Design principles for shift current photovoltaics

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While the basic principles of conventional solar cells are well understood, little attention has gone towards maximizing the efficiency of photovoltaic devices based on shift currents. By analysing effective models, here we outline simple design principles for the optimization of shift currents for frequencies near the band gap. Our method allows us to express the band edge shift current in terms of a few model parameters and to show it depends explicitly on wavefunctions in addition to standard band structure. We use our approach to identify two classes of shift current photovoltaics, ferroelectric polymer films and single-layer orthorhombic monochalcogenides such as GeS, which display the largest band edge responsivities reported so far. Moreover, exploring the parameter space of the tight-binding models that describe them we find photoresponsivities that can exceed 100 mA/W−1. Our results illustrate the great potential of shift current photovoltaics to compete with conventional solar cells.

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Cost-effective, high-performing solar cell technology is an essential piece of a sustainable energy strategy. Exploring approaches to photo-current generation beyond conventional solar cells based on pn junctions is worthwhile given that their performance is in practice constrained by the Shockley–Queisser limit. One of the most promising alternative sources of photocurrent is the bulk photovoltaic effect (BPVE) or ‘shift current’ effect, a nonlinear optical response that yields net photocurrent in materials with net polarization. Contrary to conventional pn junctions, the BPVE is able to generate an above-band-gap photovoltage, potentially allowing the performance of BPVE-based photovoltaics to surpass conventional ones. However, closed-circuit currents generated via the BPVE reported in the literature have typically been small compared with those generated in pn junction photovoltaics. Recent interest in the BPVE also stems from the proposal that it may be at work in a promising class of materials for photovoltaics known as hybrid perovskites, an extremely active field of research.

The fundamental requirement for a material to produce a current via the BPVE is that it breaks inversion symmetry, allowing an asymmetric photoexcitation of carriers. But despite considerable case-by-case study of the BPVE, the necessary ingredients to optimize a BPVE-based solar cell are not sufficiently well understood. As with conventional solar cells, band gaps in the visible (1.1–3.1 eV) and large electronic densities of states are always beneficial. In addition, to produce a solar cell that responds to unpolarized sunlight, a highly anisotropic material must be used, since otherwise there is no preferred direction for the current to flow. But beyond these natural requirements, our only guiding knowledge is that the shift current depends explicitly on the nature of the electronic wavefunctions and that it is not correlated with the material polarization in any obvious way despite the fact that both shift currents and polarization originate from inversion symmetry breaking.

In the current situation, a more generic understanding of what makes the BPVE strong is highly desirable. When tackling complex material science problems, stripping off all complications and optimizing the simplest model that captures the relevant physics often proves the best strategy, as shown for example in thermoelectricity studies. In this work, we present simple design principles for BPVE optimization based on the study of an effective model for the band edges. With this model, the band edge shift current is given by the product of the joint density of states (JDOS) and a matrix element, both given by simple expressions in terms of a few model parameters. The simplicity of the model allows us to derive the main principle that band edges with semi-Dirac type of Hamiltonians are the best starting point to obtain large band edge prefactors. In addition, by relating the effective model parameters to realistic tight-binding models, we can predict that several materials with the required band structure have larger shift currents than any reported so far.

**Results**

**Density of states in one- and two-dimensions.** In our search for materials we should look for large JDOS in systems where the band edge is closely aligned with the peak of the solar spectrum, around 1.5 eV. Since the band edge always induces a Van Hove singularity in the density of states, the requirement of a large peak in the photoresponse can be naturally better satisfied by low-dimensional materials, which generically present stronger singularities. Materials of one and two dimensions are therefore the focus of this work. Among one-dimensional materials, ferroelectric polymers are suitable candidates for shift-current photovoltaics: they strongly break inversion symmetry, some have suitable band gaps for photovoltaics applications, and they can be produced in macroscopically oriented samples. For these reasons, we consider solar cells consisting of such polymer films, shown in Fig. 1a. Two-dimensional materials also have great

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**Figure 1 | Schematics of proposed shift current photovoltaics:** (a) Three-dimensional (3D) structure of a solar cell built by stacking one-dimensional ferroelectric polymers. (b) Simplified two-band tight-binding model of a polymer. (c) 3D structure of a solar cell made by stacking two-dimensional monolayers of a monochalcogenide. The inert spacers between layers prevent the restoration of bulk inversion symmetry. (d) Simplified two-band tight-binding model for a monochalcogenide layer.
potential for photovoltaics, as shown by demonstration of a pn-
junction photovoltaic effect in dichalcogenide heterostructures42–44,
and in few-layer black phosphorus45. However, these well
known two-dimensional (2D) semiconductors have vanishing
shift currents because of either inversion or rotation symmetry.
Group IV monochalcogenides have emerged in the past years as a
new family of inversion-breaking, anisotropic 2D materials with
fascinating properties46–50, and interest in growing as thin films
of all four members of the family, GeS1–3,4, GeSe2–4,5,6,5,6 and
SnSe27–29 has now been isolated experimentally. In this work,
we show that GeS is ideally suited to realize high values of the
BPVE. Their GeS structure is shown in Fig. 1c.

