Electronic properties of the FeSe/STO interface from first-principle calculations

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Abstract
We perform first-principle calculations of the FeSe monolayer on STO with the focus on three central aspects. First, compared to experiment, the bulk lattice constant of FeSe is too small in LDA, PBEsol and Perdew–Burgke–Ernzerhof (PBE) type exchange-correlation (xc) functionals while in bulk SrTiO3 (STO) LDA over-binds, PBE under-binds and PBEsol agrees best with experiment. Thus, the strain in the FeSe monolayer on STO depends on the xc functional and, especially in the non-magnetic state, is strongly overestimated and best described in PBEsol. In agreement with earlier work, we find that the band structure of the checkerboard antiferromagnetic configuration agrees best with experiment where, in addition, the relative strain on FeSe is best described. Second, our focus is on the crystal structure of the interface itself. The FeSe/STO distance depends weakly on the presence of magnetism and PBE results agree best with recent experimental data. We find that a double TiO2-layer below the FeSe relaxes to a structure in disagreement with experimental data. On the other hand, considering the effect of oxygen-vacancies in the single TiO2 terminated slab within the virtual crystal approximation, in agreement with recent experiment, the FeSe monolayer Ti layer distance increases for a small vacancy concentration (<20%). Third, we investigate the charge-transfer to FeSe due to oxygen-vacancies in STO. Interestingly, we find negligible charge transfer for small concentrations—only above 20% a significant charge transfer is observed.

Keywords: FeSe monolayer, superconductivity, ab initio calculations, oxygen vacancy, magnetism, charge transfer

(Some figures may appear in colour only in the online journal)

1. Introduction
The discovery of superconductivity (SC) in the single monolayer of FeSe on SrTiO3 has triggered an enormous excitement in the community, first because of the very high critical temperature \( T_c \) with an ARPES gap closing at \( \sim 65 \) K and second because the missing hole pocket at the Brillouin zone center. The absence of the hole pocket directly challenges the usual explanation of SC in the Fe-based superconductors by repulsive interactions that causes a sign changing gap function on the electron-like and the hole-like Fermi surface sheets of these materials [1–3]. Measurements of the anisotropy of the gap function on the remaining electron pocket have ruled out a dominant \( d \)-wave character [4, 5]. In the search for the origin of SC in this particular material it is worth noting that the electronic structure of the FeSe monolayer is very similar to the FeSe intercalates [6, 7] or the electron doped multi-layer surfaces [8] where one also finds a critical temperature of around 40–50 K with no apparent sign of attractive interactions in these systems. Thus, we are left with the challenge to explain an apparent \( s \)-wave gapped 40 K superconductor with repulsive interactions.

One suggested explanation, recently proposed by two groups [9, 10] is that \( s_{\pm} \) pairing survives, even though the hole band is \( \sim 60 \) meV below the Fermi level and thus ‘incipient’. So far, both groups have used a very simplified model of the electronic band structure. The position of the hole band extremum is crucial since with the supposedly strong interactions in these systems, a magnetic transition is induced as soon as it approaches the Fermi level. In experiment this position corresponds to the effective doping level that can be controlled either directly by potassium dosing [11] or liquid
gating techniques [12, 13] or, effectively, by annealing steps [3]. The doping in the latter case is discussed to be caused by the occurrence of oxygen vacancies in the interface [14–16]. While the cause for SC in the FeSe intercalates is likely of purely electronic origin, in the monolayer of FeSe on STO with a higher $T_c$, on the other hand, there have been clear signs of electron-phonon interactions. Reference [17] found replicas of the Fe d-orbital bands at the Fermi level which follow the dispersion of electronic bands with an energy offset of 100 meV, which matches the energy of one optical oxygen modes in the STO substrate. The occurrence of these replica bands can be explained by noting that the polar oxygen mode will induce a dipole coupling of the electronic states in FeSe. In the model of [17], the coupling away from zero momentum transfer falls of exponentially with a length scale controlled by the distance of the FeSe from the O ions in the STO substrate making the calculation of this parameter crucial [18].

