Quasiparticle $GW$ band structures and Fermi surfaces of bulk and monolayer NbS$_2$

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In this work we employ the $GW$ approximation in the framework of the Sternheimer-GW method to investigate the effects of many-body corrections to the band structures and Fermi surfaces of bulk and monolayer NbS$_2$. For the bulk system, we find that the inclusion of these many-body effects leads to important changes in the band structure, especially in the low-energy regime around the Fermi level, and that our calculations are in good agreement with recent ARPES measurements. In the case of a free-standing monolayer NbS$_2$, we observe a strong increase of the screened Coulomb interaction and the quasiparticle corrections as compared to bulk. In this case we also perform calculations to include the effect of screening by a substrate. We report in detail the results of our convergence tests and computational parameters, to serve as a solid basis for future studies.

I. INTRODUCTION

Transition metal dichalcogenides (TMDs) have been the focus of many studies in recent years, as their physical and chemical diversity offers an ideal platform to investigate semiconductors, metals, and superconductors in layered systems using the same structural template [1–4]. Within the family of TMDs, metallic materials have attracted considerable attention due to the fact that both a superconducting phase as well as a charge density wave (CDW) phase appear in the low-temperature phase diagram [5–13]. Moreover, the fact that the increased spatial confinement in few-layer and monolayer systems, as well as the substrates they are placed on, cause important changes in the electronic structure [14], in particular in the screened Coulomb interaction, has drawn considerable interest to two-dimensional (2D) materials [15–22]. With respect to few-layer TMDs, experiments show that the superconducting critical temperature tends to decrease with decreasing number of layers [21, 23, 24]. The situation for the critical temperature of the CDW order is less clear, and a consensus on how it depends on the layer thickness has not yet been achieved [21, 24–26].

The metallic compound 2H-NbS$_2$ stands out in the TMD family, as it is superconducting with a critical temperature of ~6 K, but does not exhibit CDW order in the bulk. It has recently been proposed that bulk NbS$_2$ is actually on the verge of a CDW instability [27]. The strongly anharmonic phonon modes dominate the superconducting pairing in 2H-NbS$_2$, successfully explaining the two-gap feature observed in experiments. In Ref. 27 it is shown that accurate low-energy band structures and Fermi surfaces beyond density-functional theory (DFT) are crucial for achieving a better quantitative agreement with experiments. At variance with bulk NbS$_2$, the fabrication and experimental investigation of monolayer NbS$_2$ has not been reported yet.

In the present study, we want to expand on these findings and provide an extensive view on the electronic properties of bulk and monolayer NbS$_2$ beyond DFT by considering many-body perturbation theory in the framework of the $GW$ approximation [28–33]. In addition, as only few $GW$ calculations have been reported for metallic TMDs [34], part of this work is to examine the various convergence parameters of the $GW$ calculation for the bulk and the monolayer system. As the main focus of this work, we compare our calculations with recent angle-resolved photoemission spectroscopy (ARPES) measurements on bulk NbS$_2$ [35]. Furthermore, we assess the effects of the increased spatial confinement when going from bulk to the monolayer, and the role of substrates.

This paper is organized as follows: In Sec. II, we provide structural details about bulk and monolayer NbS$_2$, we give a short overview of the methods used in this work, and summarize the computational setup and the convergence properties of the $GW$ calculations. In Sec. III we discuss our results for the band structures, densities of states, and Fermi surfaces of bulk and monolayer NbS$_2$. In the case of bulk NbS$_2$ we compare our calculations with recent ARPES data. In Sec. IV, we offer our conclusions and identify important avenues of future research. In the appendixes we report detailed convergence tests of the $GW$ calculations with respect to plane waves, energy cutoffs, and Brillouin-zone sampling.

II. COMPUTATIONAL DETAILS

A. Structures

Bulk 2H-NbS$_2$ crystallizes in a layered hexagonal structure with space group $P6_3/mmc$. The unit cell contains two S-Nb-S layers, as shown in Fig. 1. The Nb atoms occupy the 2b Wyckoff positions (0, 0, 1/4) and the S atoms are located at the 4f positions (1/3, 2/3, z). All calculations are performed in the optimized crystal structure, with lattice parameters $a = 3.28$ Å, $c/a = 3.47$,
changes in the electronic structure due to including SOC on the level of DFT is smaller than the (Fig. 11) and monolayer NbS optimization within DFT on our der Waals (vdW) corrections at the step of the structure tion theory. We also tested the influence of including van

and solely focus on the changes of the electronic struct-
ture arising from the inclusion of many-body perturba-
tion, allowing us to neglect SOC in a first approxima-
tion when the particle number changes.[42] This per-

mits us to study a wide range of diverse materials, from
solids to molecules and nanostructures, as well as surfaces 
and interfaces [43, 44]. Important applications include
the correction of band gaps and bandwidths [45], and
while GW has traditionally been used for insulators and
semiconductors, it is expected to affect the properties of
metallic systems as well.

and magnetic fields. The predictive power is less impres-
sive when it comes to electronic excitations. For ex-
ample, Kohn-Sham DFT tends to yield too low band gaps,
as well as inaccurate band widths, densities of states, 
and effective masses [41]. Among the possible approa-
hces to overcome these limitations, such as for example hybrid 
functionals, the quasiparticle GW method has emerged 
as one of the most reliable tools across the materials
spectrum, such as semiconductors, insulators, and met-
als, bulk systems, as well as surfaces and interfaces [28–

