Heterobilayers of 2D materials as a platform for excitonic superfluidity

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Excitonic condensate has been long-sought within bulk indirect-gap semiconductors, quantum wells, and 2D material layers, all tried as carrying media. Here, we propose intrinsically stable 2D semiconductor heterostructures with doubly-indirect overlapping bands as optimal platforms for excitonic condensation. After screening hundreds of 2D materials, we identify candidates where spontaneous excitonic condensation mediated by purely electronic interaction should occur, and hetero-pairs Sb2Te3Se/BiTeCl, Hf2N2I2/Zr2N2Cl2, and LiAlTe2/BiTeI emerge promising. Unlike monolayers, where excitonic condensation is hampered by Peierls instability, or other bilayers, where doping by applied voltage is required, rendering them essentially non-equilibrium systems, the chemically-specific heterostructures predicted here are lattice-matched, show no detrimental electronic instability, and display broken type-III gap, thus offering optimal carrier density without any gate voltages, in true-equilibrium. Predicted materials can be used to access different parts of electron-hole phase diagram, including BEC-BCS crossover, enabling tantalizing applications in superfluid transport, Josephson-like tunneling, and dissipationless charge counterflow.

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Condensation to a macroscopic quantum state is a unique feature of bosonic particles that manifests in macroscopic quantum phenomena as remarkable as superfluidity and superconductivity. Experiments on these systems have affirmed our understanding of quantum theory, stimulated applications, and recent widespread interest in use for quantum computing. Apart from the extraordinary transport properties of the condensate, the topological excitations in a superfluid are ideal hunting ground for exotic particles such as ‘t Hooft-Polyakov and Dirac monopoles, or skyrmions, useful for comprehending grand unified theory but also for applications in data storage and spintronics.

Excitons are composite bosons that are bound states of an electron and hole in a solid and were predicted to undergo condensation under appropriate conditions. Compared to commonly known bosonic systems such as atomic gases and liquid He, excitons have smaller mass and their condensate should remain stable up to higher temperatures. Being created in solids by excitation with light, excitons have a short lifetime—a major obstacle to their condensation.

A fundamentally different possibility of an excitonic ground state was first discussed by Mott who noted that as valence and conduction bands of a semiconductor start overlapping (e.g., under external pressure) leading to a semi-metallic state (Fig. 1a). Coulomb attraction between the conduction band (CB) electrons and valence band (VB) holes should lead to the spontaneous formation of excitons, delaying the appearance of the metallic state. The semimetal transitions to an excitonic insulator phase, with a 2Δ gap in the excitation spectrum, as shown in Fig. 1b. The latter, also called the Bardeen-Cooper-Schrieffer (BCS) phase, corresponds to the weak coupling limit of composite boson condensate, and holds when $n\alpha^2 > 1$, where $n$ is carrier or pair density and $\alpha$ is exciton radius. At low density, $n\alpha^2 < 1$, the screening from carriers is reduced (strong coupling) and the Bose–Einstein condensate (BEC) phase forms. BEC and BCS are different limits of the same boson condensate state.

After early theoretical works on bulk semi-metallic crystals, spatial separation has been proposed as a promising way to realize excitonic instability and inverted gap quantum-well bilayer systems were considered. Having electrons and holes spaced apart is deemed essential to reduce many-body interactions that lead to thermodynamic instability near the phase transition. However, in quantum wells typically separated by dozens of Å, electron-hole interaction is weak. Moreover, surface roughness/disorder in quantum wells degrades the coherence of the excitonic state.

Recent interest in excitonic condensation has been renewed by the advent of two-dimensional (2D) materials, providing the advantage of reduced screening and atomically sharp interface. Bilayer graphene has been extensively investigated theoretically and even with some experimental evidence, however inconclusive, since the phase sought is either not observed or has very low $T_c$.