As was pointed out by [17] such a small momentum or so called forward scattering coupling is attractive in almost all pairing channels. In line with this conclusion, [19] showed that such a low momentum transfer will induce only intra-band coupling which will further enhance a possible incipient $s_\pm$ pairing state. This can explain the further enhancement of $T_c$ in the monolayers as compared to the purely electronic systems. A further theoretical understanding of this mechanism and, in particular, an extension to a more realistic electronic structure using computational methods would be desirable.

Density functional methods [20, 21] have established a good starting point for realistic calculations in the Fe-based superconductors [22–24] (see [25] for a review). However, to accurately describe the electronic structure of most FeSe systems remains difficult. DFT calculations, in particular within the generalized gradient approximation, have a tendency to overestimate the magnetic moment [25, 26]. For example, LDA [27] and PBE [28] predict an antiferromagnetic ground state of bulk FeSe at the experimental lattice configurations while the system is paramagnetic in experiment. Performing a relaxation in the paramagnetic state leads to a strongly underestimated Fe–Se bonding length and van der Waals interactions are important to accurately predict the layer separation [28]. Also for bulk FeSe the electron and hole pockets turn out too large which may be explained by the underestimation of the repulsion between the electron and hole pockets within DFT [29].

In spite of these inaccuracies, several groups have calculated properties of the monolayer FeSe on STO from first principles. Reference [30] found that for a free standing layer the checkerboard antiferromagnetic structure agrees best with experiment. Shanavas et al [15] studied the FeSe monolayer while accounting for the STO substrate. They consider vacancies in the system by replacing 20% of the surface O with F to simulate oxygen vacancies on the level of a virtual crystal approximation (VCA). While this does induce a charge transfer to the surface, it is found that the Fe d orbitals that constitute the hole pocket remain at the Fermi level.

Reference [16] used a super-cell approach to discuss the effect of an oxygen vacancy on the band structure within the non-magnetic, the checkerboard- and the stripe antiferromagnetic ordering. The super-cell approach has been used before for to study the pure STO surface [31]. In a further step, Y Wang et al [32] computed the electron-phonon coupling in the Ti–O terminated slab and in a $2 \times 1$ super cell with an oxygen vacancy. While the focus of this work is on the resolution of the momentum dependence of the electron-phonon coupling, it is also found that the vacancy causes a stronger binding between the FeSe layer and the substrate. Moreover, Coh et al [33] and Li et al [34] have calculated the electron–phonon coupling of the interface and, recently, Coh et al [35] proposed a superstructure of this interface to further enhance the phonon coupling.

Most calculations in this context have used the Perdew–Burgke–Ernzerhof (PBE) density functional [36] and all studies seem to agree that introducing vacancies binds the FeSe layer closer to the substrate and electron-dopes the FeSe layer. In a recent experimental study [37], it was discovered that upon annealing where the system turns from non-superconducting to superconducting, the binding distance of the FeSe layer, in fact, increases. This finding is in contradiction to the theoretical calculations even though comparison is difficult because the actual vacancy content in experiment is not easily determined. Reference [37] suggests that the interface is, in fact, FeSe on STO terminated by a double layer of Ti–O. Moreover, the monolayer is shown to cover the STO substrate incommensurately.

It is known that PBE tends to overestimate the binding distance while LDA type functionals are known to underestimate it [38]. This insight seems particularly important because it is common practice to fix the $x–y$ lattice constant to experiment while one implicitly allows the $z$-direction relaxation of the slab since the cell contains a large part of vacuum. This may cause a very large non-uniaxial pressure in the calculations.

In this work, we revisit the bulk calculations for both STO and FeSe and point out that the mismatch of lattice constants in $x–y$ go into opposite directions—predicted lattice parameters within the layer are too small in FeSe while in STO they obey the usual trend. As we find that PBEsol [38] is best for STO and PBE in an antiferromagnetic state is best for FeSe we compute the interface in both functionals. As oxygen vacancies play a key role in this system, we further investigate the structure and the charge transfer as a function of vacancy content within the VCA which allows us to treat small vacancy concentrations. We find for low concentrations that the layer moves away from the substrate and the doping effect on Fe is small while for higher concentrations the bond length Se–Ti shortens and charge is transferred to the FeSe layer.