31]. In this method, the exchange-correlation potential 
V_{xc} is replaced by the system’s self-energy \Sigma, and the 
QP energies are obtained by performing a perturbative 
expansion of \Sigma and the dielectric function \epsilon. By do-
ing so, this method is free of the previously mentioned
self-interactions and also reproduces the nonanalytic 
behavior when the particle number changes.[42] This per-

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All these advantages, however, require a considerably
heavier computational workload compared to DFT meth-
ods. Specifically, traditional GW approaches show a very
slow convergence with respect to unoccupied Kohn-Sham
states [46]. To deal with these issues, Refs. 32 and 33
developed a method to calculate the self-energy without
the need to consider unoccupied states. In this approach,
both the Green’s function and the screened Coulomb in-
teraction are determined by evaluating the Sternheimer 
equations in linear response [47–49], as originally pro-
posed in Ref. 50 and also demonstrated in Refs. 51 and
52. To this end, the Green’s function G(r, r’; \omega) and
the screened Coulomb interaction W(r, r’; \omega) are written as
functions of r’, and the space variable r and the frequency
\omega are considered as parameters.[53] The Green’s function
is given by

\[ \left( \hat{H} - \omega \right) G_{r, \omega} = -\delta_r , \]  

where \hat{H} represents the effective single-particle Hamilto-
nian. To obtain the first-order variations to the occupied 
electron states \Delta \psi_{\nu}^{\pm}[r, \omega] corresponding to the perturbation
\Delta V_{[r, \omega]}(r’), one has to evaluate the two Sternheimer 
equations:

\[ \left( \hat{H} - \epsilon_\nu \pm \omega \right) \Delta \psi_{\nu[r, \omega]}^{\pm} = - \left[ \theta(\epsilon_\nu - \hat{P}_\nu) \right] \Delta V_{[r, \omega]} \psi_{\nu[r, \omega]}^{\pm} . \] 

Here, the operator \hat{P}_\nu projects onto the subspace of occupied
states, with the index \nu running over only occupied
electron states. \theta(\epsilon_\nu) accounts for the partial occupation
in the case of a metallic system [54]. The first-order vari-
ation within the random-phase approximation (RPA) to

Figure 1. Ball-and-stick model of the unit cell of 2H-NbS2. 
Nb atoms are shown in red, and S atoms in green.
the single-particle density matrix $\Delta n_{\mathbf{r},\omega}$ reads

$$\Delta n_{\mathbf{r},\omega} = 2 \sum_{\nu} \psi_\nu^+ \left( \Delta \psi_\nu^+ + \Delta \psi_\nu^- \right). \tag{3}$$

In Eq. (3), the prefactor 2 takes into account the spin degeneracy and the superscript $+(-)$ refers to the positive (negative) frequency component of the induced charge. In the case of the perturbation being set to the bare Coulomb interaction, i.e., $\Delta V_{\mathbf{r},\omega}(\mathbf{r}') = \nu(\mathbf{r}, \mathbf{r}')$, the variation of the density matrix can be related to the dielectric matrix via [32]

$$\epsilon(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r}, \mathbf{r}') - \Delta n_{\mathbf{r},\omega}, \tag{4}$$

and the screened Coulomb interaction $W$ can then be obtained by inverting this matrix,

$$W(\mathbf{r}, \mathbf{r}', \omega) = \int d\mathbf{r}'' \nu(\mathbf{r}, \mathbf{r}'') \epsilon^{-1}(\mathbf{r}'', \mathbf{r}', \omega). \tag{5}$$

Another possibility to solve the Sternheimer equations would be to set the perturbation $\Delta V_{\mathbf{r},\omega}(\mathbf{r}') = W(\mathbf{r}, \mathbf{r}', \omega)$, in which case the variation of the density yields a Hartree potential screening of the bare Coulomb interaction. The disadvantage of this approach is that Eq. (2) then needs to be solved self-consistently. For small systems, as for example the NbS$_2$ compounds considered in this work, the direct method outlined in Eqs. (4) and (5) is advantageous, due to the fact that the inversion of $\epsilon$ can be performed without a significant computational overhead. On the other hand, the self-consistent approach lends itself to being employed for larger systems and in cases where memory restrictions need to be met.

In short, the Sternheimer GW method has the advantages (i) to be able to disregard all unoccupied states from the calculation, which often cause convergence problems in conventional GW approaches [55], (ii) an improved accuracy with a similar or even smaller workflow compared to traditional GW methods, and (iii) the fact that a single parameter, i.e., the kinetic-energy cutoff of the inverse dielectric matrix, controls the QP energy convergence. The above procedure also provides the complete Green’s function and screened Coulomb interaction, which enables the calculation of the complete self-energy.

In the following, we will report the results of GW calculations for bulk and monolayer NbS$_2$. These calculations have been performed at the $G_0W_0$ level with the SternheimerGW code [56]. We recalculated the Fermi level using the $G_0W_0$ quasiparticle eigenvalues to ensure the number of electrons is conserved [57]. We employed the RPA for the density response, and the frequency integration has been performed using the Godby-Needs plasmon-pole approximation [58], using an imaginary pole energy of 4 eV. The frequency integration was performed on the imaginary axis and the self-energy on the real axis was obtained with an analytic continuation using Padé approximants of order 11 [32, 33, 59]. We employed scalar-relativistic optimized norm-conserving pseudopotentials [60] including the semi-core electrons of Nb. We used the LDA exchange-correlation functional [61] in the Perdew-Zunger (PZ) parametrization [62] and an electronic smearing of 5 mRy. Our convergence studies, which we report in detail in Appendixes C and D, show that the following parameters are sufficient to describe the electronic states with an accuracy of $\sim 100$ mRy.