To understand how to optimize the photogenerated, we first
discuss how the shift current can be computed for a tight-binding
model, and then we proceed to apply this formalism to describe
a generic band edge and the response of particular materials.

**Shift current.** In this work we consider the shift current
contribution to the BPVE and we shall use both terms interchangeably (note the BPVE can have other contributions as
well6). With electric field \( E_k(\omega) \) at frequency \( \omega \) and linearly
polarized in the \( b \) direction, the shift current is a DC response of the
form

\[
J_b = \sigma_{abb}(\omega) E_b(\omega) E_b(-\omega).
\]

(1)

Defining an intensity for each polarization, \( I_{0b} = \epsilon_0 |E_b|^2/2 \), we
define the photoresponse \( \kappa_{abb} \) as the current density generated
per incident intensity \( I_0 = |\kappa_{abb}|^2 I_{0b} \) which gives \( \kappa_{abb} = 2 \sigma_{abb}/\epsilon_0 \). Note
that in conventional solar cells the current is also linear with
intensity. For a D-dimensional system, \( \kappa_{abb} \) takes the form

\[
\kappa_{abb} = C \int \frac{d^Dk}{(2\pi)^D} \sum_{nm} I_{nm} \delta(\omega_{nm} - \omega),
\]

(2)

where \( C = 4g_n \varepsilon_0 \varepsilon_r^b / \hbar^2 \epsilon_{0b} \) with \( c \) being the speed of light, \( \epsilon_0 \) the vacuum permittivity and \( g_n = 2 \) accounts for the spin degeneracy.
In what follows we set \( \hbar = 1 \). Summation of indices is explicitly
indicated using the summation symbol. The sum is over all Bloch
bands, with \( \omega_{nm} = E_n - E_m \) the energy difference between bands
\( n \) and \( m \) and \( I_{nm} = f_n - f_m \) the difference of Fermi occupations,
which we take at zero temperature. The integrand is

\[
I_{nm}^{\text{abb}} = \text{Im} \left( \phi_{nm}^b \phi_{nm}^a \right),
\]

(3)

where \( \phi_{nm}^a \) are the inter-band matrix elements of the
position operator (or inter-band Berry connections), defined as

\[
r_{nm}^a = i \langle n | \partial_x m \rangle \text{ for } n \neq m \text{ and zero otherwise, where } |n\rangle \text{ is the}
\]

estate of band } n \text{. A semiconductor denotes a generalized derivative
}

\[
r_{nm}^{\text{ab}} = \partial_k r_{nm}^{ab} - i \langle n | \partial_x m \rangle r_{nm}^{ab}, \text{ where } \phi_{nm}^a = i \langle n | \partial_k n \rangle \text{ is the diagonal}
\]

Berry connection for band } n \text{.}

**Generic two-band model.** With the aim of describing the shift
current response of the band edge of a semiconductor, next we
consider the shift current of a generic two-band model. The
Fourier transform of the real space Hamiltonian is performed
with the choice of phases \( \psi_m k(x) = \frac{1}{\sqrt{N}} \sum_k \phi_k(x) \phi^*(x-k) \) where \( \phi(x) \) is a localized orbital and \( x \) is the
position of site \( i \) in the unit cell. This choice is made in order to
naturally incorporate the action of the position operator, see
refs 60–62. The Hamiltonian matrix takes the form

\[
H = \epsilon_0 \sigma_0 + \sum_i f_i \sigma_i y,
\]

(4)

where \( \sigma_0 \) is the identity matrix, \( \sigma_x, \sigma_y, \sigma_z \) are the Pauli
matrices and \( \epsilon_0 \) and \( f_i = f_{x0}, f_{y0}, f_{z0} \) are generic functions of momenta
\( k \) (the momentum label is omitted to simplify notation).

The conduction and valence bands are given by \( E_i = \epsilon_0 + \epsilon_i \),
\( E_2 = \epsilon_0 - \epsilon \), respectively and \( \epsilon = (\sum_i f_i)^{1/2} \). Note that this basis
choice implies that the Hamiltonian matrix elements are not
periodic in the Brillouin Zone, \( H_j(k + G) \neq H_j(k) \) with \( G \) a
reciprocal lattice vector.

To compute the shift current, the direct use of equation (3)
requires the evaluation of derivatives of Bloch functions, which
can be difficult to compute numerically. Previous works9,29 have
addressed this problem with the use of identities that replace
wavefunction derivatives with sums over all states of matrix
elements of Hamiltonian derivatives. These identities are known
as sum rules and rely on the fact that momentum and velocity
operators are proportional in the plane wave basis \( p = mv \), which
is not true in the tight-binding formalism. In this work we derived
a generalized sum rule appropriate for tight-binding models
(see Methods section), from which the integrand equation (3) can
be evaluated for any two-band model in terms of the Hamiltonian
derivatives only. The result is

\[
I_{12}^{\text{abb}} = - \sum_{ijm} \frac{1}{4\epsilon^2} \left( f_m j_i f_j a - f_m j_i f_j a \right) \epsilon_{ijm},
\]