Fig. 1 Exciton condensation in broken-gap 2D bilayer heterostructures. a Band alignment in a semi-metallic system with distinct electron and hole pockets necessary for exciton condensation. b For such a system with a negative gap ($E_F$) or when $E_F < E_L$ (the exciton binding energy), the semi-metallic state becomes unstable and opens a gap for an arbitrarily weak electron-hole attraction. The semimetal now transitions to an excitonic insulator, with a gap of $2\Delta$ in the excitation spectrum. c For a broken-gap band alignment, the electron is transferred to the conduction band of the acceptor layer B, with a hole remaining in the valence band on the donor layer A. In a staggered-gap alignment, band overlap can be tuned by external perturbation.
lattice-matched monolayer 2D semiconductors with either a broken gap (type III) or staggered gap (type II) alignment. For a broken-gap band alignment shown in Fig. 1c, the electron is transferred to the conduction band of the acceptor layer, with a hole remaining in the valence band on the donor layer. Band overlap can also be tuned through external perturbation, as shown in Fig. 1c, starting from the staggered gap lineup.

Results

Model Hamiltonian analysis of 2D bilayer heterostructure. In order to guide and accelerate such search of suitable material pairs based on their band alignment, we first perform a model Hamiltonian analysis (see "Methods") for estimating the optimal effective mass and carrier density. In a bilayer heterostructure with carrier density \( n \), embedded in vacuum and separated by distance \( d = 3 \text{ Å} \), the electron and hole states are on different layers and have distinct effective masses. To estimate the binding energies (\( E_b \)) of individual interlayer excitons in such vdW heterostructures, we adopt the RPA form of the screened potential suitable for bilayers. The effective mass Hamiltonian for an electron-hole pair in parabolic bands was constructed and diagonalized using the Gaussian basis set (see "Methods" for details). Figure 2a shows the calculated room-temperature binding energies of interlayer excitons as a function of reduced mass \( \mu \) and carrier density. Although the potential is always attractive, the model predicts essentially no binding for densities side, and electron-hole plasma on the high density side. The estimated critical temperatures (details in "Methods"). Overall, Fig. 2b represents a semi-quantitative phase diagram for excitonic particles and denotes optimal \( n \) to realize an excitonic condensate phase (see Supplementary Fig. 9 for all other phases). Apart from the phases shown in Fig. 2b, a gas of excitons can also transition to an electron-hole liquid (EHL) state, thereby preventing the realization of an excitonic condensation (BKT/BCS). However, in our bilayer case with electrons and holes spatially separated, the excitons act as oriented electric dipoles with a repulsive interaction between them. The repulsion is important because it prevents the occurrence of EHL state and excitonic BKT/BCS can be realized at low densities. However, at high densities, the EHL state might be more stable.