For bulk NbS$_2$ we employed a kinetic-energy cutoff for the plane waves of the ground-state DFT calculation of 40 Ry (cf. Appendix C1), a $12 \times 12 \times 4$ k mesh (cf. Appendix C2), an energy cutoff of 10 Ry for the dielectric matrix (cf. Appendix C3), and an energy cutoff of 25 Ry for the exchange part of the self-energy (cf. Appendix C4). For monolayer NbS$_2$ we employed a kinetic-energy cutoff for the plane waves of the ground-state DFT calculation of 40 Ry (cf. Appendix D1), a $24 \times 24 \times 1$ k mesh (cf. Appendix D2), an energy cutoff of 10 Ry for the dielectric matrix (cf. Appendix D3), and an energy cutoff of 25 Ry for the exchange part of the self-energy (cf. Appendix D4).

We calculated the QP corrections to the Kohn-Sham eigenvalues for the bulk structure for a $6 \times 6 \times 2$ Brillouin-zone (BZ) grid and used maximally localized Wannier functions [63–65] to interpolate this data onto a fine 60 × 60 × 20 BZ grid. For the monolayer, we interpolated from a coarse $8 \times 8 \times 1$ BZ grid to a fine 160 × 160 × 1 BZ grid. In the case of the monolayer, the Coulomb interaction has been truncated in the z direction to account for the two-dimensional nature of the system.

III. RESULTS AND DISCUSSION

A. Bulk NbS$_2$

At first, we want to take a close look at the electronic band structures in the bulk compound. Compared to the LDA electronic structure, the inclusion of many-body interaction effects slightly increases the bandwidth of bulk $2H$-NbS$_2$ for the electronic states up to $\pm 7$ eV around the Fermi level [cf. Fig. 2(a)]. This increase originates mainly from the unoccupied bands being pushed to higher energies. We observe that at the $\Gamma$ point, the S $p_z$ and the Nb $d_{z^2}$ states are pushed apart by the inclusion of electron-electron interactions. This is in contrast to the LDA case, where they are very close in energy. The single electron band crossing the Fermi level around the M point within LDA, which is of in-plane Nb $d_{xy}/d_{x^2−y^2}$ orbital character, is renormalized to lower energies. We will discuss the resulting change of the topology of the Fermi surface in more detail later in this paper. For the time being we only mention that the changes to the electronic structure, mostly around the M point, lead to a decrease of the DOS at the Fermi level by 18% [Fig. 2(d)]. As is pointed out in Ref. 27, this leads to a decreased electron-phonon coupling, and in turn to a lower critical superconducting temperature in this compound. At the
is not explicitly $k$ dependent, which is in first approximation true for the Fermi-surface bands in NbS$_2$. $Z_{n,k}$ can be related to the velocity renormalization [67] via $1 - Z_{n,k}^{-1} = (v_{n,k} - v_{n,k}^0) / v_{n,k}$, with $v_{n,k}$ and $v_{n,k}^0$ being the interacting and noninteracting electron velocity, respectively. For bulk NbS$_2$, we find a renormalization of the electron velocity at the Fermi level of around $-51\%$. The Fermi velocity, as well as the mass renormalization around the Fermi level and the size of the Fermi surfaces, would be experimentally accessible by quantum oscillation measurements, like the de Haas van Alphen effect [68]. However, we are not aware of any such measurements for NbS$_2$.

Plotting the QP corrections as function of the LDA eigenenergies, as depicted in Fig. 3(c), shows that the states above the Fermi level are experiencing a larger shift due to the inclusion of many-body perturbations compared to those below the Fermi level.

In Fig. 4, we compare the QP band structure with ARPES measurements from Ref. 35. We combined the reported experimental results obtained with horizontally and vertically polarized photons in Fig. 4(b). In order to account for the finite resolution in experiment, we broadened our band structure with Lorentzians with an energy-dependent full width at half maximum $\Gamma$, i.e., $\Gamma = \gamma |E - E_F| + \Gamma_0$ with $\gamma = 0.15$ and $\Gamma_0 = 0.15$ eV, to approximately match the experimental broadening. Our calculations agree with the ARPES measurements, reproducing all the major features observed in the experiments. In particular, the two excitations slightly above and below $-2$ eV at $\Gamma$ and their further dispersion in the direction of the $K$ point match the measurements nicely, as do the two partly occupied bands close to the Fermi level. The $S_{p_z}$ band seems not to be visible in the ARPES data, probably due to a vanishing transition matrix element for the incident light beam. We further observe that a rigid shift of the Fermi level by $300$ meV would bring the calculations in excellent agreement with the experiments, as shown in Fig. 4(c).

This energy shift corresponds to adding $0.47$ electrons per formula unit (f.u.) to the system, and could be explained by intrinsic doping effects or an imperfect stoichiometry of the sample. For example, the stoichiometry Nb$_{1.05}$S$_2$ would match the observed shift of $300$ meV. Taking into account the accuracy of our GW calculations ($\sim 100$ meV) and possible shifts in the band structure due to electron-phonon interaction ($\sim 50$ meV) in the most favorable way, our calculations would also be in agreement with a stoichiometry of Nb$_{1.05}$S$_2$. These compositions for Nb$_{1.05}$S$_2$ are well within a range that has been realized in experiments [69]. Another possible source for the observed energy shift could be due to the fact that the $G_0W_0$ approach employed here is not a fully self-consistent method, hence the starting point of the calculation, i.e., the choice of the DFT functional, can be expected to slightly affect our results. Furthermore, as mentioned before, the $G_0W_0$ method does not conserve the particle number and the Fermi energy has

$K$ point, we find that the unoccupied Nb $d_{xy/z^2-y^2}$ band is pushed to higher energies.