(5)

where the compact derivative notation \( f_m j_i \equiv \partial_k f_i \) and \( \epsilon_{ij} \equiv \partial_k \epsilon \) is used. Equation (5) is one of the main results of this work.
Several general principles to maximize the band edge shift current
can be derived from this expression. A straightforward one is that,
since this expression does not depend on \( \epsilon_0 \), particle-hole
asymmetry does not influence the shift current at all. Therefore \( \epsilon_0 \) is
set to zero from now on. The additional term that appears only
for tight-binding models in this more general sum rule is \( f_m j_i \),
which is absent in previous formulations. For a direct band
gap, this term dominates the response exactly at the band edge,
since to lowest order in \( k \) the first term always has constant
contribution, while the second one is at least linear in \( k \) for any
model due to the energy derivative \( \epsilon_k \). For this term to be
finite, the three Pauli matrices in the Hamiltonian must have constant,
linear and quadratic coefficients, in any order. Satisfying this
low-energy constraint can be taken as another general principle in
the search for materials with large shift current.

More explicit guidelines can be obtained by considering an
explicit low-energy model with a direct band gap at a time
reversal invariant momentum. Expanding the Hamiltonian around
it we get

\[
H = \left( \delta + \frac{1}{2} \epsilon_{kk}^a \right) \sigma_x + v_F E \sigma_y + \left( \Lambda + \beta \epsilon_{kk}^a \right) \epsilon_{kk}^a \sigma_x.
\]

(6)

Time reversal symmetry \( H(-k) = H(k) \) prevents quadratic
terms in \( \sigma_x \) and we have taken the linear term to be in the \( x \)
direction without loss of generality. Note this type of linear term
requires the breaking of any \( C_n \) rotation symmetry with \( n > 2 \).
The band gap of this model is \( E_g = 2\epsilon_{kk}^a \). Evaluating equation (5)
we get

\[
I_{12}^{xx}(\omega) = 4v_F \left( \alpha + \beta \epsilon \right) + O(k^2),
\]

(7)

\[
I_{12}^{yy}(\omega) = 2v_F \left( \alpha + \beta \epsilon \right) + O(k^2),
\]

(8)

while \( I_{12}^{xy} = I_{12}^{yx} = 0 + O(k^2) \). Also note that in order to have a
non-zero shift current quadratic terms in \( \sigma_x \) or \( \sigma_y \) are required. In
2D, the fact that \( I_{12}^{xx} \) is in general non-zero means that the current
need not be in the direction of the electric field polarization.

The shift current close to the band edge can now be obtained by
substituting equations (7) and (8) into equation (2), which gives

\[
\kappa_{abb}(\omega) = C \frac{I_{12}^{abb}(\omega) N(\omega)}{E(\omega - E_g)}, \quad (\omega - E_g)/E_g \ll 1,
\]

(9)
where \( N(\omega) = \int \frac{d\mathbf{k}^D}{(2\pi)^D} \delta(\omega_{kk} - \omega)/(2\pi)^D \) is the JDOS. Equation (9) provides an analytical formula for \( \omega \) close to the band edge for a very general class of models. This simple expression allows one to disentangle the contributions of the shift current integrand and the JDOS and hence to optimize them independently.

To maximize the response we therefore require band structures where the JDOS has a strong singularity. It is well known that in the one-dimensional (1D) case, the generic JDOS diverges as a square root, \( N(\omega) \propto (\omega - E_\text{g})^{-1/2} \). 1D systems such as polymers or nanowires or systems in the quasi-1D limit will in general have a large response. In 2D, the band edge JDOS has a finite jump of \( \frac{\pi}{\mathbf{C}_0}a^3 \) for vanishing momentum \( \mathbf{k} \). A singular \( N(\omega) \) thus occurs in 2D when the inverse effective mass vanishes. In the effective model in Equation (6), this happens when \( \delta = 0 \), which realizes what we may call a gapped semi-Dirac dispersion\(^3\), since the coefficients of \( \sigma_x \) and \( \sigma_y \) are linear and quadratic in momentum, respectively. In such a case we have \( N(\omega) \propto (\omega - E_\text{g})^{-1/4} \) (full expressions for \( N(\omega) \) may be found in the Methods section).

For materials with large JDOS, the current can be further enhanced by appropriately tuning the parameters in Equations (7) and (8). This is mostly easily discussed if these parameters can be related to microscopic lattice models. In the next section, we discuss tight-binding models for simple materials that realize the described types of band structures.

### Material realizations and lattice models

As a realization of the 1D case, we consider ferroelectric polymers that break inversion symmetry such as polyvinylidene fluoride or disubstituted polycateniene\(^9,40,64\). This system is described by the tight-binding model schematically shown in Fig. 1b, defined in terms of two types of hoppings, \( t_1 \) and \( t_2 \), alternating on-site potentials \( \Delta \), and orbital centres at \( x = 0 \) and \( x = x_0 \). With our choice of basis functions, the Hamiltonian is specified by

\[
H = t_1 e^{i\mathbf{k}\mathbf{a}_1} + t_2 e^{-i\mathbf{k}\mathbf{a}_1} + \Delta
\]

and \( t_2 = \Delta \), where \( a = 10 \) Å is the lattice constant and the distance between closest neighbours is ref. 64 \( x_0 \approx 0.48 \) Å. For estimates of the tight-binding parameters, we consider the example of disubstituted polyacetylene that was experimentally realized in ref. 39, with a band gap of 2.5 eV. For regular polycateniene, where \( \Delta = 0 \), the hopping parameters and band gap have been estimated as ref. 64 \( t_1 \approx 2.85 \) eV, \( t_2 \approx 2.15 \) eV, \( E_g = 1.4 \) eV. Assuming the same hopping for the disubstituted version, we use \( \Delta = 1.0 \) eV to match the observed band gap. Note that the dispersion does not depend on \( x_0 \).