Identifying optimal 2D bilayer heterostructures. The densities to realize excitonic condensation should be achievable with existing 2D materials. We search the 2D material database to identify optimal materials by first recalculating and comparing valence and conduction band positions with respect to the vacuum level. The database contains a list of 2D materials that can be exfoliated from experimentally known 3D compounds. Next, after pre-selecting candidate pairs, we calculate the band gaps of 23 heterostructures with broken and staggered band alignments, as shown in Fig. 3. The pairs were chosen so that their lattice mismatch \( \Delta \varepsilon < 2\% \), and each layer has a band gap \( > 0.3 \text{ eV} \). Band gaps in heterostructures range from \(-0.22 \text{ eV} \) to \( 0.1 \text{ eV} \), with negative values indicating greater overlap. Assuming effective masses are same, higher band overlap corresponds to higher carrier density, and different heterostructures can be used to access distinct regions of the phase diagram. According to Fig. 2b, \( n \sim 10^{10} \text{ cm}^{-2} \) is an optimal range of carrier density for excitonic condensation, and the corresponding optimal initial band overlaps are \( 1 \text{ meV} < W_0 < 391 \text{ meV} \), assuming \( \mu = 0.1 \text{ m}_e \) and \( d = 3 \text{ Å} \) (see "Methods" for details). The final overlap in a heterostructure is \( W \) = \( 1 \text{ meV} < W < 120 \text{ meV} \). We select three materials pairs \( \text{Sb}_2\text{Te}_2\text{Se}/\text{BiTeCl} \), \( \text{Hf}_2\text{N}_2\text{I}_2/\text{Zr}_2\text{N}_2\text{Cl}_2 \), and \( \text{LiAlTe}_2/\text{BiTeI} \) marked in Fig. 3, in which final calculated band overlaps after forming heterostructures are \( 67 \text{ meV} \), \( 47 \text{ meV} \), and \( 38 \text{ meV} \), respectively. Materials with small band gaps can show...
Projected LDA band structures of Fig. 4c of the Hf$_2$N$_2$I$_2$/Zr$_2$N$_2$Cl$_2$ band structure, which also shows VBM and CBM decreases but remains, at ~0.05 eV, as seen in level. After a bilayer is formed, the energy overlap between the TiSe$_2$, and the calculated BCS gaps tors, with the VBM of freestanding Hf$_2$N$_2$I$_2$ at instability. In Fig.4a, b the band structures of individual Hf$_2$N$_2$I$_2$/Zr$_2$N$_2$Cl$_2$ layers are plotted. Both materials are semiconductors, with the VBM of freestanding Hf$_2$N$_2$I$_2$ at ~-4.57 eV and the CBM of Zr$_2$N$_2$Cl$_2$ at ~-4.88 eV, with respect to the same vacuum level. After a bilayer is formed, the energy overlap between the VBM and CBM decreases but remains, at ~-0.05 eV, as seen in Fig. 4c of the Hf$_2$N$_2$I$_2$/Zr$_2$N$_2$Cl$_2$ band structure, which also shows that the electron-doped conduction band at the K point is located on the Zr$_2$N$_2$Cl$_2$ layer, while hole-doped valence band on the Hf$_2$N$_2$I$_2$ layer. As there is little interlayer mixing in either the valence or conduction bands, a bilayer becomes polar. The band structure of Hf$_2$N$_2$I$_2$/Zr$_2$N$_2$Cl$_2$ resembles in fact that of monolayer 1T-TiSe$_2$ (Fig. 4d), both being indirect-gap semimetals with the VBM and CBM lying at different valleys in the Brillouin zone.

**Fig. 3 Hetero-bilayers band alignments.** Relative positions of valence (left upward columns) and conduction bands (right downward columns) in 2D heterostructures for $\Delta_r < 2\%$, $-0.22$ eV $< \Delta \epsilon < 0.1$ eV, $E_g > 0.3$ eV. The five bilayers considered in detail in this work are highlighted with thicker outline, and the calculated BCS gaps $\Delta$ for heterostructures 1, 2, and 3 are shown.

**Fig. 4 Band structures and phonon spectra of 2D Hf$_2$N$_2$I$_2$, Zr$_2$N$_2$Cl$_2$, Hf$_2$N$_2$I$_2$/Zr$_2$N$_2$Cl$_2$, and 1T TiSe$_2$.** Band alignment in a Hf$_2$N$_2$I$_2$ and b Zr$_2$N$_2$Cl$_2$. Projected LDA band structures of e Hf$_2$N$_2$I$_2$/Zr$_2$N$_2$Cl$_2$ heterostructure, and d 1T TiSe$_2$. LDA phonon dispersions with electron-phonon couplings $\lambda$ of e 1T TiSe$_2$, and f Hf$_2$N$_2$I$_2$/Zr$_2$N$_2$Cl$_2$ heterostructure. The area of the gray and red circles is proportional to the coupling strength $\lambda$.

excitonic instability provided that $E_g < E_h$, and can also in principle exhibit condensation.