To better distinguish between the different effects the GW corrections have on the DFT electronic structure, we show the exchange-correlation potential $V_{xc}$, the exchange and correlation parts of the self-energy, $\Sigma_x$ and $\Sigma_c$ respectively, as well as the QP strength $Z_{n,k} = (1 - \partial \text{Re} \Sigma_{n,k} / \partial E)^{-1}$ and the QP correction (before the Wannier interpolation) as a function of the DFT eigenvalues in Fig. 3. The data points belonging to the Fermi-surface bands have been colored according to their largest orbital contribution, as detailed in Fig. 2. While $V_{xc}$ is in very good approximation decreasing linearly with increasing DFT eigenvalue, $\Sigma_x$ is increasing with an abrupt change around the DFT Fermi level, as depicted in Figs. 2(a) and 2(b) respectively. It is worth noting that $\Sigma_x$ follows the standard trend of the exchange self-energy for the homogeneous electron gas, as is typical for metals exhibiting superconducting or magnetic phases at low temperatures [66]. The reverse trend to $\Sigma_x$ is found for $\text{Re} \Sigma_c$, as shown in Fig. 3(c).

We find that in our calculations $Z_{n,k}$ ranges from 0.54 to 0.71, showing that GW corrections decrease the QP strength considerably. In the case that the self-energy

![Figure 2](image.png)

Figure 2. Comparison of the band structure (a), (c) and DOS (b), (d) of bulk 2H-NbS$_2$ on the level of DFT (dashed magenta) and with GW renormalization (solid black). In (c) and (d) we additionally provide the projection of the electronic states onto the S $p_z$ (blue), the out-of-plane Nb $d_{z^2}$ (green), and the in-plane Nb $d_{xy/z^2-y^2}$ (red) orbitals.
In the following, we want to take a detailed look at the changes of the Fermi surface, once GW corrections are taken into account. In Fig. 5 we illustrate the three sheets forming the Fermi surface: a disk-shaped pocket centered at the Γ point (S\textsubscript{Γ}\textsubscript{1}) originating from S\textsubscript{pz} orbitals; another Γ centered, tube-shaped pocket (S\textsubscript{Γ}\textsubscript{2}) of Nb\textsubscript{d\textsubscript{z}^2} character; and a K-centered, triangular-shaped pocket (S\textsubscript{K}). The latter has Nb\textsubscript{d\textsubscript{z}^2} character at the M point, but changes gradually to Nb\textsubscript{d\textsubscript{xy}/\textsubscript{dx^2−y^2}} when moving along the surface. When electron-electron interactions are taken into account at the level of GW [Fig. 5(b)], S\textsubscript{Γ}\textsubscript{1} shrinks considerably, while S\textsubscript{Γ}\textsubscript{2} becomes more rounded and grows in diameter. Another important aspect of many-body corrections is the fact that the triangular S\textsubscript{K} no longer extends up to the M point and it is no longer connected to the neighboring S\textsubscript{K} Fermi surfaces.

In order to compare our Fermi surfaces with those from experiments, we broaden the QP energies close to the Fermi level by a Lorentzian with an energy-dependent width, as detailed before, to mimic the energy and momentum resolution of ARPES measurements (Fig. 6). As the experiments do not resolve the out-of-plane component, we also average over k\textsubscript{z}. Independent of the method, the S\textsubscript{Γ}\textsubscript{1} Fermi surface is indiscernible from the background, in agreement with experiments [35], where the polarization of the incident beam probably has vanishing dipole matrix elements with the p\textsubscript{z} orbitals, as mentioned before. Only the Nb d orbitals provide visible contributions to the Fermi surface, and due to the more rounded and disconnected S\textsubscript{K} Fermi surface, the GW calculation yields a better agreement with ARPES measurements than the LDA. Again, by rigidly shifting our GW results by 300 meV, as shown in Fig. 6(c), we obtain very good agreement with experiments.

B. Monolayer NbS\textsubscript{2}

We now want to focus our attention on the monolayer of NbS\textsubscript{2}. In contrast to the bulk, the monolayer is comprised of only one formula unit, and due to the fact that
Figure 6. Fermi surfaces of bulk NbS$_2$ calculated within LDA (a) and GW (b), broadened with Lorentzians and averaged over $k_z$. In panel (c), we have shifted the Fermi level by 300 meV, corresponding to the electronic states shown in Fig. 4(c). For comparison with experiments, the measured ARPES Fermi surface from Ref. 35 is reproduced in panel (d). Panel (d) is reprinted with permission from Ref. 35. Copyright (2016) by the American Physical Society.