2. Computational details

We model the surface by placing an FeSe monolayer on a slab of three layers of SrTiO$_3$. Periodic replicas in $z$-direction are separated by $>10$ Å of vacuum to eliminate axillary interaction. All subsequent DFT calculations were performed with Quantum ESPRESSO [39] using ultra-soft GBRV pseudo
potentials [40]. Accurate convergence was achieved within a plane wave cutoff of 50 and 200 Ry for wave function and charge density unless otherwise noted. We sample the Brillouin zone using a $6 \times 6$ Monkhurst–Pack grid [41] with a Methfessel–Paxton smearing [42] of 0.02 Ry. We use a very strict condition of $5 \times 10^{-5}$ Ry au$^{-1}$ and $10^{-6}$ Ry for force and total energy convergence during relaxations. Especially when oxygen vacancies are considered, the asymmetric slab shows a dipole moment. In order to remove spurious interaction with the periodic replicas, an axillary compensating dipole is introduced in the vacuum. Reference [43] concluded that the the octahedral, ferro-electric distortion is suppressed near the surface and in general not important for the electronic structure. Based on this insight, we approximate the ferro-electric distorted STO with a cubic unit cell.

3. Bulk calculations

In preparation for the calculation of the FeSe monolayer on STO interface, we consider the individual bulk materials in this section. The cutoff for FeSe could be reduced to 45 and 180 Ry for wavefunction and charge density with a k point sampling of $6 \times 6 \times 4$ and $4 \times 4 \times 4$ for STO. We performed a relaxation for all three functionals while starting from a tetragonal phase in the non-magnetic (NM) phase or an orthorhombic and antiferromagnetically broken symmetry. The resulting structures are given in table 1. The relaxation within the LDA always lead to the non-magnetic structure, i.e. the broken symmetries were restored to numerical accuracy.

Results for STO are more in line with the usual hierarchy of bonding lengths where LDA underestimates, PBE overestimates and PBEsol is closest to experiment. In FeSe, however, all functionals underestimate the in-plane lattice constant, especially if the NM state is considered. Calculated lattice constants for LDA are in good agreement with earlier work [46]. Reference [28] finds that the stripe antiferromagnetic state, that has in fact the lowest energy, shows an even better agreement of the $a_{\text{FeSe}}$ and $b_{\text{FeSe}}$ lattice constants. However, since earlier work on the FeSe/STO

### Table 1. Structural parameters for the bulk materials cubic STO and FeSe for the three functional in comparison with experiment. For FeSe we allow a checkerboard antiferromagnetic order (AFM). Within LDA, the structure converged to one that has a non-magnetic (NM) ground state.

|          | LDA   | PBEsol | PBE   | Exp  |
|----------|-------|--------|-------|------|
|          | NM    | AFM    | NM    | AFM  |      |
| $a_{\text{STO}}[\text{Å}]$ | 3.842 | 3.892  | 3.937 | 3.907 [44] |
| $a_{\text{FeSe}}[\text{Å}]$ | 3.589 | 3.631  | 3.685 | 3.716 | 3.765 [45] |
| $b_{\text{FeSe}}[\text{Å}]$ | 3.589 | 3.623  | 3.685 | 3.709 | 3.754 [45] |
| $c_{\text{FeSe}}[\text{Å}]$ | 5.301 | 5.476  | 6.336 | 6.206 | 5.479 [45] |
| $\mu_{\text{Fe}}$ | 0     | 1.370  | 1.397 | 1.377 | 1.447 | 1.462 [45] |

Figure 1. Relaxed structure of the double Ti–O layer within PBE on the left and with the single layer Ti–O terminated slab on the right. Parts of the cell on the top that contain vacuum are removed from the plot.

Figure 2. Total energy difference of the slab as a function of $x – y$ compression for the xc-functionals LDA, PBEsol and PBE. The total energy depends quadratically (fit) on the lattice constant and reaches its minimum at $a_{\text{lat}} = 3.822$, 3.847 and 3.880 Å for LDA, PBEsol and PBE, respectively. The experimental monolayer FeSe lattice constant of 3.86 Å is shown in the plot.
interface agrees that the electronic structure of the checkerboard antiferromagnetic state agrees best with experiment, we focus on this phase and its bulk properties as calculated with DFT methods. In the following, we shall always refer to the checkerboard order as the AFM state. Reference [28] also points out that van der Waals interactions are crucial to compute out of plane, $c_{FeSe}$, lattice constant correctly. That the same conclusion holds for the monolayer on STO is not immediately clear, since, especially if there is charge transfer, other effects are likely dominant.

