Strain effects on the spin-orbit induced band structure splittings in monolayer MoS$_2$ and graphene.

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The strain effects on the spin-orbit induced splitting of the valence band maximum and conduction band minimum in monolayer MoS$_2$ and the gap in graphene are calculated using first-principles calculations. The dependence of these splittings on the various symmetry types of strain is described by means of an effective Hamiltonian based on the method of invariants and the parameters in the model are extracted by fitting to the theory. These splittings are related to acoustic phonon deformation potentials, or electron-phonon coupling matrix elements which enter the spin-dependent scattering theory of conduction in these materials.

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I. INTRODUCTION

Graphene and monolayer MoS$_2$ are both interesting materials for spin-dependent electronic devices\cite{1,2}. In spite of their similarities, they also have significant differences. As is well known, graphene has a linear dispersion near the Dirac points and has inversion symmetry. MoS$_2$ has a gap of about 1.8 eV and the absence of inversion symmetry in monolayer MoS$_2$ leads to an interesting relation of the spins and the valley degrees of freedom. Both valence band and conduction band edges in the $K$ and $K'$ valleys of the Brillouin zone are split purely by spin-orbit coupling. Because of the time-reversal symmetry between $\psi_{k\sigma}$ and $\psi_{-k-\sigma}$, the up and down spin states in opposing valleys are reversed. This relation leads to the possibility of valley control of the carriers by means of circularly polarized excitation.\cite{3,4} On the other hand, spin transport in this material depends on the intra-valley and inter-valley scattering, which arises from the electron-phonon coupling. As is also well known in graphene, ripples play an important role in 2D materials.\cite{5} These ripples are governed by out-of-plane long-wavelength phonon distortion; the so-called flexural acoustic mode. This mode is associated with the dynamic out-of-plane shear strain. Thus, by studying the splittings and shifts of the energy bands with strain, it is possible to extract deformation potential constants that set the amplitudes of various electron-phonon scattering processes.\cite{6,7} The present study is motivated by this connection.

Strain induced changes in the band gap of MoS$_2$ have been the subject of several recent papers.\cite{8,9} The emphasis of those papers is on the strain engineering of the band structure. While we will also present some results on the band gaps with strain, our emphasis is on studying the effect of different types of strain on the band edge spin-orbit splittings in MoS$_2$. Closely related, the spin-orbit coupling in graphene leads to the opening of a gap at the Dirac point.\cite{10} The size of this spin-orbit coupling induced gap in graphene is extremely small and has been somewhat controversial with different estimates resulting from different tight-binding models and first-principles calculations.\cite{11,12} Here, we present first-principles calculations of this spin-orbit induced gap, and from its dependence on strain we recover the scattering constant for intrinsic spin flips in graphene.\cite{13} This connection is made via a new strain term that we introduce to the $K$-point effective Hamiltonian in graphene.

In the theory of electron-phonon scattering, absolute deformation potentials of individual bands play a role.\cite{14,15} The so-called absolute hydrostatic deformation potentials lead to shifts of the bands and cannot be extracted from a single bulk calculation because the reference potential in a periodic crystal is ill-defined.\cite{16,17} An interface calculation is needed between a strained and unstrained region in order to obtain the dipole potential alignment between the two and hence the absolute shifts of the bands. On the other hand, splitting of the bands due to traceless components of the strain tensor are obtainable from a single unit cell calculation, appropriately strained. In this paper, we focus only on deformation potentials which can be extracted from band splittings. It also means that we cannot obtain inter-valley matrix elements in this manner. In spite of these restrictions, the present study should be of interest, because the splittings studied under strain are in principle also directly observable experimentally.

Before embarking on the theory we note that it may be surprising that the spin-orbit splitting would depend on strain at all. After all, the spin-orbit coupling is a relativistic effect resulting mostly from the inner parts of the atom and hence be mostly an atomic property. However, the strain affects the mixing of different atomic orbitals (e.g., different Mo-$d$ orbitals and S-$p$ orbitals in the eigenstates), and as a result the effective splitting does depend measurably on strain. While these effects
are indeed rather small, they present a challenge to the computational accuracy. Nevertheless, systematic errors of density functional theory in its usual local density approximation cancel out in these energy differences (band splittings) and differences of differences (strain induced changes in the splittings). This fact makes it possible to calculate the splittings as long as a sufficiently accurate basis set is used to find the eigenvalues of the crystal potential (i.e., the band structure). The all-electron linearized band structure methods like the full-potential linearized muffin-tin orbital method (FP-LMTO) satisfies the requirements.