We calculate the phonon spectra and band structure of Hf$_2$N$_2$I$_2$/Zr$_2$N$_2$Cl$_2$ (see Supplementary Fig. 3 for two other heterobilayers), which is instructive to compare with the monolayer 1T-TiSe$_2$, well studied$^{32–35}$ as a possible candidate for excitonic instability. In Fig. 4a, b the band structures of individual Hf$_2$N$_2$I$_2$ and Zr$_2$N$_2$Cl$_2$ layers are plotted. Both materials are semiconductors, with the VBM of freestanding Hf$_2$N$_2$I$_2$ at ~4.57 eV and the CBM of Zr$_2$N$_2$Cl$_2$ at ~4.88 eV, with respect to the same vacuum level. After a bilayer is formed, the energy overlap between the VBM and CBM decreases but remains, at ~0.05 eV, as seen in Fig. 4c of the Hf$_2$N$_2$I$_2$/Zr$_2$N$_2$Cl$_2$ band structure, which also shows that the electron-doped conduction band at the K point is located on the Zr$_2$N$_2$Cl$_2$ layer, while hole-doped valence band on the Hf$_2$N$_2$I$_2$ layer. As there is little interlayer mixing in either the valence or conduction bands, a bilayer becomes polar. The band structure of Hf$_2$N$_2$I$_2$/Zr$_2$N$_2$Cl$_2$ resembles in fact that of monolayer 1T-TiSe$_2$ (Fig. 4d), both being indirect-gap semimetals with the VBM and CBM lying at different valleys in the Brillouin zone. Similar to 1T-TiSe$_2$, the valence and conduction bands are mainly composed of $p$ and $d$ orbitals, with the VBM originating from iodine $p$ states of Hf$_2$N$_2$I$_2$ layer, and smaller contributions from nitrogen $p$ states of Hf$_2$N$_2$I$_2$, whereas the CBM originates from zirconium $d$ states, with smaller contributions from $p$ states of N and Cl of Zr$_2$N$_2$Cl$_2$ (see Supplementary Fig. 7). Notably, the valence and conduction bands of 1T-TiSe$_2$ are strongly coupled to phonons$^{16,34,46}$, namely, the bands of TiSe$_2$ are coupled to atomic displacements at modulation vector $Q = \Gamma\mathrm{M}$, in Fig. 4e; resulting charge-density wave (CDW) is accompanied by lattice reconstruction. This resembles the Peierls instability which opens the band gap, debatably driving this material to a conventional insulator state$^{34–36}$. In contrast, such instability is absent in Hf$_2$N$_2$I$_2$/Zr$_2$N$_2$Cl$_2$, where valence and conduction bands, located at different layers, are decoupled. The phonon spectrum of Hf$_2$N$_2$I$_2$/Zr$_2$N$_2$Cl$_2$ in Fig. 4f attests to its stable structure; electron-phonon coupling, largest at K and $\Gamma$ points, is too weak to cause unstable modes. A CDW is expected due to the modulation vector $Q = \Gamma\mathrm{K}$, however, due to weak electron-phonon coupling, there will not be any lattice distortion. The spontaneous excitonic condensation in this material will be mediated by purely electronic interaction. Thus, excitonic condensation would not be hampered by the phonon instability in a Hf$_2$N$_2$I$_2$/Zr$_2$N$_2$Cl$_2$ bilayer or, for that matter, in other vdW bilayers (this was further
affirmed by additional supercell calculations, see 3.2 in Supplementary Note 3).