From this analysis, we conclude that we can expect the structure of the STO to be best described within the PBEsol functional while PBE will perform better for the FeSe monolayer. In the following we will compare the performance of these functionals within the AFM and NM state while we include oxygen vacancies at the last stage.

### 4. Double Ti–O$_x$ layer

In this section, we follow the suggestion of [37] and consider a slab terminated by a double layer of Ti–O below the FeSe monolayer. We model the system with a slab of three layers of cubic STO and add an additional Ti–O layer below the FeSe. The relaxed structure within PBE is shown in figure 1. It turns out, that the FeSe layer is poorly bound and $\approx$5 Å far away from the substrate in this configuration, both in PBEsol and PBE. In fact, it was not possible to relax the system to the required low forces and the constrained on forces had to be reduced to $1.5 \times 10^{-3}$ Ry au$^{-1}$ indicating that the minimum in the potential energy surface is very shallow. While the binding may become closer if van der Waals interactions are considered, we also observe a reconstruction of the double Ti–O where the Ti of the topmost layer moves towards the substrate which is different from the layer found in [37] where the layers keep their general structure and the separation of the Ti–O$_x$ layers, instead, increases as compared to bulk STO. The effect of close binding of the double Ti–O layers is consistent within all tests performed on this system and in disagreement with the structure reported in [37]. We determine from the DFT perspective that the single Ti–O, terminated STO is the more likely configuration.

### 5. Binding distance and $x$ – $y$ relaxation

DFT functionals usually disagree in the predicted lattice constant with experiment up to within a few percent. In a bulk geometry, one can let the unit cell relax to represent the minimum in total energy which yields the equilibrium structure. In the present surface geometry, it is particularly

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**Table 2.** Comparison of relaxed NM structure and excess charge within the three functionals at experimental and energy optimal ($E – o$) in plane lattice constant. $\rho_{Fe}$, $\rho_{Se-O}$ and $\rho_{Se-C}$ are the excess charge according to a Bader surface analysis at a Fe site, a Se site in direction of the substrate and a Se site in direction of the vacuum, respectively. $\alpha$ is the Fe–Se bonding angle and $d_{TiSe}$ the bonding distance of the Ti to Se.

| Functional | $h_{FeSe}$ (Å) | $\alpha$ (Deg) | $d_{TiSe}$ (Å) | $\rho_{Fe}$ (e/u.c.) | $\rho_{Se-O}$ (e/u.c.) | $\rho_{Se-C}$ (e/u.c.) |
|------------|----------------|----------------|----------------|---------------------|------------------------|------------------------|
| LDA        | 1.201          | 116.79         | 2.860          | 0.407               | −0.395                 | −0.363                 |
| LDA $E – o$| 1.242          | 113.97         | 2.860          | 0.371               | −0.356                 | −0.329                 |
| PBEsol     | 1.229          | 115.61         | 2.964          | 0.431               | −0.418                 | −0.392                 |
| PBEsol $E – o$ | 1.257 | 113.68         | 2.963          | 0.420               | −0.421                 | −0.366                 |
| PBE        | 1.280          | 113.18         | 3.162          | 0.460               | −0.465                 | −0.412                 |
| PBE $E – o$| 1.280          | 113.18         | 3.164          | 0.461               | −0.472                 | −0.409                 |