Using Equations (2) and (5) we can now compute the shift current for this 1D model. Expanding about the low energy momentum \( k_0 = \pi/a \) and performing a constant rotation of the Pauli matrices, we obtain an effective model as equation (6) with parameters \( k_0 = 0 \) and \( \delta = t_1 - t_2 \), \( \nu_0 = (t_1 - t_2) x_0 + t_2 a_2 \), \( x_\perp = \left[ t_2 (a_1 - x_0)^2 - t_1 x_0^2 \right]/2 \).

To be able to compare the responsivity of these materials to that of a three-dimensional system, we consider a stack of polymers as depicted in Fig. 1a, separated by a distance \( d \) which we take to be equal to the lattice constant of the polymer \( d = a \). The photoresponsivity is then \( \kappa^{\text{ab}} = \kappa^{DD}/d^2 \). The typical photoresponsivity spectrum of this model with this convention is shown in Fig. 2a.

For the 2D case, we require a layered material that breaks both inversion and rotational symmetries. The most popular of the recently isolated 2D semiconductors break either inversion (BN, MoS\(_2\)) or rotational symmetries (black phosphorus\(^65\), ReS\(_2\) (ref. 66)), but not both. An inversion symmetry breaking version of the strongly anisotropic black phosphorus, a group V element, can be obtained combining elements of the IV and VI groups.

These group IV monochalcogenides, such as GeS, are predicted to be stable in the monolayer form with the orthorhombic structure of black phosphorus\(^66,67\).

These materials can be described with a tight-binding model similar to the one used for black phosphorus\(^65\)-\(^68\). While the GeS unit cell contains two Ge–S pairs at different heights, a unit cell with a single Ge–S pair can be used when the physics to be probed is insensitive to the heights of the atoms (see Methods for a detailed explanation). The two band Hamiltonian is specified by

\[
f_{\mathbf{k}} + i f_{\mathbf{k}} = -e^{-i\mathbf{k}\cdot\mathbf{a}_1} \left[ t_1 + i t_2 \Phi(\mathbf{k}) + t_1 \Phi^*(\mathbf{k}) \right], \quad \mathbf{a}_0 = (x_0, 0)
\]

and \( \Phi(\mathbf{k}) = (e^{i\mathbf{k}\cdot\mathbf{a}_1} + e^{i\mathbf{k}\cdot\mathbf{a}_2}) \), and \( f_{\mathbf{k}} = \Delta \). \( a_1 \) and \( a_2 \) are the lattice vectors. See Fig. 1d for the definition of the hopping integrals.

Again note the dispersion is independent of \( x_0 \). The specific values of the tight-binding parameters for GeS have been obtained by fitting an \textit{ab-initio} calculation as described in the Methods section, where the coefficients of the low-energy model near the band edge are also shown. Note in this lattice structure there is a mirror symmetry \( y \rightarrow -y \), which is represented as the identity, and restricts \( x_{\perp 0} = y_{\perp 0} = 0 \). This is so because both conduction and valence bands are even under the symmetry, as it also happens in black phosphorus. This is also the result of our \textit{ab-initio} calculation.) This symmetry still allows a linear term of the form \( k_x \sigma_x \) crucial for the semi-Dirac type of band structure. In this model, the semi-Dirac limit is realized when

\[
t_1 = -2(t_2 + t_3)^{1/2}
\]

We consider a stack of monolayers separated by \( d = a \), as shown in Fig. 1c. In this case, we consider an inert spacer layer between the GeS layers to avoid the restoration of inversion symmetry that would occur if we were to stack GeS into its natural bulk form. The three-dimensional photoresponsivity of this model, given by \( \kappa^{DD} = \kappa^{ab}/d \), is computed using equations (2) and (5). To make contact with the 1D case we consider a stacking distance \( d = a_0 = (|a_1| + |a_2|)^{1/2} \) and \( x_0 = 0.18a \). The results are shown in Fig. 2b. We see that both \( \kappa^{xx} \) and \( \kappa^{yy} \) are in general finite, and the polarization average is also finite due to the strong anisotropy.

The response of the monochalcogenides is large because they are close in parameter space to the gapped semi-Dirac Hamiltonian. This is best illustrated by considering the evolution of a fictitious system where the hoppings are tuned (with \( t_0 = 0 \) for simplicity) to the semi-Dirac case \( |t_1|/t_2 = 2 \), where the divergence of the response is clearly appreciated. This evolution is shown in Fig. 2c.