The plan of the paper is as follows. In Sec. II we derive effective Hamiltonian forms using the method of invariants. In Sec. III we present details of the first-principles computational method employed. In Sec. IV we present the first-principles results on the splittings under the effective Hamiltonians, we employ the method of invariants.23,25,29–31 This group theoretical framework provides the terms allowed by symmetry. Simply put, the strain tensor is decomposed in irreducible representations of the point group of the k-point where the band splitting of interest occurs. The Hamiltonian must belong to the fully symmetric irreducible representation (IR). Group theory thus determines which terms, linear or quadratic in the strain component, are allowed in the Hamiltonian. In the case of MoS$_2$, the states near the splitting are determined by a $2 \times 2$ Hamiltonian while in the case of graphene, the Dirac cone is represented by a $4 \times 4$ Hamiltonian, including both the orbital pseudospin and real spin degrees of freedom. The theory thus predicts linear or quadratic dependence of the band splittings on different types of strain.

A. MoS$_2$ effective Hamiltonian

In the absence of strain, the spin-orbit split states at the K-point band edges in MoS$_2$ are described by a $2 \times 2$ matrix, conveniently expressed in terms of the Pauli matrices and unit matrix:

$$H_0 = \hat{E}1 + \frac{1}{2} \Delta_0 \sigma_z.$$  

Here $\hat{E}$ is the average of up and down spin bands without spin-orbit splitting and as an arbitrary constant it can be set to zero. $\Delta_0$ is the spin-orbit splitting. The same form applies to the valence band maximum (VBM) and conduction band minimum (CBM) although of course the value of $\Delta_0$ is rather different. We distinguish them by means of a subscript v or c for VBM and CBM, respectively. It is much smaller for the CBM ($\Delta_{0c} = 3.36$ meV) than for the VBM ($\Delta_{0v} = 146$ meV) because the CBM states are derived mostly from the Mo-$d_{3z^2-r^2}$ orbital which has quantum number $L_z = 0$, and hence zero spin-orbit coupling. It is only because of the small deviation of the Mo atomic potential from spherical symmetry due to the crystal structure, and because of the small components from $S p_x$, $p_y$ orbitals that it is not zero. On the other hand, the VBM consists of $d_{xy}$, $d_{yz}$ like states. The strain adds terms $b(\epsilon)$ on the diagonal and $a_i(\epsilon)$ on the off-diagonal of the form

$$H_{\text{strain}} = \frac{1}{2} b(\epsilon) \sigma_z + \frac{1}{2} \sum_{i=x,y} a_i(\epsilon) \sigma_i.$$  

We employ symmetrized strain-tensor components, $\epsilon_{ij} = (du_i/dx_j + du_j/dx_i)/2$, where $u_i$ is the displacement of the $i$-th cartesian coordinate$^{[4]}$. The strain dependent splitting of $H_0 + H_{\text{strain}}$ becomes

$$\Delta(\epsilon) = \sqrt{[\Delta_0 + b(\epsilon)]^2 + |a(\epsilon)|^2}.$$  

Next, we specify the dependence of $b(\epsilon)$ and $a(\epsilon)$ for different symmetry components of the strain tensor. The flexural modes or out-of-plane strain-tensor components ($\epsilon_{xx}$ and $\epsilon_{yy}$) are odd with respect to the mirror-plane passing through the MoS$_2$ layer. Accordingly, they can only contribute even terms to the diagonal and odd terms to the off-diagonal parts of the effective Hamiltonian. Hence, to lowest non-zero order,

$$a_i(\epsilon_{iz}) \approx a_1 \epsilon_{iz}, \quad b(\epsilon_{iz}) \approx b_2 \epsilon_{iz}^2.$$  

Contrary to the out-of-plane case, in-plane strain components ($\epsilon_{xx}$, $\epsilon_{yy}$) are even with respect to the horizontal mirror-plane. The off-diagonal terms must necessarily be zero and cannot lead to spin-flip scattering, whereas the leading diagonal term is linear in strain,

$$a_i(\epsilon_{ij}) = 0, \quad b(\epsilon_{ij}) \approx b_1 \epsilon_{ij} + b_2 \epsilon_{ij}^2 + \ldots.$$  

