\cos (\xi) \cos (kv \cos (\phi) \xi) e^{-k^2 A_0 \xi^2 / 2\beta})
\]

Simplifying above expression with the terms involving \( \xi \): Let,

\[
y \equiv \cos \phi
\]
\[
\cos(\xi) \cos(kvy) e^{-k^2 A_G/2\beta} = \int_{-\infty}^{\infty} dx \left[ \frac{1}{2} \cos \{ \xi(kvy + 1) \} e^{-k^2 A_G/2\beta} + \frac{1}{2} \cos \{ \xi(kvy - 1) \} e^{-k^2 A_G/2\beta} \right]
\]

Since,
\[
\int_{-\infty}^{\infty} e^{-x^2} \cos(xb) = \frac{\sqrt{\pi}}{\sqrt{\beta}} e^{-b^2/4a}
\]

So, after integrating over \( \xi \) we get:
\[
E = \frac{\alpha}{4 \sqrt{\pi} \sinh\left( \frac{\beta}{2} \right)} \cdot \frac{\sqrt{\beta}}{A_0} \times \int d\phi dk \frac{k}{|k|} \cos(\phi) e^{kvy/2\beta} e^{-k^2 B_0/k^2 A_0} (e^{-\beta k^2_B/2\beta^2} + e^{-\frac{\beta}{2} k^2_B/k^2 A_0})
\]

Simplifying the exponent of \( e^{kvy/2\beta} \), we get:
\[
-\frac{\beta}{2} \left( \frac{yv}{\sqrt{A_0}} - \frac{k}{2} + \frac{1}{k} \right)^2 - \frac{k^2}{4} + 1
\]

Similarly, the exponent of \( e^{kvy/2\beta} \), we get:
\[
-\frac{\beta}{2} \left( \frac{yv}{\sqrt{A_0}} - \frac{k}{2} - \frac{1}{k} \right)^2 - \frac{k^2}{4} - 1
\]

We have used \( k\sqrt{A_0} \equiv k \), so that \( \int dk \to \frac{1}{\sqrt{A_0}} \int dk \)

Using the above simplifications in the expression of \( E \) and substituting back \( y \equiv \cos(\phi) \) with further algebraic simplifications we get:
\[
E = \frac{\alpha}{4 \sinh\left( \frac{\beta}{2} \right)} \cdot \frac{\sqrt{\beta}}{\pi} \cdot \frac{1}{A_0} \int_{0}^{2\pi} d\phi \cos(\phi) \int_{0}^{\infty} dk \frac{k}{|k|} \]

\[
\times \exp\left( -\frac{\beta k^2}{8A_0} \left[ \frac{4B_0}{\beta^2} - A_0 \right] \right)
\]

\[
\times \left( e^{-\frac{\beta}{2}} \exp\left( -\frac{\beta}{2} \left( \frac{\cos(\phi) v}{\sqrt{A_0}} - \frac{k}{2} + \frac{1}{k} \right)^2 \right) \right)
\]

\[
+ e^{\frac{\beta}{2}} \exp\left( -\frac{\beta}{2} \left( \frac{\cos(\phi) v}{\sqrt{A_0}} - \frac{k}{2} - \frac{1}{k} \right)^2 \right)
\]

which is the form used in the analysis.

**ORCID iDs**

Ramji Singh 🐦 https://orcid.org/0000-0003-4211-7306

**References**

[1] Geim A K and Novoselov K S 2007 The rise of graphene Nat. Mater. 6 Nature Publishing Group 183–91
[2] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Electric field effect in atomically thin carbon films Science 306 666–9
[3] Jin Z, Li X, Mullen J T and Kim K W 2014 Intrinsic transport properties of electrons and holes in monolayer transition-metal dichalcogenides Phys. Rev. B 90 045422
[4] Chen P F and Wu Y R 2021 Calculation of field dependent mobility in MoS₂ and WS₂ with multi-valley monte carlo method 2021 Int. Symp. on VLSI Technology, Systems and Applications (VLSI-TSA), pp 1–2
[5] Cheng L and Liu Y 2018 What limits the intrinsic mobility of electrons and holes in two dimensional metal dichalcogenides J. Am. Chem. Soc. 140 17895–900
[6] Fiori G et al 2014 Electronics based on two-dimensional materials Nat. Nanotechnol. 9 768–79
[7] Zhang W, Huang Z, Zhang W and Li Y 2014 Two-dimensional semiconductors with possible high room temperature mobility Nano Res. 7 1731–7
[8] Frohlich H 1954 Adv. Phys. 3 325–61
[9] Stroscio M A and Dutta M 2001 Phonons in Nanostructures (Cambridge, U.K.: Cambridge Univ. Press)
[10] Sohier T, Calandra M and Mauri F 2016 Two-dimensional Frohlich interaction in transition-metal dichalcogenide monolayers: theoretical modeling and first principles calculation’s Phys. Rev. B 94 085415
[11] Thornber K K and Feynman R P 1970 Velocity acquired by an electron in a finite electric field in a polar crystal Physical Review. B, Solid State 1 4099–114
[12] Singh R, Dutta M and Stroscio M A 2020 Thornber-feynman carrier-optical-phonon scattering rates in wurtzite crystals J. Phys. Condens. Matter 33 015301
[13] Singh R, Dutta M and Stroscio M A 2021 Electron-optical-phonon scattering rates in cubic group III-nitride crystals: path-integral corrections to fermi golden rule matrix elements Semicond. Sci. Technol. 36 025017
[14] Feynman R P 1955 Slow electrons in a polar crystal Phys. Rev. 660–5
[15] Feynman R P, Hellwarth R W, Iddings C K and Platzman P M 1962 Mobility of slow electrons in a polar crystal Phys. Rev. 127 1004–17
[16] Huybrechts W 1978 Ground-state energy and effective mass of a polaron in a two-dimensional surface layer Solid State Commun. 28 Elsevier Ltd 95–7
[17] Peeters F M, Xiaoguang W and Devreese J T 1986 Ground-state energy of a polaron in n dimensions Physical Review. B, Condensed Matter 33 American Physical Society 3926–34
[18] Peeters F M and Devreese J T 1987 Scaling relations between the two- and three-dimensional polarons for static and dynamical properties Physical Review. B, Condensed Matter American Physical Society 36 4442–5
[19] Dmitriev A P, Kachorovskii V Y, Shur M and Stroscio M 2000 Electron runaway and negative differential mobility in two-dimensional electron gas in elementary semiconductors Solid State Communications 113 565–8
[20] Huang Z, Zhang W and Zhang W 2016 Computational search for two-dimensional MX2 semiconductors with possible high electron mobility at room temperature Materials MDPI AG 9 716–716
[21] Laturia A, Van de Put M I and Vandenberghe W G 2018 Dielectric properties of hexagonal boron nitride and transition metal dichalcogenides: from monolayer to bulk npj 2D Mater Appl. 2 61–7
[22] Petousis I, Mrdjenovich D, Ballouz E, Liu M, Winston D, Chen W, Graf T, Schladt T D, Persson K A and Prinz F B 2017 High-throughput screening of inorganic compounds for the discovery of novel dielectric and optical materials Scientific Data 4 160134
[23] Mitin V V, Kochelap V A, Dutta M and Stroscio M A 2019 Introduction to Optical and Optoelectronic Properties of Nanostructures (Cambridge: Cambridge University Press)