### Further optimization

After describing the representative tight-binding models with large JDOS, we may now address a more systematic analysis of the photoresponsivity. First, we consider exploring the phase diagram of the monochalcogenides by sweeping \( |t_1|/t_2 \) in parameter space while the band gap is fixed at 1.89 eV by choosing \( \Delta \) appropriately and \( t_5 = 0 \) for simplicity. Figure 3a shows the polarization averaged photoresponsivity, \( \kappa_\perp = (\kappa^{xx} + \kappa^{yy})/2 \), for the parameters \( x_0 = 0.18a \) and \( \theta = 0.69 \). This phase diagram summarizes nicely the most physically relevant regimes where the shift current is large due to a divergent JDOS, namely the 1D limit where \( |t_1| \ll t_2 \), and the semi-Dirac regime where \( |t_1| \sim 2t_2 \). In this phase diagram, the point corresponding to \( t_1 \) and \( t_2 \) of GeS is shown as a white circle with blue outline.

Next we illustrate a very important feature of the behaviour of the shift current integrand. Equations (7) and (8) depend generically on the hoppings and lattice parameters. The energy does not depend on the parameter \( x_0 \) but the wavefunctions do. In Fig. 3b, we show the peak photoresponsivity as a function of \( |t_1|/t_2 \) and \( x_0 \). A large response is observed in the semi-Dirac limit \( |t_1|/t_2 \sim 2 \). However, a very strong dependence on \( x_0 \) and even a...
The emergence of a singularity is observed. In the three figures, solid lines show the shift current components as computed from the tight-binding model, and a dashed line in each subfigure shows the respective diagram. (\(t_1 = 2.85, t_2 = 2.15, \Delta = 1.0\) in eV, showing the square root divergence of the current at the band edges. (b) Various non-zero components of the responsibility tensor for a stack of 2D monochalcogenides with parameters \(t_1 = -2.33, t_2 = 0.61, t_3 = 0.13, \Delta = 0.41\) in eV and \(x_0 = 0.52\) Å. A large peak is observed in \(\chi_{\text{xxx}}\) at the band edge. (c) Responsivity for \(\Delta = 0.8\) eV, \(x_0 = 0.6\) Å, \(t_3 = 0\) and different hopping ratios \(|t_1|/t_2\) approaching the semi-Dirac limit. The emergence of a singularity is observed. In the three figures, solid lines show the shift current components as computed from the tight-binding model, and a dashed line in each subfigure shows the xxx shift current component as predicted by the effective low energy model valid near the edge equation (9).

Figure 2 | Frequency dependence of photoresponsivity. (a) Responsivity for a stack of disubstituted polyacetylene polymers with tight-binding parameters \(t_1 = 2.85, t_2 = 2.15, \Delta = 1.0\) in eV, showing the square root divergence of the current at the band edges. (b) Various non-zero components of the responsibility tensor for a stack of 2D monochalcogenides with parameters \(t_1 = -2.33, t_2 = 0.61, t_3 = 0.13, \Delta = 0.41\) in eV and \(x_0 = 0.52\) Å. A large peak is observed in \(\chi_{\text{xxx}}\) at the band edge. (c) Responsivity for \(\Delta = 0.8\) eV, \(x_0 = 0.6\) Å, \(t_3 = 0\) and different hopping ratios \(|t_1|/t_2\) approaching the semi-Dirac limit. The emergence of a singularity is observed. In the three figures, solid lines show the shift current components as computed from the tight-binding model, and a dashed line in each subfigure shows the xxx shift current component as predicted by the effective low energy model valid near the edge equation (9).

The location of GeS on the phase diagram is marked by a white circle with blue outline. Regions for which the gap cannot be kept at \(\Delta = 0\) dramatically sign change is also observed. The dependence on \(x_0\) dramatically illustrates the fact that the shift current depends not only on the band structure but also on the wavefunctions. This can be seen explicitly in the fact that the effective mass \(m_e^{-1} = 4\alpha^2_0 t_1 t_2/E_g\) is independent of \(x_0\), but the combination \(\frac{\nu_{\text{olec}}}{\alpha_0}\) appearing in the shift current integrand is not. In particular \(\alpha_0\) vanishes for \(x_0 = \alpha_0/|1 + (|t_1|/2t_2)|^{1/2}\), which means that regardless of the JDOS, the band edge response can actually be zero. This behaviour is characteristic of Berry connections, which depend explicitly on the positions of the sites in the unit cell.

**Discussion**

In this work, we have shown how an effective model for the band edge enables a clean separation of the two factors that contribute to a large shift current: the standard JDOS and the shift current matrix element. This model also allows us to readily identify materials with semi-Dirac-like Hamiltonians as those where both factors can be made large. Several other general conclusions can be drawn from the form of the effective shift current integrand in equations (7) and (8). First, since the \(1/\omega^3\) factor becomes \(1/E_g^3\) at the band edge, materials with smaller gaps are expected to have larger shift currents. A second conclusion is that while looking for materials with large JDOS is a good guiding principle, the shift current integrand depends on other microscopic details that can change the response dramatically. Within our simple model, the shift current can be maximized by bringing the two sites of the unit cell closer together, which is a requirement that the monochalcogenides satisfy well. Materials that may perform even better than GeS may be searched for exploring different chemical compositions, alloying or by strain engineering.