For the VBM under out-of-plane strain $\epsilon_{iz}$, the zero strain splitting is large compared to the strain terms and one might thus think that the term $b_2 \epsilon_{iz}^2$ may be entirely neglected. In that case expanding the square root, one obtains

$$\Delta_v(\epsilon_{iz}) = \Delta_{0v} + \frac{a_1^2 \epsilon_{iz}^2}{2 \Delta_{0v}},$$  

which predicts a quadratic increase of the spin-orbit splitting with strain. However, we find that the splitting actually decreases. This implies that $b_2 \epsilon_{iz}^2$ cannot be
neglected and has negative $b_{2c}$, because it is the only contribution that can reduce the splitting. So keeping this important term, we can write

$$\Delta_\epsilon (\epsilon_{iz})^2 = \Delta_{0c}^2 + (a_{iz}^2 + 2b_{2c}\Delta_0)\epsilon_{iz}^2 + b_{2c}^2\epsilon_{iz}^2.$$  \hspace{1cm} (7)

For the CBM and out-of-plane strain, the zero-strain splitting is much smaller so that the strain may become dominant and give rise to a linear strain dependence,

$$\Delta_\epsilon (\epsilon_{iz}) \approx |a_{1c}|\epsilon_{iz}.$$  \hspace{1cm} (8)

except for very small strains, where it should still look quadratic.

Turning to in-plane strains, there are no off-diagonal terms and the leading term is linear in strain, so we simply have

$$\Delta_\epsilon (\epsilon_{ij}) = \Delta_{0c} + b_{1c}\epsilon_{ij} + b_{2c}\epsilon_{ij}^2.$$  \hspace{1cm} (9)

However, the $b_{1c}$ for $\epsilon_{xy}$ vanishes, in which case the dependence is again quadratic on strain. In Appendix A we derive this exact cancelation of $b_{1c}$ for $\epsilon_{xy}$, and also the analytical expression of $b_{1c}$ for $\epsilon_{ii}$. The latter is shown to result from competition between first and second order perturbation terms. For the conduction band, where the spin-orbit splitting is small, the linear in strain term turns out to be also small for tensional strain in the plane. Thus, the quadratic term can become dominant for sufficiently large strains. We will see that in fact $b_{2c}$ is negative in that case.

### B. Graphene effective Hamiltonian

To write the strain-dependent Hamiltonian in graphene, we invoke the transformation properties of the states and strain tensor in its $K$ point. This information is summarized in Table IV (Appendix B). The states in the edges of the conduction and valence bands of the Dirac point transform as $\Gamma^7$ and $\Gamma^9$. Each of these two-dimensional IRs reflects the sublattice orbital degeneracy (pseudospin) and real spin degeneracy due to the space inversion symmetry. Table IV also includes invariants that tell us that the coupling between the edge states and strain can be written in the following Hamiltonian form

$$H = \begin{pmatrix}
  (a(\epsilon) + \frac{\Delta_0}{2^5}) & 0 & b(\epsilon) & i\epsilon(\epsilon) \\
  0 & (a(\epsilon) + \frac{\Delta_0}{2^5}) & i\epsilon(\epsilon) & b(\epsilon) \\
  (b^*(\epsilon)) & (ic^*(\epsilon)) & (b^*(\epsilon)) & (b^*(\epsilon)) \\
  -(ic^*(\epsilon)) & a(\epsilon) & 0 & a(\epsilon) - \frac{\Delta_0}{2^5}
\end{pmatrix}.$$  \hspace{1cm} (10)

$\Delta_D$ is the strain independent gap induced by spin-orbit coupling. This gap separates the edge states of the conduction and valence bands in the Dirac point. The diagonal strain term, $a(\epsilon)$, is an hydrostatic deformation potential that merely shifts the Dirac point relative to the average electrostatic potential. Its magnitude scales with the local changes in the density of electrons in response to contraction or dilatation of the unit-cell. The connection with strain components follows the transformation properties of the identity IR ($\Gamma^1$),

$$a(\epsilon) = \Xi_d [(\epsilon_{xx} + \epsilon_{yy}) - \frac{1}{2}(\epsilon_{xx}^2 + \epsilon_{yy}^2)].$$  \hspace{1cm} (11)

The hydrostatic term comprises linear (quadratic) components of in-plane (out-of-plane) strain. These terms share a single deformation potential constant ($\Xi_d$) because graphene has only one atomic layer; unlike MoS$_2$ which has some intrinsic thickness, in undistorted graphene all atoms lie in the same plane. This fact means that a flexural strain ($\epsilon_{xz}, \epsilon_{yz}$) can be viewed as a mere stretch of the membrane. Using elementary geometry, it is readily seen that $\epsilon_{xz}^2/2$ or $\epsilon_{yz}^2/2$ correspond to $\epsilon_{xx}$ or $\epsilon_{yy}$. To represent this physics, we also use $\epsilon_{iz} = \partial u_z/\partial x_i$ to define the out-of-plane tensor component in graphene.