Discussion

H$_2$N$_2$I$_2$/Zr$_2$N$_2$Cl$_2$ has a finite modulation vector Q = ΓK, however, Sb$_2$Te$_3$Se/BiTeCl$_3$, and LiAlTe$_2$/BiTe exhibit a zero modulation vector (see Supplementary Fig. 3). This results in band crossing between electron and hole states and also hybridization in Sb$_2$Te$_3$Se/BiTeCl$_3$, and LiAlTe$_2$/BiTe (for details see 3.1 in Supplementary Note 3). Single-particle level band hybridization can lead to interband tunneling processes and may fix the phase of the order parameter and destroy superfluidity$^{47}$. However, these tunneling processes can be suppressed by using suitable dielectrics such as hBN in between the two layers and superfluidity can be achieved. From the band structures calculated using LDA functional, we further extract the effective masses (see Supplementary Table 1) and calculate the n in three hetero-bilayers, in order to estimate the critical temperatures for excitonic condensation, marked in Fig. 2b as circled 1, 2 and 3 (see 1.2 in Supplementary Note 1 for the value of n obtained with another functional). We find n to be $>$10$^{12}$ cm$^{-2}$, with H$_2$N$_2$I$_2$/Zr$_2$N$_2$Cl$_2$ highest T$_c$ of $\approx$ 31 K. While the method-dependent spread of n values as estimated by different functionals would yield different estimates for T$_c$, it should not affect the conclusion about the feasibility of excitonic condensation in these heterostructures. Building upon Mott’s earlier ideas$^{44}$, external factors such as strain, and possibly gating or changing the interlayer distance (yet not to weaken binding interaction), can fine-tune the carrier density, to access different regions of the phase diagram, and increase the T$_c$ (see Supplementary Note 2 for details). For example, a field of $\sim$1 V/mm can change the carrier density by $\sim$10$^{12}$ cm$^{-2}$, and can quite noticeably shift T$_c$ of materials in Fig. 2b diagram. Similar perturbation can even be used to tune the band overlap in the hetero-bilayers lying on the flanks of Fig. 3, which were rendered above as suboptimal for excitonic condensation, if those are more readily synthesizable.

In summary, our quantitative analysis demonstrates that Sb$_2$Te$_3$Se/BiTeCl$_3$, H$_2$N$_2$I$_2$/Zr$_2$N$_2$Cl$_2$, LiAlTe$_2$/BiTe, H$_2$N$_2$I$_2$/SnS$_2$ and possibly other 2D hetero-bilayers can serve as a platform for realizing an excitonic ground state, in true equilibrium systems (with no need of light-excitation or even static applied voltages). The van der Waals spacing ensures that the lattice thermodynamic stability is preserved, with bands edges being decoupled from the atomic displacements, offering a better material-host for excitonic condensation as compared to recently considered monolayer 1T-ITSe$_2$, likely prone to Peierls instability, which hamper exciton condensation. Moreover, the type-III broken gap ensures that no applied gate-voltage is required for doping, contrary to other studied hetero-bilayers. To map the electron-hole system behaviors in a hetero-bilayers, we construct a phase diagram, which for realistic materials suggests excitonic condensation at tens of K at densities 10$^{11}$-10$^{12}$ cm$^{-2}$. Various parts of the phase diagram, and most importantly the BEC-BCS crossover can in principle be reached through further tuning by external electric field and strain. We expect the materials predicted here to show superfluid transport properties such as enhanced Josephson-like interlayer tunneling$^{35}$, and dissipation-less charge flow$^{48}$, which have been experimentally observed in other bilayer designs and have potential for next-generation electronics and logic devices$^{49}$. Excitons have spin degree of freedom and the spin polarization states of the excitons can also act as a qubit$^{5}$. Moreover, excitonic ferromagnetism$^{50}$ may arise from a mix of the single and triplet pairing states, which can be used to generate spin currents vital in spintronics. An interesting realization can be possible in nested cylindrical hetero-bilayers, where additional flexoelectric offset$^{51}$ must be taken into account.