Our results were made possible by the derivation of a new sum rule appropriate for tight-binding models. With this sum rule, our work can be easily extended to tight-binding models with more than two bands, or systems where the minimum direct gap is not at a time-reversal invariant momentum. We expect that the formalism developed here will provide the necessary link to combine ab-initio methods with effective models, allowing for more in-depth, systematic study of shift current photovoltaics.
Our results should be compared with known ferroelectric materials that have been recently studied. In the visible range of frequencies, $\omega \lesssim 3\text{ eV}$, we find peak values of 0.1 mAW$^{-1}$ in BiFeO$_3$ (ref. 30), 1 mAW$^{-1}$ in hybrid perovskites$^{13}$ and a maximum 10 mAW$^{-1}$ in BaTiO$_3$ (ref. 14) or NaAsSe$_2$ (ref. 15). The realistic materials that we propose present larger responsivities, with the additional advantage that the peak is by construction at the band edge. Moreover, as Figs 2c and 3b show, peak responses on the order of several hundreds of mAW$^{-1}$ could be achieved with materials closer to the semi-Dirac regime.

To compare with conventional photovoltaic mechanisms, the total current per intensity of a crystalline Si solar cell exposed to sunlight is about 400 mAW$^{-1}$ (ref. 71).

Given these numbers, our work is a sign that shift current photovoltaics capable of surpassing conventional solar cells may be close at hand, and a push to investigate their full potential using methods discussed in this work—along with established techniques—is warranted. We believe that the simple principles derived in our work will serve as a guide for both theory and experiment in the development and optimization of the next generation of shift current photovoltaics.

**Methods**

**Shift current.** To make contact with previous work, we note the shift current integrand in equation (3) is sometimes expressed in terms of the phase of the inter-band matrix element $i_{\alpha \beta}^\phi = |\psi_{\alpha}^b| |\psi_{\beta}^o|$ as $i_{\alpha \beta}^\phi = |\phi_{\alpha}^b| |\phi_{\beta}^o| R_{\alpha \beta}^\phi$, where

$$R_{\alpha \beta}^\phi = \partial_{E_{\alpha}} \phi_{\alpha}^o - \partial_{E_{\beta}} \phi_{\beta}^o.$$  

(10)

Our results should be compared with known ferroelectric materials that have been recently studied. In the visible range of frequencies, $\omega \lesssim 3\text{ eV}$, we find peak values of 0.1 mAW$^{-1}$ in BiFeO$_3$ (ref. 30), 1 mAW$^{-1}$ in hybrid perovskites$^{13}$ and a maximum 10 mAW$^{-1}$ in BaTiO$_3$ (ref. 14) or NaAsSe$_2$ (ref. 15). The realistic materials that we propose present larger responsivities, with the additional advantage that the peak is by construction at the band edge. Moreover, as Figs 2c and 3b show, peak responses on the order of several hundreds of mAW$^{-1}$ could be achieved with materials closer to the semi-Dirac regime.

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Given these numbers, our work is a sign that shift current photovoltaics capable of surpassing conventional solar cells may be close at hand, and a push to investigate their full potential using methods discussed in this work—along with established techniques—is warranted. We believe that the simple principles derived in our work will serve as a guide for both theory and experiment in the development and optimization of the next generation of shift current photovoltaics.

**Methods**

**Shift current.** To make contact with previous work, we note the shift current integrand in equation (3) is sometimes expressed in terms of the phase of the inter-band matrix element $i_{\alpha \beta}^\phi = |\psi_{\alpha}^b| |\psi_{\beta}^o|$ as $i_{\alpha \beta}^\phi = |\phi_{\alpha}^b| |\phi_{\beta}^o| R_{\alpha \beta}^\phi$, where

$$R_{\alpha \beta}^\phi = \partial_{E_{\alpha}} \phi_{\alpha}^o - \partial_{E_{\beta}} \phi_{\beta}^o.$$  

(10)

Figure 4 | Tight-binding fit to ab initio for GeS. Dispersion of conduction and valence bands of GeS near $\Gamma$ computed ab initio (red dots). A black line shows the tight-binding fit for comparison.

Two-band model. For the case of two bands, $m = 1, 2$, the product rule for the shift current integrand in equation (3) leads to the simplified expression

$r_{nm}^{\phi \tau} = \frac{1}{\omega_{12}} \text{Im} \left[ -v_{12}^\psi v_{12}^\phi (v_{12}^\tau - v_{12}^\phi) + v_{21}^\psi (v_{12}^\phi - v_{12}^\psi) \right].$  

(17)

To evaluate this expression we compute the wave functions of $H$

$$\psi_{\alpha} = \frac{1}{\sqrt{2E_{\alpha}}} \left(-\eta \sqrt{\epsilon - \eta f_{\alpha}} e^{i\phi_{\alpha}} \sqrt{\epsilon + \eta f_{\alpha}} \right).$$  