Contrary to the diagonal strain term, the off-diagonal terms in Eq. (10) affect the size of the gap according to

$$E_g = \sqrt{\Delta_D^2 + 4\Xi_o^2[(\epsilon_{xx} - \epsilon_{yy})^2 + 4\epsilon_{xy}^2]}.$$  \hspace{1cm} (12)

$b(\epsilon)$ and $c(\epsilon)$ are shear-strain components that couple the edge states ($\Gamma^7 \times \Gamma^9 = \Gamma^6$). The coupling between states of similar spin possesses $\Gamma^6$ symmetry, and its form reads

$$b(\epsilon) = \Xi_o [\epsilon_{xx} - \epsilon_{yy} + 2i\epsilon_{xy} - \epsilon_{xz}^2 - \epsilon_{yz}^2 + 3\epsilon_{xx}\epsilon_{xy} - 2ie_{xx}\epsilon_{zy}].$$  \hspace{1cm} (13)

Again, we may see that this coupling comprises linear (quadratic) components of in-plane (out-of-plane) strain. The spin-independent deformation potential constant, $\Xi_o$, is often described by means of a fictitious vector potential due to changes in the hopping energy between nearest neighbor orbitals. Importantly, as shear strain does not change the unit-cell area to leading order, this parameter is not associated with local changes in the density of electrons. Hence, it can be calculated via density functional theory in the local density approximation. Compared with previous works, our contribution to the strain Hamiltonian of graphene is the spin-orbit coupling term in the anti-diagonal of Eq. (10). It possesses $\Gamma^5$ symmetry due to the coupling between states of opposite spin, and its form reads

$$c(\epsilon) = \epsilon_{so}(\epsilon_{yz} + i\epsilon_{xz}).$$  \hspace{1cm} (14)

Contrary to the spin-independent terms, this term comprises linear out-of-plane strain. We will make use of this feature to extract its magnitude. The importance of the spin-orbit coupling deformation potential constant, $\epsilon_{so}$, is realized from the fact that it is directly related to the intrinsic spin relaxation in graphene. Putting these pieces together, the change of the gap in response to pure in-plane strain becomes

$$E_g = \sqrt{\Delta_D^2 + 4\Xi_o^2[(\epsilon_{xx} - \epsilon_{yy})^2 + 4\epsilon_{xy}^2]}.$$  \hspace{1cm} (15)
Similarly, the change of the gap in response to pure outof-plane strain becomes

\[ E_o = \sqrt{\Delta_0^2 + \Xi_0^2 (\epsilon_{xx}^2 + \epsilon_{zz}^2)} + 4 \epsilon_{so}^2 (\epsilon_{yy}^2 + \epsilon_{zz}^2). \] (16)

In the following, we will use Eqs. (15) and (16) to determine the corresponding shear deformation potential parameters \( \Xi_0 \) and \( \epsilon_{so} \) by fitting to first-principles calculations including appropriate strain combinations.

### III. COMPUTATIONAL METHOD

Density functional theory is used in the local density approximation following the von-Barth-Hedin parametrization. The band structures are calculated using the full-potential linearized muffin-tin orbital (FP-LMTO) method as described in Refs. [37] and [38]. A double \((\kappa, R_{sm})\) basis set is used, including \(spd\) and \(spd\) for the first and second set respectively. Here, \( \kappa^2 = \tilde{E} - \nu_{mnt} \) represents the kinetic energy of the smoothed Hankel function, or its decay length, while the \( R_{sm} \) is a smoothing radius (See Bott et al. in Ref. [39]). Brillouin zone integrations are carried out using a 13×13×3 and 14×14×7 k-point sets for graphene and MoS\(_2\), respectively. Augmentation is carried out inside the muffin-tin spheres up to \( l_{max} = 4 \).

The LDA underestimates the gap significantly in MoS\(_2\) [22] but for the changes in the splitting considered here, it is sufficient to consider the quasiparticle self-energy shift to be independent of strain. Similarly, in graphene the LDA underestimates the Fermi velocity or slope of the Dirac cone. Using the quasiparticle-self-consistent GW method [20] we obtain a change of the Dirac cone slope from 0.8±0.1×10\(^6\) m/s in LDA to 1.1±0.1×10\(^6\) m/s in good agreement with van Schilfgaarde and Katsnelson [11]. For the present purposes of deriving the strain dependent deformation potentials, the LDA results are deemed sufficiently accurate.