Methods

First principles DFT calculation

Band structures, phonon frequencies, and electron-phonon coupling coefficients were calculated from density functional theory using LDA functional, as implemented in the Quantum Espresso package$^{52}$. Fully relativistic ultrasoft pseudopotentials were used to represent ionic cores and were obtained from the pslibrary$^{53}$ (version 1.0.0, https://dalcinor.github.io/pslibrary/). The pseudopotentials and 60 Ry kinetic energy cutoff was used for all materials except those with Li, Mg, La, Zn, Cu, and Na. For the latter few, we used the cutoffs above the recommended minima, all higher than 60 Ry. A k-grid of 81 x 81 x 1 was used for Brillouin zone sampling. BFGS algorithm was used for structural relaxation. The structure was relaxed until the Hellmann–Feynman forces on the atoms were less than 2.6 meV/Å. A vacuum of 20 Å was used along the direction perpendicular to the 2D sheet to reduce the interaction between the periodic images. Spin-orbit coupling was included in all calculations. The response of the material to an external electric field (Supplementary Fig. 2) was calculated using the Vienna Ab Initio Simulation Package (VASP)$^{54}$ implementation. A cutoff of 600 eV for the plane-wave basis was used. Ion-electron interactions were reproduced by all-electron pseudopotentials. The values as estimated by different functionals would yield different estimates for T$_c$, it is known to fortuitously capture well the interlayer van der Waals interactions$^{55}$. Additionally, semiempirical Grimme’s DFT-D2 van der Waals correction to PBE functional was used to estimate the equilibrium interlayer distance and a good agreement with LDA functional was obtained.

We considered all 258 easily-exfoliable layers, with a small unit cell (66 atoms/ unit cell) from the materials cloud database, as selected by its creators$^{45}$. Among these, 135 were found to have hexagonal lattices, and their pairs-combinations were tested for lattice match. The lattice constant matching is important for excitonic condensation. In a heterostructure with a large difference in lattice constant, the materials are incommensurate, preventing zero-momentum exciton formation and excitonic condensation. This is analogous to the disappearance of excitonic condensation upon twisting the heterobilayers MoSe$_2$/WS$_2$, observed recently$^{51}$; upon twisting, the lattices become incommensurate with momentum mismatch between the hole and electron valleys in the materials, the interlayer excitons formed thus have a large momentum, which destroys condensation.

Model Hamiltonian analysis - exciton binding energy

The model Hamiltonian within the effective mass approximation for an electron-hole pair in a bilayer semiconductor is given by

$$H = -\hbar^2 / (2m_e) \left( \partial^2 / \partial x^2 - \hbar^2 / (2m_h) \right) \partial^2 / \partial y^2 + V_{eh}(r)$$

(1)

Here, $m_e$ and $m_h$ are the reduced masses in x and y directions, respectively, and $V_{eh}(r)$ is the attractive Coulomb potential as given by Eq. (2),

$$V_{eh}(r) = -\frac{2e^2}{\epsilon} \left( \frac{1}{r} + \frac{1}{r_0} \right)$$

(2)

and $r_0$ is the 2D screening wave number assumed to be unity in this work, $\epsilon$ is the background dielectric constant assumed to be unity in this work, $\hbar$ is the Planck constant, and $r$ is the effective mass. In a two-dimensional metal with parabolic bands, the screening wave number is independent of density at zero temperature. However, at finite $\beta$, the screening is both density- and temperature-dependent, with increasing temperature leading to reduced screening (for details see 1.1 in Supplementary Note 1); $r_0$ of 300 K is assumed here. $V_{eh}(r)$ was obtained from $V_{eh}(q)$ using Fourier transform. The excitonic binding energies $E_b$ and wavefunctions were obtained by finding the eigenvalues and eigenfunctions of the effective mass Hamiltonian (Eq. (1)). Gaussian basis set of size 6 was used to expand the ground-state excitonic wavefunction, and calculate the exciton-wavefunctions and energy of the Hamiltonian. The expansion was optimized using the downhill simplex algorithm. The parameters for model Hamiltonian analysis were extracted from the heterostructures, not the constituent layers.