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**Figure 3.** LDA band structure at the STO bulk experimental (a) and energy optimal (b) $x$ – $y$ lattice constant. Colors indicate the projection on atomic orbitals as indicated on the right of each plot and the size of each dot corresponds to the overlap of the particular wavefunction with the given atomic orbital.
important to verify that a strain imposed by the choice of unit cell does not alter the chemical bonding structure since, as opposed to a bulk geometry, the strain on the slab in the $z$-direction is zero due to the vacuum. If all the chemical bonds in the system obey the trend, choosing the experimental lattice constant of cubic STO and using the LDA xc functional will tend to stretch the slab and planes will move closer together. In figure 2 we show the total energy of the surface plus slab geometry (compare figure 1, right) as a function of $x - y$ lattice parameter. The total energy depends quadratically on the distance to the optimal value over a rather large range. From the quadratic fits, we determine that equilibrium lattice constants of $3.822, 3.847$, and $3.880$ Å for LDA, PBEsol, and PBE, respectively. It is interesting to note that bulk STO has a lattice constant of $3.9065$ Å \cite{44} while \cite{37} found a significantly smaller value for the FeSe layer of $\sim 3.86$ Å. While this implies a significant expansion as compared to bulk FeSe (compare table 1), it is still much

|           | $h_{FeSe}$ (Å) | $\alpha$ (Deg) | $d_{TSB}$ (Å) |
|-----------|----------------|----------------|----------------|
| PBE       | 1.371          | 109.86         | 3.129          |
| PBEsol    | 1.306          | 112.45         | 2.947          |
| Exp NS \cite{37} | 1.33 ± 0.02 | 111.0 ± 0.09 | 3.34 ± 0.05 |

Figure 4. Comparison of the band structure of the NM in (a) and (c) with the AFM state in (b) and (d) within PBEsol (a) and (c) and PBE (b) and (c). We use the same color coding as in figure 3. Lattice parameters are energy optimal for the NM and the experimental $a_{lat} = 3.905$ Å for the AFM state.

Table 3. Structure and charge in the AFM state. We use the experimental lattice parameter $a_{lat} = 3.905$ Å and relax the system for fixed unit cell.

|           | $\rho_{Fe}$ (e/uc) | $\rho_{Se-O}$ (e/uc) | $\rho_{Se-V}$ (e/uc) |
|-----------|-------------------|----------------------|----------------------|
| PBE       | 0.570             | -0.560               | -0.530               |
| PBEsol    | 0.527             | -0.526               | -0.483               |
smaller than the bulk STO lattice constant in the cubic phase. The reason is for this discrepancy is, in fact, that the underlying STO is incommensurate with the surface layer and has a slightly larger lattice constant.

As noted earlier, all functionals considered in this work tend to shrink the FeSe in the (x – y)-direction. The energy optimal configuration represents a well defined compromise between these two components of the system. In fact, reducing the STO layer number in the slab to one, we find further reduced optimal $a_{\text{lat}}$ values of 3.788, 3.810 and 3.841 Å which reflects the growing influence of the FeSe layer.

We take the energy optimal lattice constant as a compromise between bulk and surface stress. In table 2 we show the bonding structure and charge transfer according to a Bader analysis. We find that the bonding distance of the FeSe layer to the slab $d_{\text{FeSe}}$ does not depend on the x – y stress, but significantly on the functional. With the bonding distance being 2.86 Å and the Fe–Se distance 1.2 Å we find a step height of 5.26 Å in LDA that slightly increases to 5.34 Å if the energy optimal x – y lattice constant is used. Both of these values are much too short as compared to the 5.5 Å measured in the original STM study [1]. Comparison of this step height within PBE and especially PBEsol is much better.

While the separation distance of FeSe from the STO substrate does not depend on strain, the FeSe internal structure parameters show significant signs of strain within PBEsol and, even more so, in the LDA when the experimental lattice parameter are used. This is apparent in an opening of the bonding angle $\alpha$ and a reduction of the Se height $h_{\text{Se}}$. The energy optimal and experimental lattice parameter are very close for PBE. Performing the calculation with the energy optimal lattice constant, we find more similar structure parameters among the functionals. If the mismatch between calculated layer—and substrate lattice parameter were independent on the functional, the tensile strain should be unaffected whether we perform the calculation in LDA, PBEsol or PBE at an energy optimal lattice parameter. However, we still observe a tendency to open the bonding angle and increase the Se position as compared to the Fe layer changing the functional from PBE to PBEsol and LDA, indicating that the relative tensile strain increases. Without O-vacancies the FeSe layer is nearly neutral within the Bader analysis in all these calculations.