### IV. RESULTS

#### A. MoS\(_2\)

Figure 1a shows the splitting of the valence band as a function of out-of-plane strain. As already mentioned, the splitting decreases as function of strain. The fitted parameters to Eq. (7) are \( a_1v = 573 \) meV and \( b_2v = -2.42 \) eV. Figure 1b shows the splitting of the conduction band as a function of out-of-plane strain. We can see that it behaves nearly linear for sufficiently large strain. The parameters were obtained by directly fitting the square-root behavior and resulted in \( a_{1c} = 774 \) meV and \( b_{2c} = 263 \) meV.

Next, we consider the in-plane strains. As predicted in Eq. (9) for \( \epsilon_{xy} \) with vanishing \( b_1 \), both VBM and CBM splittings are quadratic in \( \epsilon_{xy} \). This behavior is shown in Figs. 3a and 3b. By fitting Eq. (9) to the calculated data, \( b_2 \) parameters are found to be \(-2.67 \) eV and \(-3.45 \) eV for VBM and CBM, respectively. In case of tensile strain \( (\epsilon_{xx}) \), the splitting for both VBM and CBM show the combination of linear and quadratic in \( \epsilon_{xx} \) characters. However, the positive linear coefficient \( (b_1) \) of VBM, which is 115 meV, is more than ten times larger than the one for the CBM, which is 8.85 meV. In contrast, their negative quadratic coefficients \( (b_2) \), \(-1.92 \) eV for the VBM and \(-1.81 \) eV for the CBM, are of the same order of magnitude. Therefore, the fit of the VBM splitting in Fig. 2a is dominated by the linear term while the fit of CBM splitting in Fig. 2b is quickly dominated by the quadratic term when \( \epsilon_{xx} \) is larger than 0.001. Furthermore, the CBM splitting goes through a maximum as function of in-plane tensile strain. All of the parameters mentioned above are tabulated in Table I.

We also consider the gaps as function of strain in Figs. 1c, 2c, and 3c. Band gaps as function of strain are fitted
FIG. 2: (a) valence band splitting, (b) conduction band splitting, and (c) band gap of monolayer MoS$_2$ as a function of tensile strain ($\epsilon_{xx}$)

with a quadratic function

$$\Delta_g(\epsilon) = \Delta^0_g + c_1 \epsilon + c_2 \epsilon^2,$$

(17)

and the resulting parameters are summarized in Table I.

We can see that the tensile in-plane strain $\epsilon_{xx}$ has a much stronger effect on the band gap than the shear strains. The linear decrease of the gap of about 59 meV/% strain is close to the calculated value reported by Conley et al.\textsuperscript{42}

The quadratic terms however are not negligible for the shear strains and seem to be of similar magnitude for each strain although it is negative for out of plane strain and positive for in-plane strain.

B. Graphene

First, we note that we obtain a spin-orbit induced gap at the Dirac point of about 26 $\mu$eV in the absence of strain. This result is in good agreement with the linearized augmented plane wave (LAPW) calculations by Gmitra \textit{et al.}\textsuperscript{21}

In Fig. 3 we show the gap squared as function of strain squared for in-plane and out-of-plane strain. Different in-plane strains, $\epsilon_{xx}$, $\epsilon_{xx} - \epsilon_{yy}$, $\epsilon_{xy}$ gave somewhat different results for the extracted fitting parameters because of numerical effects. We use these to estimate the uncertainty on the extracted parameters, given in Table III. In a separate Figure 5 we show the small strain behavior as function of $\epsilon_{xx}$ and as function

| Strain   | Parameter | VBM    | CBM     |
|----------|-----------|--------|---------|
| $\epsilon_{xx}, \epsilon_{yy}$ | $a_1$  | 573 meV | 774 meV |
|          | $b_2$     | -2.42 eV | 263 meV |
| $\epsilon_{xx}, \epsilon_{yy}$ | $b_1$  | 115 meV | 8.58 meV |
|          | $b_2$     | -1.92 eV | -1.81 eV |
| $\epsilon_{xy}$ | $b_2$     | -2.67 eV | -3.45 eV |
|          | $\Delta_0$ | 146 meV | 3.36 meV |

TABLE I: Parameters for monolayer MoS$_2$
TABLE II: Parameters for the change in band gap of monolayer MoS$_2$.

| Strain | $c_1$ (meV) | $c_2$ (eV) |
|--------|-------------|------------|
| $\epsilon_{xx}$ | $-175$ | $-34.9$ |
| $\epsilon_{xx}$ | $-5.87$ | $30.5$ |
| $\epsilon_{yy}$ | $13.5$ | $42.4$ |

of $\epsilon_{yz}^2$, which clearly shows that there is no linear spin-orbit term for the in-plane strain case but only for the out-of-plane strain case. We note that for strains of the order of 0.001, the $c_{so}$ term is comparable in magnitude with the $\Xi_o$ term. The linear fit in the small strain region gives an uncertainty of about 8% on the slope parameter or on $c_{so}$.