Figure 7. Comparison of the band structure (a), (c), and DOS (b), (d) of monolayer $2H$-NbS$_2$ on the level of LDA (dashed magenta) and with GW renormalization, neglecting and including substrate effects (solid black and dotted blue lines, respectively). In (c), the orbital contributions of the out-of-plane Nb $d_{z^2}$ and in-plane Nb $d_{xy/d_{x^2-y^2}}$ are given by the size of the colored markers in green and red, respectively. The results of this calculation are shown as solid black lines in Fig. 7, where one can observe a considerable reduction of the GW corrections. This becomes even more apparent when looking at $V_{xc}$, $\Sigma_x$, $\text{Re}[\Sigma_x(E_0)]$, $Z_{n,k}$, and the QP corrections, as provided in Fig. 8, where the results of the calculations with (without) substrate are shown as circles (squares). The overall behavior of these quantities as a function of the respective DFT eigenvalues is very similar to the bulk case, i.e., $V_{xc}$ is in good approximation linearly decreasing with increasing $E_0$, while $\Sigma_x$ is increasing with a steep slope for values close to $E_F$, closely following the trend of a homogeneous electron gas [66]. The reverse trend of $\Sigma_x$ is found for...
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want to mention at this point that our calculations for monolayer NbS2 are in

good agreement with those presented in Ref. 34 for mono-

LDA eigenvalues, as shown in Fig. 8(e). We

ascribe this behavior to the fact that the Coulomb inter-
nation of the LDA eigenvalues, as shown in Fig. 8(e). We

also observe that a Fermi-level shift of 300 meV

we proposed that such a shift could arise from unintentional doping in the experimen-

tal sample.

For the monolayer system, we observe a strong in-
crease of the screened Coulomb interaction as compared to bulk due to its two-dimensional nature, and we have

shown that the consideration of a substrate via changing the dielectric constant on one side of the monolayer re-

sults in a marked reduction of the interaction potential and the effects of the many-body corrections. When we

take into account the screening from the substrate, the
electronic bandwidth is smaller than in the free-standing case, and the DOS at the Fermi level is larger. This in

turn also means that the electron-phonon coupling and superconducting properties will be sensitive to the choice

of substrate. As another example of the importance of substrate effects, we find that the ratio of the effective

masses is 1.7 times larger for the NbS2 monolayer on a substrate compared to the free-standing monolayer. As

we are not aware of any experimental work on monolayer NbS2, these calculations provide a first insight into the

electronic properties of this compound beyond DFT.

In summary, this work highlights the importance to in-
clude many-body perturbation theory corrections in the study of metallic TMDs. These corrections will lead to

improved carrier velocities and densities of states, and are crucial for a more accurate understanding of charge

transport and superconductivity in these compounds.

IV. CONCLUSIONS

In this work, we employed the Sternheimer GW method to perform a detailed investigation of the electronic prop-
erties of bulk and monolayer NbS2, using many-body perturbation theory in the framework of the GW approxima-
tion. We document in the appendixes convergence stud-
ies for the monolayer on a substrate and the steeper electron bands around the Fermi level. The Fermi surface do-

not change when comparing the free-standing monolayer with the monolayer on a substrate.

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tific Cluster (VSC), and the Cambridge Service for
Figure 8. (a) Exchange-correlation potential $V_{xc}$, (b) exchange-part $\Sigma_x$ of the self-energy, (c) real part of the correlation self-energy $\Sigma_c$ at the DFT eigenvalues $E_0$, (d) QP renormalization factor $Z_{n,k}$, and (e) QP corrections of monolayer NbS$_2$ for all $k$ points of the coarse Wannier grid as a function of $E_0$ for the free-standing monolayer (squares) and with considered substrate (circles). The data points that belong to the Fermi-surface bands have been colored according to their largest orbital character (cf. Fig. 7), and the dashed red line in panel (e) serves as a guide to the eye.

Figure 9. Spectral function for a monolayer of NbS$_2$ with (left) and without (right) substrate, along the high-symmetry $\Gamma$-$K$ path. The GW quasiparticle peaks are broadened using Lorentzians of energy-dependent width.

Figure 10. Fermi surfaces for monolayer NbS$_2$, calculated within LDA (a) and GW (b), where the band structure has been broadened with Lorentzians. The effects of a substrate on the GW Fermi surface are negligible (not shown).

Appendix A: Effect of SOC

In Figs. 11 and 12 we provide a comparison of the DFT band structure with (dashed blue) and without (solid red) SOC for bulk and monolayer NbS$_2$, respectively. For these calculations, fully relativistic optimized norm-conserving Vanderbilt pseudopotentials [79, 80] within PZ [62] that include the semi-core electrons of Nb have been used. As one can see, SOC leads to band splittings around the $K$ point. For the bulk, we calculate a splitting of $\sim 74$ meV and for the free-standing monolayer a splitting of $\sim 52$ meV. These values are within the accuracy of our GW results, and are therefore neglected.

Appendix B: Effect of van der Waals corrections

In this appendix we discuss the effects of including van der Waals corrections on the band structure of bulk NbS$_2$. In Fig. 13, we show as solid black lines the band structure at the level of GW without considering vdW effects, while for the dashed magenta line we have included vdW interactions according to the semiempirical Grimme D2 corrections [81]. As can be appreciated in this figure, the changes to the band structure are small, and the DOS in the low-energy range is almost identical. The most marked difference is the fact that with vdW corrections, the S $p_z$ close to the $\Gamma$ point falls below the Fermi energy.

This can also be observed in Fig. 14, where we show the GW spectral function with and without vdW corrections during the structure optimization. Apart from the QP band coming from S $p_z$ states, the two spectral functions are almost indistinguishable.

Moving on to the Fermi surfaces shown in Fig. 15, we find that, apart from very small, the structure optimized with vdW corrections leads to very similar results for the GW spectral function at low energies.
Appendix C: Convergence studies for bulk NbS$_2$

1. Plane wave cutoff for ground state DFT calculations

First, we test the convergence of our $GW$ calculations with respect to the kinetic-energy cutoff $E_k$ for the plane waves used in the ground-state DFT calculation. We report the results of this study in Table I, where we show the inverse of the diagonal element of the dielectric matrix $\epsilon_i = \epsilon_{G_i, G_i}(\mathbf{q}, \omega)$ with $G_i = (i, 0, 0)2\pi/a$, evaluated at $\mathbf{q} = \Gamma$ and $\omega = 0$.