BCS mean field gap equation

Analogous to the BCS algebra, the order parameter $\Delta$ is obtained by solving the below equations self-consistently$^{21,43}$

$$\tilde{\Delta}_q = \tilde{\Delta}_q - \tilde{\Delta}_q + (1 - \tilde{\Delta}_q) \left( V_{eh}(k - \tilde{\Delta}_q) - \tilde{\Delta}_q \right)$$

(3)

$$\tilde{\Delta}_q = \frac{\tilde{\Delta}_q + \Delta q}{\tilde{\Delta}_q}$$

(4)

$$\Delta_q = -\frac{(1 - \tilde{\Delta}_q) V_{eh}(k - \tilde{\Delta}_q) \Delta_q}{\tilde{\Delta}_q}$$

(5)

Here, $V_{eh}(q)$ is the attractive Coulomb potential as given by Eq. (2), $V_{eh}(q) = (2\pi n_s/\pi) [q + s + \pi^2 n_s^2 (q + s)^2 - 2\pi n_s^2 (q + s)^2]$ $^{50}$, $n_s = 1/2 [k_0^2 / (2m_e + \hbar^2 / 2m_e)]$, $\mu$ = 1/2[\epsilon - $\epsilon_{\nu}^2 / \epsilon_{\nu}^2(1 + s/d)]$, $\epsilon_{\nu}$ here is chemical potential for excitons, $\Sigma = \Sigma_0 (1 - \tilde{\Delta}_q / \tilde{\Delta}_q)$ and
\[ q = |k - k'| \] The order parameter (\( A \)) in Eq. (5) is the gap function. It is zero in the normal state and non-zero in the excitonic insulating state. A value of 2\( A \) denotes the gap in the excitonic insulator ground state. The form of BCS Eq. (5) remains the same when the modulation vector \( Q \) is finite, as \( Q \) does not enter the expression. This is because in \( \epsilon_k \) (which depends on \( E_k(\sigma) \) conduction band (electron) dispersion and \( E_k(\pi) \) valence band (hole) dispersion) \( k \) is referred to the respective band extrema. We do not include spin degrees of freedom and thus neglect any spin-triplet excitonic order. All quantities in Eqs. (3)–(5) are assumed to be isotropic i.e. functions of magnitude of \( k \) and these equations are solved self-consistently to determine \( E_0 \) and \( A_0 \). Subsequently, critical temperature is obtained from the maximum value of \( A_0 \). The mean field calculations give an approximate depiction of the excitonic condensate phase diagram and quantum Monte Carlo can be appropriate for a much higher accuracy.

**Charge transfer model**

For an isolated pair of materials with parabolic bands and VBM-CMB overlap \( W_0 \), the charge transfer can be estimated using a parallel-plate capacitor model as

\[ \frac{W_0}{e} = \frac{C_0}{C_1} \left( 1 + \frac{C_1}{C_2} \right) \]

where \( C_0 = e_0/\epsilon \) is the classical and quantum bilayer capacitances, respectively. One has \( \frac{W_0}{e} = \frac{\epsilon_0}{\epsilon_1} \left( 1 + \frac{C_2}{C_1} \right) \) for numerical estimates. In a stacked heterostructure, with a new band overlap \( W \), the density is expressed as

\[ \frac{n}{2} = \frac{e_0}{W} \left( 1 + \frac{C_2}{C_1} \right) \frac{\epsilon_2}{\epsilon_1} \left( 1 + \frac{C_3}{C_2} \right) \text{or} \frac{\epsilon_2}{n} \text{[10}^{13} \text{cm}^{-2} \text{]} = \frac{W}{e} \left[ 1 + 0.18 \phi(\text{md}) + 0.02/\mu \right] \]

for numerical estimates.

**Data availability**

The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary information files. An archive with optimized geometries for heterostructures listed in Fig. 3 is provided as Supplementary dataset 1. The data in the dataset is deposited on the Zenodo database https://doi.org/10.5281/zenodo.3822513.

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**Author contributions**
S.G., A.K., and B.I.Y. conceived the project. S.G. and A.K. identified and refined the structures from the databases and performed all first-principles simulations. All authors contributed to the writing of the paper.

**Competing interests**
The authors declare no competing interests.

**Additional information**
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