V. CONCLUSIONS

The strain-dependent spin splittings of MoS$_2$ and graphene are systematically studied. The spin-orbit induced splittings of the valence-band maximum, conduction-band minimum and the gap in MoS$_2$ as well as the spin-orbit induced gap in graphene were studied as function of strain using first-principles calculations. Various spin-dependent and spin-independent deformation potentials were extracted, in comparison with strain Hamiltonians governed by the method of invariants. The importance of these deformation potentials is that they directly dictate the strength of intrinsic spin-flip and momentum scattering due to electron-phonon interaction. The obtained spin-dependent deformation potential for graphene $c_{so} \approx 3$ meV, rather than the much smaller Dirac gap ($\sim 26$ $\mu$eV), is the important parameter in studying the intrinsic spin relaxation in graphene. Similarly, sizable spin-dependent deformation potentials on the order of atomic spin-orbit coupling ($\gtrsim 0.1$ eV) render strong electron spin relaxation in MoS$_2$, despite the tiny spin splitting in its conduction band minimum ($\sim 3.4$ meV).

TABLE III: Parameters obtained from fittings for graphene.

| $\Delta_D$ (meV) | $\Xi_o$ (eV) | $c_{so}$ (meV) |
|-----------------|--------------|---------------|
| $26 \pm 1$      | $9.5 \pm 0.5$ | $2.9 \pm 0.3$ |

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Appendix A: Detailed derivation of in plane spin-dependent deformations of MoS$_2$

The expressions of $b_1$ in Eq. (9) are obtained through perturbation theory and method of invariants. The general perturbation brought by in-plane strain is

$$H_{strain}^{in} = \sum_{i,j=x,y} r_i \frac{\partial V}{\partial r_j} \epsilon_{ij},$$

$$= \frac{1}{2} \left( x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} \right) (\epsilon_{xx} + \epsilon_{yy})$$

$$+ \frac{1}{2} \left( x \frac{\partial V}{\partial y} - y \frac{\partial V}{\partial x} \right) (\epsilon_{xy} - \epsilon_{yx})$$

$$+ \frac{1}{4} \left[ \left( x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} \right) + i \left( x \frac{\partial V}{\partial y} - y \frac{\partial V}{\partial x} \right) \right]$$

$$\times \left[ (\epsilon_{xx} - \epsilon_{yy}) - i(\epsilon_{xy} + \epsilon_{yx}) \right]$$

$$+ \frac{1}{4} \left[ \left( x \frac{\partial V}{\partial y} - y \frac{\partial V}{\partial x} \right) - i \left( x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} \right) \right]$$

$$\times \left[ (\epsilon_{xx} - \epsilon_{yy}) + i(\epsilon_{xy} + \epsilon_{yx}) \right], \quad (A1)$$

where the first two terms both transform as $K_1$ which is the identity irreducible representation (IR) of the $K$-point $C_{3y}$ group. The last two terms transform as $K_{2,3}$ IRs. For simplicity, we have omitted the $p_xp_y\delta_{ij}/m$ terms in $H_{strain}^{in}$ (they transform the same as $r_i \partial V/\partial r_j$). Using the one-dimension nature of all the IRs in $C_{3y}$ ($K_1 \times K_1^* = K_1$), intra-band coupling via the invariants $(\epsilon_{xx} + \epsilon_{yy})\sigma_z$ or $(\epsilon_{xy} - \epsilon_{yx})\sigma_z$ is symmetry-allowed in all of the bands. The corresponding integral constant of this intra-band coupling comes from second-order perturbation (one due to strain and another due to spin-orbit) as well as from first-order perturbation (strain-modified spin-orbit interaction). Below, we show that the two parts cancel out partially for a general integral constant associated with $\epsilon_{ij}\sigma_z$ of spin-independent band $K_n$. The first-order perturbation due to strain-modified spin-orbit interaction reads

$$\lambda\langle K_n | \nabla (r_i \frac{\partial V}{\partial r_j}) \times \mathbf{p} | z | K_n \rangle$$

$$+ \lambda\langle K_n | - \delta_{xi} \frac{\partial V}{\partial r_j} p_y + \delta_{yi} \frac{\partial V}{\partial r_j} p_x | K_n \rangle$$

$$+ \lambda\langle K_n | - \delta_{yi} \frac{\partial V}{\partial r_x} p_j + \delta_{xi} \frac{\partial V}{\partial r_y} p_j | K_n \rangle$$