(18)

with $n = 1, 2$, $\eta = (-1)^n$, and $\phi_{\alpha} = \text{arctan}(f_{\alpha})$. The required matrix elements are

$v_{12}^\phi = \langle \phi_{\alpha}^b | (\epsilon_{\alpha} + X \sigma_{\alpha}) | \psi_{\alpha}^o \rangle = \sum_{i} f_{\alpha} \epsilon_{i} s_{i},$  

(19)

and

$v_{12}^{\eta \phi} = \langle \phi_{\alpha}^{b} | (\epsilon_{\alpha} \sigma_{\alpha}^{\eta} + X \sigma_{\alpha}^{-\eta}) | \psi_{\alpha}^{o} \rangle = \sum_{i} f_{\alpha} \epsilon_{i} s_{i},$  

(20)

where the off diagonal matrix element $s_{i} = \langle \psi_{\alpha} | \delta_{i} | \phi_{\alpha} \rangle$ is

$s_{i} = \left( \frac{\cos \phi_{\alpha} + \sin \phi_{\alpha} \sin \phi_{\alpha} \sin \phi_{\alpha}}{i \cos \phi_{\alpha} - \frac{\sqrt{\epsilon + \eta f_{\alpha}}}{\sqrt{\epsilon - \eta f_{\alpha}}} \left( \frac{\sqrt{\epsilon + \eta f_{\alpha}}}{\sqrt{\epsilon - \eta f_{\alpha}}} \right) \right),$  

(21)

and the diagonal velocity matrix elements are computed from equation (15). The imaginary part in equation (17) can be taken using $\text{Im}[s_{i}] = -\sum_{o} \epsilon_{m} \text{Im} \epsilon_{m} / \epsilon$ and this leads to equation (5) in the main text.

**Joint density of states.** To compute the J DOS, we first start with the 1D case. Close to the band edge, we expand the energies of conduction and valence bands as

Table 1 | Ab initio and tight-binding parameters for GeS.

| Parameter | Ab initio | Tight-binding |
|-----------|-----------|---------------|
| $E_{g}$   | 1.89 eV   | 1.89 eV       |
| $m_{v,c}$ | -0.064 eV$^{-1}$ Å$^{-2}$ | 0.079 eV$^{-1}$ Å$^{-2}$ |
| $m_{c,v}$ | 0.079 eV$^{-1}$ Å$^{-2}$ | -0.340 eV$^{-1}$ Å$^{-2}$ |
| $m_{c,c}$ | 0.171 eV$^{-1}$ Å$^{-2}$ | 3.565 Å$^{3}$ |
| $\gamma$  | 2.529 Å$^{2}$ | 2.529 Å$^{2}$ |

| Parameter | Ab initio | Tight-binding |
|-----------|-----------|---------------|
| $\Delta$  | 0.41 eV   | -2.33 eV      |
| $t_{1}$   | 0.61 eV   | 0.13 eV       |
| $t_{2}$   | 0.07 eV   | -0.09 eV      |
| $t_{3}$   | 0.52 Å    | 0.52 Å        |

First row: input ab initio parameters and the second row: tight-binding parameters obtained from the fitting.
$E_i \approx E_i^0(k) + k^2/2m_{ci}$, so that $\omega_{12} = E_1 - E_2 \approx E_1 + k^2/2m_1$, where the total effective mass $m_{ci}^{-1} = [m_{c1}]^{-1} + [m_{c2}]^{-1}$ is given by

$$m_{ci}^{-1} = 4(\nu_f + 2\nu_g + 2\nu_o)\Delta / E_g,$$

and solve for $k(o) = \sqrt{2m_1(o - E_1)}$. Rescaling $2m_1$ we get

$$N^{1D}(o) = \sqrt{2m_1} \int \frac{dk}{2\pi} \frac{k(k - k(o))}{1 \text{MeV/k}} = \frac{\sqrt{2m_1} \theta(o - E_1)}{\sqrt{2m_1} \theta(o - E_1)},$$

where we get the expected 1D singularity. For the generic 2D case, we again expand $\omega_{12} \approx E_1 + k^2/2m_1 + k^2/2m_2$, where $m_2$ is still given by equation (22) and

$$m_2^{-1} = \frac{1}{2}(\nu_f + \nu_g + \nu_o)\Delta / E_g.$$

We consider the case when $m_2 > 0$, $m_1 > 0$, so that the minimum does lie at $k = 0$. By rescaling $2m_1$ and $2m_2$, we get in polar coordinates

$$N^{2D} = \sqrt{4m_1m_2} \int \frac{dk}{2\pi} \left( \frac{k(k - k(o))}{1 \text{MeV/k}} \right) \frac{d\theta}{\theta},$$

which is the expected constant result. Finally, the semi-Dirac case occurs in 2D when $m_2 = 0$, which is the absence of second neighbour hopping occurs exactly at $\Delta = 0$. In this case, we keep the complete expression for $\omega_{12} = (\tau_1 + \tau_2 + \tau_3)^2 + \nu_g^2 + \Delta^2)/2$. In polar coordinates we have

$$N^{2D} = \int \frac{dk}{2\pi} \frac{k(k - k(o))}{1 \text{MeV/k}} \frac{d\theta}{\theta},$$