In figure 3 we compare the band structure with a projection on atomic orbitals for LDA with (a) and without (b) strain on the unit cell. As can be seen, the hole pocket at $\Gamma$ becomes slightly bigger as we relax the system while the heavier, filled hole band below the Fermi level moves down in energy. At the M point, the electron pocket slightly moves up in energy as we relax. At the example of LDA, where the differences between energy optimal and experimental lattice parameters are largest, we find that additional strain seems to improve comparison with experiment although this has likely to be attributed to smaller hoppings within the Fe layer and not a better description of the strong interactions in this material.

Because the LDA structure describes neither the STO nor the FeSe correctly, in the following, we focus on the two other functionals PBE and PBEsol. Turning our attention to the magnetic state, in table 3 we give the structural and charge analysis. We fix the lattice constant to the experimental cubic STO bulk value of 3.905 Å. The total size of the 1 unit cell thick layer is computed to be 5.87 and 5.56 Å which, especially for PBEsol compares well with the original measurement of 5.5 Å in [1]. However, comparison with recent experimental data [37] reveals that the binding distance of the layer from the substrate is too short while the structural parameters for the layer itself appear to be somewhat in between the results for PBEsol and PBE. Comparison may be complicated, because for example the vacancy concentration in the normal state is unknown while our calculation assumes the stoichiometric structure.

In figure 4, we compare the magnetic and non-magnetic electronic bands within PBEsol and PBE at their respective energy optimal lattice configuration. We find that the differences between PBE and PBEsol are minor. Allowing for an AFM state where we use the experimental lattice parameters, on the other hand strongly shifts down the hole band and the resulting band structure compare much better with ARPES data [17] than the NM data. PBE shows a slightly higher Fermi level than PBEsol, thus making the agreement even better.
6. Oxygen vacancies

In the following we want to investigate the effects of oxygen vacancies. In order to allow for a more continuous variation of the concentrations, also with access to low deficiency percentages that within the super cell approach are beyond our computational power, we use the VCA.

It is not straightforward to simulate the absence of an atom within the VCA. Reference [15] used a virtual mixture of 20% of F with O to achieve an excess charge that turned out to electron-dope the FeSe layer. However, while this replacement may simulate the effective charge doping well, the local disordered potential of the interface is likely different. Alternatively one could change the nuclear number of e.g. the Ti atoms to simulate dangling bonds due to the presence of vacancies [47]. Here, we choose to mix the oxygen pseudo potential with vacuum, i.e. we scale the potential and the charge with a parameter $x$.

All the atoms in the top STO layer are replaced with this virtual potential. The evolution of the structure parameters of the interface are shown in figure 5. We subtract from a value shown in figure 5 the value at zero percentage such as $\Delta \alpha (x) = \alpha (x\%) - \alpha (0\%)$. As can be seen, the variations of the FeSe internal structural parameters are almost unaffected by the vacancy doping for low concentrations. As an interesting effect, we find that instead of binding closer, at first for low vacancy concentrations, the FeSe moves away from the substrate upon vacancy doping. This trend is most pronounced in PBE, even though PBEsol also shows this behavior. Then, at an already large concentration of 20%, the trend is reversed and the binding distance shortens again. We show the difference $\Delta d_{Se-O} = z_{Se} - z_O$ as a function of vacancy doping. $\Delta d_{Se-O}$ follows $\Delta h_{TiSe}$ and thereby reflects the fact, that the layer shifts upwards while the substrate remains intact. At about 30%, $\Delta d_{Se-O}$ starts increasing while $\Delta h_{TiSe}$ decreases. This points out that the Ti binds to Se and not any more to O. This may have to be attributed to our unrealistic description of the potential in this region by the VCA.