$$= \lambda\langle K_n | r_i \frac{\partial (\nabla \times \mathbf{p})}{\partial r_j} | K_n \rangle$$

$$+ \lambda\langle K_n | (\delta_{yi} \frac{\partial V}{\partial r_x} + \delta_{xi} \frac{\partial V}{\partial r_y}) p_j | K_n \rangle, \quad (A2)$$

where $\lambda = h/4m_0^2c^2$. Eq. (A2) assumes rigid-ion approximation, but it retains the correct symmetry and does not affect the result qualitatively. The second-order perturbation part reads,

$$2\text{Re} \left[ \langle K_n | (r_i \frac{\partial V}{\partial r_j} + \frac{p_i p_j}{m}) \sum_{n'} | K_{n'} \rangle \langle K_{n'} | \lambda (\nabla \times \mathbf{p})_z | K_n \rangle \right] \frac{E_{K_n} - E_{K_{n'}}}{E_{K_{n'}} - E_{K_{n''}}}, \quad (A3)$$

where $K_{n'}$ is other bands at $K$ point excluding the $K_n$ band. Using the fact that $\frac{\partial V}{\partial r_j} = |p_j\rangle \langle H|$, we get that

$$2\text{Re} \left[ \langle K_n | r_i \frac{\partial V}{\partial r_j} \sum_{n'} | K_{n'} \rangle \langle K_{n'} | \lambda (\nabla \times \mathbf{p})_z | K_n \rangle \right] \frac{E_{K_n} - E_{K_{n'}}}{E_{K_{n'}} - E_{K_{n''}}}.$$

Dispensing with the identity operator altogether, we get

$$-\frac{i}{\hbar} \langle K_n | r_i p_j \lambda (\nabla \times \mathbf{p})_z - \lambda (\nabla \times \mathbf{p})_z r_i p_j | K_n \rangle$$

$$= -\lambda \langle K_n | r_i \frac{\partial (\nabla \times \mathbf{p})}{\partial r_j} | K_n \rangle$$

$$+ \lambda \langle K_n | (\delta_{yi} \frac{\partial V}{\partial r_x} - \delta_{xi} \frac{\partial V}{\partial r_y}) p_j | K_n \rangle. \quad (A5)$$

This term cancels out the first-order perturbation part [Eq. (A2)], and the net result from adding Eqs. (A2) and (A3) is

$$2\text{Re} \left[ \langle K_n | \frac{p_i p_j}{m} \sum_{n'} | K_{n'} \rangle \langle K_{n'} | \lambda (\nabla \times \mathbf{p})_z | K_n \rangle \right] \frac{E_{K_n} - E_{K_{n'}}}{E_{K_{n'}} - E_{K_{n''}}} \quad (A6)$$

Therefore, by Eq. (A1) and the argument that followed it, the integral constant $b_{1,z}$ associated with shear strain drops ($p_xp_y - p_xp_y = 0$), while the integral constant associated with dilation strain remains ($p_xp_x + p_yp_y = 0$). In practice, $\epsilon_{xy} - \epsilon_{yx}$ is treated as 0 since rotation does not induce energy perturbation, and the accompanied deformation potentials are not evaluated. The above derivation justifies this practice from the detailed interaction Hamiltonian, while Eq. (A6) times two gives the detailed expression for $b_1$ with $i = j$.

Finally, when $| K_n \rangle$ is dominated by orbitals with zero angular momentum (e.g., lowest conduction band of MoS$_2$), the majority of $b_1$ vanishes, since $(\nabla \times \mathbf{p})_z | d_{z^2} \rangle = 0$. So $b_1$ is small in this case and is proportional to the small components from $S p_z, p_y$ orbitals, and the small deviation of the Mo atomic potential from spherical symmetry due to the crystal structure.
TABLE IV: Character table of the $D_{3h}$ point double group.\textsuperscript{13} It is used to construct the strain-dependent Hamiltonian in the $K$ point of graphene. \{x, y, z\} and \{R_x, R_y, R_z\} represent components of a polar and axial vectors, respectively. The $x$-axis is defined along the zigzag edge direction and the $y$-axis is along the armchair direction. A strain tensor component $\epsilon_{ij}$ transforms as the product of the $i$-th and $j$-th components of a polar-vector.