In Table II, we show the values of $\Sigma_x$ of the four QP states at $\Gamma$ closest to the Fermi level as a function of the cutoff value. As one can see, our target accuracy of $< 100$ meV is already met for 30 Ry. The maximum deviation falls below 30 meV for a cutoff of 40 Ry.

2. Brillouin zone sampling

In Sternheimer$GW$, there are three BZ grids to consider: (i) the grid used to sample the exchange, (ii) the grid used to sample the correlation, and (iii) the grid used to sample the dielectric response (in our calculations, this grid is set to be the same as for the exchange). The dependence of the correlation part of the self-energy on the number of points used to sample the Brillouin zone is shown in Fig. 16, where we plot the inverse of the first four diagonal elements of $\epsilon_i = \epsilon_{G_i, G_i}(\mathbf{q}, \omega)$ with $G_i = (i, 0, 0)2\pi/a$ evaluated at $\mathbf{q} = \Gamma$ and $\omega = 0$.

While the convergence of the correlation part is quite
Figure 13. Band structure of bulk NbS$_2$ with included GW corrections, where the structure has been optimized at the DFT level with (dashed, magenta) and without (black, solid) van der Waals corrections.

Figure 14. Comparison of the GW spectral function of bulk NbS$_2$ (a) without and (b) with vdW corrections during the structure optimization. The spectral functions have been calculated by broadening the QP energies with a Lorentzian of energy-dependent width, as in Fig. 4.

Figure 15. GW Fermi surfaces of bulk NbS$_2$ calculated (a) without and (b) with van der Waals corrections during the structure optimization. The spectral functions have been calculated by broadening the QP energies with a Lorentzian of energy-dependent width, as in Fig. 6.

Table II. $\Sigma_x(\mathbf{k})$ of the four electronic states closest to the Fermi energy at $\mathbf{k} = \Gamma$ (at the DFT level) as a function of the kinetic-energy cutoff $E_k$ for the plane waves of the DFT ground-state calculation. For these calculations, we used an $8 \times 8 \times 4$ k grid, an energy cutoff in the dielectric matrix of 10 Ry, and an energy cutoff of 20 Ry in the exchange part of the self-energy.

| $E_k$ (Ry) | band 1 (eV) | band 2 (eV) | band 3 (eV) | band 4 (eV) |
|---|---|---|---|---|
| 30 | -16.83 | -11.61 | -13.70 | -10.77 |
| 40 | -16.82 | -11.55 | -13.73 | -10.72 |
| 50 | -16.82 | -11.52 | -13.75 | -10.71 |
| 60 | -16.81 | -11.51 | -13.75 | -10.70 |
| 70 | -16.82 | -11.51 | -13.75 | -10.70 |

Figure 16. The inverse of the first four diagonal elements of $\epsilon_i = \epsilon_{G_i,0}^{\mathbf{q}=\mathbf{q}}(\mathbf{q},\omega)$ with $G_i = (i,0,0)2\pi/a$, evaluated at $\mathbf{q} = \Gamma$ and $\omega = 0$, as a function of the number of $\mathbf{k}$ points. The vertical dashed line indicates the value for the $12 \times 12 \times 4$ BZ grid used in the final calculations.

smooth, the exchange part of the self-energy is more difficult to converge with respect to the number of BZ points. We notice that achieving convergence for the two bands closest to the Fermi level is particularly difficult, while the convergence of the other states is very fast. In Fig. 17 we show $\Sigma_x$ at $\Gamma$ as a function of the number of BZ points $n_k$, where we have connected with a blue line those points that have a common $n_{k_x,y}/n_{k_z} = 3$ ratio, similar to the lattice vector lengths’ ratio. The vertical dashed lines indicate the values for a $27 \times 27 \times 9$ BZ grid, which we consider converged. The large deviations between single points and the bulging downwards of the blue curve are largely due to finite-size effects coming from the $k_z$ sampling. As calculations for a $27 \times 27 \times 9$ grid are at the moment not feasible, we chose a $12 \times 12 \times 4$ grid that allows for reasonably fast calculations while still maintaining an accuracy of $< 100$ meV relative to the $27 \times 27 \times 9$ grid.
Figure 17. $\Sigma_x$ at $\Gamma$ of the four electronic states closest to the Fermi energy (at DFT level) as a function of the number of BZ grid points. The vertical dashed line indicates the value for the $12 \times 12 \times 4$ k grid used in the final calculations. Data points that have a common ratio $n_{k_x,y}/n_{k_z} = 3$ are connected with a blue line.

3. Energy cutoff $E_c$ for the correlation part of the self-energy $\Sigma_x$

In Table III we report the convergence of the diagonal elements of the screened Coulomb interaction matrix $W_i = W_{G_i,G_i}(q,\omega)$ with $G_i = (i,0,0)2\pi/a$, evaluated at $q = \Gamma$ and $\omega = 0$, as a function of the energy cutoff $E_c$ of the dielectric matrix.