We now rescale $\nu_g$, $\nu_o$, instead, solve for $k$

$$k(o) = \left[ -\nu_f^2 - \nu_g^2/\cos \theta \pm \sqrt{\nu_g^2 \cos^2 \theta + \nu_o^2 - E_g^2} \right]^{1/2} / 2,$$

and get

$$N^{2D} = \frac{\sqrt{4m_1m_2}}{\pi} \int \frac{dk}{2\pi} \frac{k(k - k(o))}{1 \text{MeV/k}} \frac{d\theta}{\theta} = \frac{\left( \nu_f^2 + \nu_g^2 \right) \cos \theta - \nu_o^2}{\sqrt{\nu_g^2 \cos^2 \theta + \nu_o^2 - E_g^2}}.$$

The tight-binding Hamiltonian takes the form $H = \varepsilon_0 + \sum \sigma \beta_i(k)$ with coefficients

$$\varepsilon_0 = -2\varepsilon_{12} \left( \cos \alpha_1 \cdot k + \cos \alpha_2 \cdot k \right),$$

$$f_q = -e^{i\Phi(k)} [t_1 + t_2 \Phi(k)] + t_1 \Phi^*(k),$$

where, as defined in the text, $\Phi(k) = (\epsilon^{\alpha_1} k + \epsilon^{\alpha_2} k)$. Our tight-binding fit is intended to reproduce faithfully the bands and wavefunctions close to the band edge, where the effective low-energy model applies. This model is given by

$$H = \left( \nu_1 k^2 + \nu_2 k^2 \right) T + \left( \delta + \nu_1 k^2 + \nu_2 k^2 \right) \sigma_x + \nu_3 \sigma_y + \Delta \sigma_z,$$

where a constant term is omitted as it can be absorbed in the chemical potential. The effective model parameters are related to the tight-binding parameters as

$$\gamma_a = 2\nu_a^2,$$

$$\gamma_y = (2\nu_1 + 4\nu_2) \sigma_y,$$

$$\delta = \nu_1 - 2\nu_0 - 2\nu_0,$$

$$\nu_3 = -2\nu_0 (2\nu_1 - 2\nu_0 - 2\nu_0) x_0,$$

$$x_0 = t_2 (x_1 - x_0)^2 - t_1 x_0^2 + 6 (x_1 - x_0)^2 x_1^2,$$

$$x_0 = t_2 (x_1 - x_0) x_1.$$

The key to obtain a reliable tight-binding parameterization is that, since the shift current depends sensitively on the actual wavefunctions, the tight-binding model should be fitted to wavefunction-dependent quantities in addition to the band energies. The simplest gauge invariant quantity that depends on wavefunction phases is the bracket of two covariant derivatives

$$Q_{\alpha\beta} = \langle D_{\alpha} u_{\beta} D_{\alpha} u_{\beta} \rangle,$$

and get

$$\Omega(k) = \varepsilon_0 \text{Im} \left[ \langle \sigma_3 \sigma_1 \rangle / \langle \sigma_3 \rangle \right] = \nabla \times A.$$

The Berry curvature around $\Gamma$ for the tight-binding model is given by

$$\Omega = \nu y (\nu x A - \nu y A) / \left( \Delta + \delta^2 + \nu^2 \right)^{1/2},$$

Since $\Omega$ vanishes at the origin, we take $\varepsilon_0 \Omega$ as one extra input for the fit. The quantum metric is defined as

$$g_{\alpha\beta} = \text{Re} \left[ \langle \delta_{\alpha\beta} \delta_{\alpha\beta} \rangle / \langle \delta_{\alpha\beta} \rangle \right] - A_{\alpha} A_{\beta},$$

and get

$$g_{\alpha\beta} = \nu y / \left( \Delta + \delta^2 + \nu^2 \right)^{1/2},$$

so we take $g_{\alpha\beta}$ as another extra input for the fit.

In summary, we take as $ab$-initio input parameters the gap, the four effective masses and the lowest order Berry curvature and quantum metric, $\nu y \Omega$ and $g_{\alpha\beta}$. The difference in effective masses for electron and hole bands, accounted for the term $\varepsilon_0$, can be fitted independently with the hoppings $t_1$ and $t_2$. Since $\varepsilon_0$ has no impact in the shift current response, the hoppings $t_1$ and $t_2$ are not considered in the main text. The rest of the input is fitted with $t_1$, $t_2$, and $t_3$, the on-site potential $\Delta$ and $x_0$, and the results of the fit are shown in Table 1. While $x_0$ is in fact known from the lattice structure of GeS to be 0.62 Å, obtaining it independently from the tight-binding fit, which gives a close value of 0.52 Å provides an additional check of the validity of the model.

**Data availability.** The data that support the findings of this study are available from the corresponding author upon request.

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Author contributions

A.M.C. and B.M.F. contributed equally to the work. A.M.C., B.M.F., F.d.J. and J.E.M. carried out the analytical and numerical analysis. S.C. carried out all ab-initio computations. All authors contributed to the results and the writing of the manuscript.

Additional information

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