| $D_{3h}$ | E | $E^\pm$ | $C_3^\pm$ | $C_3^z$ | $\sigma_h$ | $S_3^+$ | $S_3^-$ | $C_3^\sigma$ | $S_3^\sigma$ | $\sigma_v$ | $\sigma_v \sigma_i$ | \textit{invariants} |
|---------|---|---------|---------|---------|---------|---------|---------|---------|---------|---------|----------------|----------------|
| $A_1'$ | $\Gamma_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | $z^2, x^2 + y^2, x(3y^2 - x^2)$ |
| $A_2'$ | $\Gamma_2$ | 1 | 1 | 1 | 1 | 1 | 1 | $-1$ | $-1$ | $R_x, g(3x^2 - y^2)$ |
| $A_1''$ | $\Gamma_3$ | 1 | 1 | 1 | 1 | $-1$ | $-1$ | 1 | $-1$ | $z$ |
| $E'$ | $\Gamma_5$ | 2 | 2 | $-1$ | $-1$ | 2 | 1 | 1 | 0 | \{R_x, R_y\}, \{y, -xz\} |
| $E'$ | $\Gamma_6$ | 2 | 2 | $-1$ | $-1$ | 2 | $-1$ | $-1$ | 0 | \{x, y\}, \{x^2 - y^2, -2xy\} |
| $E_1$ | $\Gamma_7$ | 2 | $-2$ | 1 | $-1$ | 0 | $\sqrt{3}$ | $-\sqrt{3}$ | 0 | \{iR_x - R_y \downarrow, iR_x + R_y \uparrow\} |
| $E_2$ | $\Gamma_8$ | 2 | $-2$ | 1 | $-1$ | 0 | $-\sqrt{3}$ | $\sqrt{3}$ | 0 | 0 |
| $E_3$ | $\Gamma_9$ | 2 | $-2$ | 2 | 0 | 0 | 0 | 0 | 0 | \{iR_x + R_y \uparrow, iR_x - R_y \downarrow\} |

TABLE V: Character table of the $C_{3h}$ point double group.\textsuperscript{13} It is used to construct the strain-dependent Hamiltonian in the $K$ point of MX$_2$. The function notations are defined in the same way as in Table IV.

| $C_{3h}$ | E | $C_3^+$ | $C_3^-$ | $\sigma_h$ | $S_3^+$ | $S_3^-$ | $E$ | $C_3^\sigma$ | $S_3^\sigma$ | \textit{invariants} |
|---------|---|---------|---------|---------|---------|---------|---|---------|---------|----------------|
| $A'$ | $K_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | $R_x, x^2 + y^2, z^2$ |
| $2E'$ | $K_2$ | 1 | $\omega$ | $\omega^*$ | 1 | $\omega$ | $\omega^*$ | 1 | $\omega$ | $x - iy, 2xy - i(x^2 - y^2)$ |
| $1E'$ | $K_3$ | 1 | $\omega^*$ | 1 | $\omega$ | $\omega^*$ | 1 | $\omega$ | $x + iy, 2xy + i(x^2 - y^2)$ |
| $A''$ | $K_4$ | 1 | 1 | $-1$ | $-1$ | 1 | 1 | 1 | $-1$ | $-1$ |
| $2E''$ | $K_5$ | 1 | $\omega$ | $-\omega$ | $-\omega^*$ | 1 | $\omega$ | $-\omega$ | $-\omega^*$ | $R_x - iR_y, yz + izx$ |
| $1E''$ | $K_6$ | 1 | $\omega$ | $-\omega$ | $-\omega^*$ | 1 | $\omega$ | $-\omega$ | $-\omega^*$ | $R_x + iR_y, yz - izx$ |
| $1E_3$ | $K_7$ | 1 | $-\omega$ | $-\omega^*$ | $i$ | $i\omega$ | $i\omega^*$ | $-1$ | $i\omega$ | $i\omega^*$ | $\uparrow_z$ |
| $2E_3$ | $K_8$ | 1 | $-\omega$ | $-\omega$ | $-\omega^*$ | $i$ | $i\omega$ | $i\omega^*$ | $-1$ | $i\omega$ | $i\omega^*$ | $\downarrow_z$ |
| $2E_2$ | $K_9$ | 1 | $-\omega$ | $-\omega^*$ | $i$ | $i\omega$ | $i\omega^*$ | $-1$ | $i\omega$ | $i\omega^*$ |
| $1E_2$ | $K_{10}$ | 1 | $-\omega$ | $-\omega$ | $-\omega^*$ | $i$ | $i\omega$ | $i\omega^*$ | $-1$ | $i\omega$ | $i\omega^*$ |
| $1E_1$ | $K_{11}$ | 1 | $-1$ | $-i$ | $i$ | $i$ | $-1$ | $1$ | $i$ | $i$ |
| $2E_1$ | $K_{12}$ | 1 | $-1$ | $-i$ | $i$ | $i$ | $-1$ | $1$ | $i$ | $i$ |

$\omega = \exp(2\pi i/3)$.

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