Table III. Diagonal elements of the screened Coulomb interaction $W_i = W_{G_i,G_i}(q,\omega)$ with $G_i = (i,0,0)2\pi/a$, evaluated at $q = \Gamma$ and $\omega = 0$, as a function of the energy cutoff $E_c$ for the dielectric matrix. For these calculations, we used an $8 \times 8 \times 4$ k grid and a plane-wave cutoff of 40 Ry.

| $E_c$ (Ry) | $W_2$ | $W_4$ | $W_{10}$ | $W_{14}$ |
|-----------|-------|-------|----------|----------|
| 6         | -0.9013 | -0.6964 | -0.5344 | -0.5071 |
| 8         | -0.9010 | -0.6961 | -0.5337 | -0.5066 |
| 10        | -0.9008 | -0.6950 | -0.5334 | -0.5065 |
| 12        | -0.9006 | -0.6944 | -0.5333 | -0.5064 |
| 14        | -0.9006 | -0.6940 | -0.5335 | -0.5063 |
| 16        | -0.9005 | -0.6936 | -0.5331 | -0.5064 |

In Table IV we show the convergence behavior of the $GW$ quasiparticle energies at $\Gamma$ closest to the DFT Fermi energy as a function of the energy cutoff $E_c$ for the dielectric matrix. The convergence is relatively fast, allowing us to choose a value of 10 Ry for all subsequent calculations.

Table IV. Quasiparticle eigenvalues of the four electronic states at $\Gamma$ closest to the Fermi energy (at DFT level) as a function of the energy cutoff $E_c$ for the dielectric matrix. For these calculations, we used an $8 \times 8 \times 4$ k grid, a plane-wave cutoff of 40 Ry, and an energy cutoff for the exchange part of 20 Ry.

| $E_c$ (Ry) | band 1 (eV) | band 2 (eV) | band 3 (eV) | band 4 (eV) |
|-----------|-------------|-------------|-------------|-------------|
| 6         | 7.67        | 14.26       | 11.61       | 16.56       |
| 8         | 8.28        | 9.47        | 10.78       | 12.00       |
| 10        | 8.27        | 9.43        | 10.56       | 11.70       |
| 12        | 8.24        | 9.39        | 10.40       | 11.54       |
| 14        | 8.20        | 9.36        | 10.31       | 11.44       |
| 16        | 8.19        | 9.34        | 10.26       | 11.41       |

4. Energy cutoff $E_x$ for the exchange part of the self-energy $\Sigma_x$

In order to test the dependence of our results on the energy cutoff $E_x$ of the exchange part of the self-energy, we again inspected its values for electronic states closest to the Fermi level at the $\Gamma$ point (see Table V). While the deviations between calculations with cutoffs of 20 and 35 Ry are larger than 100 meV for three of the bands, these discrepancies are reduced to $< 50$ meV if a cutoff of 25 Ry is chosen.

Table V. $\Sigma_x(k)$ of the four electronic states at $\Gamma$ closest to the Fermi energy (at DFT level) as a function of the energy cutoff $E_x$. For these calculations, we used an $8 \times 8 \times 4$ k grid, an energy cutoff in the dielectric matrix of 10 Ry, and a plane-wave cutoff of 40 Ry.

| $E_x$ (Ry) | band 1 (eV) | band 2 (eV) | band 3 (eV) | band 4 (eV) |
|-----------|-------------|-------------|-------------|-------------|
| 20        | -16.81      | -11.51      | -13.75      | -10.70      |
| 25        | -16.88      | -11.61      | -13.77      | -10.80      |
| 30        | -16.90      | -11.65      | -13.78      | -10.84      |
| 35        | -16.91      | -11.66      | -13.78      | -10.85      |

Appendix D: Convergence studies for monolayer NbS$_2$

1. Plane wave cutoff for ground state DFT calculations

In Table VI we report the convergence of the diagonal elements of the screened Coulomb interaction $W_i = W_{G_i,G_i}(q,\omega)$ with $G_i = (i,0,0)2\pi/a$, evaluated at $q = \Gamma$ and $\omega = 0$, as a function of the kinetic-energy cutoff $E_k$ for the plane waves of the DFT ground-state calculation, and in Table VII the convergence of $\Sigma_x(k)$ for the three electronic states at $k = \Gamma$ closest to the Fermi energy. The convergence with respect to the kinetic-energy cut-
off is quite fast, allowing us to choose a value of 40 Ry to achieve an accuracy < 100 meV.

The screened Coulomb interaction $W_i = W_{G,G_i}(q,\omega)$ with $G_i = (i,0,0)2\pi/a$, evaluated at $q = \Gamma$ and $\omega = 0$, as a function of the kinetic energy cutoff $E_k$ for the plane waves of the DFT ground state calculation. For these calculations, we used a $24 \times 24 \times 1$ k-grid, an energy cutoff in the dielectric matrix of 10 Ry and an energy cutoff of 20 Ry in the exchange part of the self-energy.

| $E_k$ (Ry) | $W_2$ (eV) | $W_4$ (eV) | $W_6$ (eV) |
|-----------|------------|------------|------------|
| 20        | -0.6721    | -0.2595    | -0.2423    |
| 30        | -0.6741    | -0.2600    | -0.2433    |
| 40        | -0.6737    | -0.2598    | -0.2430    |
| 50        | -0.6735    | -0.2598    | -0.2429    |
| 60        | -0.6734    | -0.2597    | -0.2428    |

2. Brillouin zone sampling

In Table VIII we report the convergence of diagonal elements of the screened Coulomb interaction $W_i = W_{G,G_i}(q,\omega)$ with $G_i = (i,0,0)2\pi/a$, evaluated at $q = \Gamma$ and $\omega = 0$, as a function of the number of BZ-points $n_k$ used to sample the Brillouin zone. For these calculations, we used an energy cutoff in the dielectric matrix of 10 Ry and an energy cutoff of 20 Ry in the exchange part of the self-energy.