Even though the charge transfer to Fe is rather small (compare figure 5(b)), in the general trend vacancies electron-dope the Fe. On the other hand, according to the Bader analysis, the charge on the Se close to the STO first increases before it decreases below the initial value. Variations are one order of magnitude larger as compared to the Fe atom. Charges on the vacuum side of the FeSe layer are highly oscillatory which is because of the low density and low density variation in the vacuum so that the Bader analysis is problematic.
There is a small antiferromagnetic polarization induced in the FeSe film for low vacancy concentrations. Again, the effect is only prominent in PBEsol. For the stoichiometric interface (figures 9(a) and (f)), we find a predominately covalent bond, where the charge is pulled in between the Ti and the Se atom. There is also a charge redistribution among the Fe d orbitals visible. Then, the bond obtains an ionic character at 10% and 20% (figures 9(b), (c) and (g), (h)), where charge from the Se part of the FeSe layer is pulled to the STO region before a more covalent nature reappears in figures 9(d) and (i) while for even higher vacancy concentrations of 40% (figures 9(e) and (j)) charge is predominately pulled from the STO region to form a covalent bond of Ti with Se that also has a partly ionic character visible by the blue regions close to the Ti atom. The only significant difference between the two functionals is the strength of the bond, which turns out to be weaker in PBE.

7. Discussion and conclusion

In conclusion, we have focused on three aspects of the first-principle calculation of the FeSe/STO system. First, we find that the electronic and lattice structure of the FeSe monolayer on STO in the antiferromagnetic state is in much better agreement with experimental findings than the non magnetic calculation. This goes hand in hand with the observation that the binding distance is strongly underestimated in the nonmagnetic state and thus puts a unrealistically large artificial strain on the FeSe in a calculation that uses bulk STO as a lattice constant. This effect is minimal in PBEsol within the magnetic state that seems to be predicting the layer internal structure best.

Second, while magnetism is important to describe the internal structure of the FeSe layer within DFT, the binding
distance to STO is weakly affected by it. Here, however, we observe large differences in the functionals predicting from short to long bond lengths: LDA, PBEsol and PBE. Comparing the calculated step height from the FeSe covered to uncovered STO areas with the original experimental value of 5.5 Å¹, we find that PBEsol agrees best. Compared to more detailed recent experimental data, and assuming the non-superconducting sample is in the 0% oxygen vacancy limit, the distances are all too short with the minimal error of 6.3% in PBE.

As an interesting observation we find that the FeSe layer separation from STO, in fact, increases at first upon increasing the oxygen vacancy concentration. The effect is present in PBE as well as PBEsol even though weak in the latter case. Assuming that the annealing steps in are mainly causing oxygen vacancies to form, this is in line with experiment where the separation increases significantly from ~3.34 to ~3.57 Å. We believe that this effect is caused by the tendency of O vacancies to reduce the strength of the covalent bond Se to Ti at low concentrations. In the calculations, PBE tends to soften the covalent bonds at a point where the charge transfer due to vacancies have not created a compensating ionic bonding. Ordered vacancies in a super-cell calculation may locally distort the bonding structure much more than the same vacancy percentage in the disordered experimental system where we would expect a more isotropic influence on electronic properties. This may explain why a super cell calculation results in a strengthening of a covalent bond that is suppressed if the deficiencies is disordered. The homogeneous averaged potential, however, is better described within the VCA.

Third, we have investigated the charge transfer induced by oxygen vacancies. Surprisingly, for low vacancy percentages (~<20%), we observe no net charge transfer to the Fe sites. Only for higher concentrations we recover the doping effect, that was previously observed in super-cell calculations. The results for the binding distance can be interpreted in the sense that experimentally we are in the low vacancy regime. Thus, this result indicates that the experimentally observed doping is caused by other sources than oxygen vacancies.

Note, that the incommensurate alignment of STO with the FeSe, as seen in the data of, may weaken the covalent bonding of FeSe to STO and, thus, explain why PBE calculations of the bond length agree better with experiment in our commensurate approximation of the system.

We believe that more experimental data would be desirable to investigate the precise nature of the interface. For example, concluded that the STO is terminated by a double layer of Ti–O. Here, we found that a relaxation within DFT starting from the suggested positions leads to an incorrect description of the system where the double layer Ti–O,
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Note added in proof. During the proof stage of this article we became aware of [49], that performed a similar calculation for the double TiO$_2$ layer. While both studies agree that without oxygen vacancies the coupling of FeSe to the substrate is weak, the relaxed structure of [49] is in better agreement with experiment.

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