| $n_k$ (Ry) | $W_2$ (eV) | $W_4$ (eV) | $W_6$ (eV) |
|------------|------------|------------|------------|
| 8^2        | -0.6788    | -0.2600    | -0.2431    |
| 12^2       | -0.6711    | -0.2596    | -0.2429    |
| 16^2       | -0.6723    | -0.2597    | -0.2430    |
| 20^2       | -0.6736    | -0.2598    | -0.2430    |
| 24^2       | -0.6737    | -0.2598    | -0.2430    |
| 28^2       | -0.6737    | -0.2599    | -0.2430    |
| 32^2       | -0.6738    | -0.2599    | -0.2430    |
| 36^2       | -0.6738    | -0.2599    | -0.2430    |

Figure 18. $\Sigma_e(k)$ of the three electronic states at $k = \Gamma$ closest to the Fermi energy (at DFT level) as a function of the number of BZ points $n_k$. The vertical dashed line indicates the value for the $24 \times 24 \times 1$ BZ grid used in the final calculations.

3. Energy cutoff $E_c$ for the correlation part of the self-energy $\Sigma_c$

In Table IX we report the convergence of diagonal elements of the screened Coulomb interaction $W_i = W_{G,G_i}(q,\omega)$ with $G_i = (i,0,0)2\pi/a$ evaluated at $q = \Gamma$ and $\omega = 0$, as a function of the energy cutoff $E_c$ for the dielectric matrix.

In Table X we show the convergence behavior of the $GW$ quasiparticle energies at $\Gamma$ closest to the DFT Fermi energy as a the energy cutoff $E_c$ for the dielectric matrix. Convergence is very fast, allowing us to choose a value of 10 Ry for the energy cutoff $E_c$. 

Table VII. $\Sigma_e(k)$ of the three electronic states at $k = \Gamma$ closest to the Fermi energy (at DFT level) as a function of the kinetic-energy cutoff $E_k$ for the plane-waves of the DFT ground state calculation. For these calculations, we used a $12 \times 12 \times 1$ k grid and an energy cutoff in the dielectric matrix of 10 Ry.

| $E_k$ (Ry) | band 1 (eV) | band 2 (eV) | band 3 (eV) |
|-----------|------------|------------|------------|
| 20        | -16.03     | -9.82      | -10.29     |
| 30        | -16.04     | -9.87      | -10.34     |
| 40        | -16.03     | -9.84      | -10.30     |
| 50        | -16.02     | -9.82      | -10.29     |
| 60        | -16.02     | -9.81      | -10.28     |
Table IX. Diagonal elements of the screened Coulomb interaction $W_i = W_{G_i, G_i}(q, \omega)$ with $G_i = (i, 0, 0) 2\pi/a$, evaluated at $q = \Gamma$ and $\omega = 0$, as a function of the energy cutoff $E_c$ for the dielectric matrix. For these calculations, we used a $24 \times 24 \times 1 \mathbf{k}$ grid and a plane-wave cutoff of 40 Ry.

| $E_c$ (Ry) | $W_2$  | $W_4$  | $W_6$  |
|-----------|--------|--------|--------|
| 6         | -0.6575| -0.2487| -0.2043|
| 8         | -0.6571| -0.2485| -0.2042|
| 10        | -0.6569| -0.2484| -0.2041|
| 12        | -0.6568| -0.2484| -0.2041|
| 14        | -0.6568| -0.2484| -0.2041|

Table X. Quasiparticle eigenvalues of the three electronic states at $\Gamma$ closest to the Fermi energy (at DFT level) as a function of the energy cutoff $E_c$ for the dielectric matrix. For these calculations, we used a $12 \times 12 \times 1 \mathbf{k}$ grid, a plane-wave cutoff of 40 Ry, and an energy cutoff for the exchange part of 20 Ry.

| $E_c$ (Ry) | band 1 (eV) | band 2 (eV) | band 3 (eV) |
|-----------|-------------|-------------|-------------|
| 6         | -2.77       | 0.89        | 3.29        |
| 8         | -2.78       | 0.65        | 2.93        |
| 10        | -2.81       | 0.44        | 2.71        |
| 12        | -2.87       | 0.30        | 2.57        |
| 14        | -2.92       | 0.19        | 2.46        |
| 16        | -2.94       | 0.16        | 2.42        |

4. Energy cutoff $E_x$ for the exchange part of the self-energy $\Sigma_x$

In Table XI we report the convergence of $\Sigma_x(\mathbf{k})$ of the three electronic states at $\Gamma$ closest to the Fermi energy (at DFT level) as a function of the energy cutoff $E_x$. We find again that not the electronic state crossing the Fermi level, but the one below, shows the slowest convergence. Still, by choosing $E_x = 25$ Ry, we can achieve an accuracy of $< 50$ meV.

Table XI. $\Sigma_x(\mathbf{k})$ of the three electronic states at $\mathbf{k} = \Gamma$ closest to the Fermi energy (at DFT level) as a function of the energy cutoff $E_x$. For these calculations, we used a $12 \times 12 \times 1 \mathbf{k}$-grid, an energy cutoff in the dielectric matrix of 10 Ry and a plane wave cutoff of 40 Ry.

| $E_x$ (Ry) | band 1 (eV) | band 2 (eV) | band 3 (eV) |
|-----------|-------------|-------------|-------------|
| 15        | -15.80      | -9.47       | -9.97       |
| 20        | -16.03      | -9.84       | -10.30      |
| 25        | -16.11      | -9.93       | -10.40      |
| 30        | -16.14      | -9.96       | -10.43      |
| 35        | -16.14      | -9.97       | -10.44      |

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