

Multiscale modelling of charged impurities in two-dimensional materials

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Abstract

Charged impurities influence functional properties of two-dimensional materials and a detailed theoretical understanding of charged defects is required to enable a rational design of defect-engineered nanomaterials for applications in ultrathin devices. To achieve this goal, we have developed multiscale approaches that combine atomistic first-principles theories, such as density-functional theory, with coarse-grained continuum models, such as effective mass models. This allows us to model large supercells which are required to accurately describe the slow decay of the screened defect potential and the defect-induced changes in the electronic properties of the two-dimensional host material. I will describe the results of our multiscale calculations for charged defects in doped graphene and in transition-metal dichalcogenide monolayers which have revealed novel mechanisms for controlling and tuning the electronic structure of two-dimensional materials.

Keywords: electronic structure theory, multiscale modelling, two-dimensional materials, defects.

1. Introduction

Two-dimensional (2D) materials exhibit many fascinating properties that could give rise to new generations of nanodevices for energy, communication and medical technology. Examples include ultrahigh electron mobilities in graphene field-effect transistors [1, 2] or extraordinary sunlight absorption in transition-metal dichalcogenide monolayers [3].

Defects are always present in real devices and therefore it is necessary to understand how they affect the properties of 2D materials. Often, defects deteriorate intrinsic properties, e.g. scattering by charged defects reduces the electron mobility [4, 5]. On the other hand, defects can also enhance properties or even introduce completely new functionality. The rational design of functionality using defects, known as defect engineering, has been a cornerstone of conventional semiconductor technology for decades, for example in the creation of silicon p-n junctions.

In 2D materials, a variety of defects exist, such as vacancies or substitutional atoms, that can also be found in 3D systems. Other types of impurities, such as adsorbed atoms and molecules, play a much more important role in 2D materials because of their extreme surface-to-volume ratio [6]. Experimentally, defects in 2D materials can be probed using various techniques,

including transport measurements, scanning tunnelling spectroscopy or via optical techniques.

In this review paper, I will describe the work of my research group to gain insight into the properties of charged defects in 2D materials using theory and simulation. Modelling charged impurities is particularly challenging because their properties are determined by physico-chemical processes occurring on multiple length scales: charge transfer is determined by the short-ranged overlap of frontier orbitals, while the screened potential of the charged defect is affected by the long-ranged dielectric response of the 2D substrate. To capture this interplay, we have developed multiscale theories that combine first-principles methods, such as *ab initio* density-functional theory, with coarse-grained approaches, such as interacting continuum models.

The paper is organized as follows: first, I will describe the multiscale methods that we have developed to calculate properties of charged defects in 2D materials. Then, I will describe some results for charged adsorbates on doped graphene and for charged impurities in transition-metal dichalcogenides. Finally, I will summarize our findings and describe future work.

2. Methods

Modelling charged impurities in 2d materials is challenging because of the complex interplay of short-ranged chemical effects, such as defect geometry and the alignment of frontier orbitals of the defect and the 2D host material which determines the direction and amount of charge transfer, and long-ranged physical effects, such as the dielectric response of the 2D material to the presence of the charged defect. Different methods exist to describe either the short-ranged chemical effects or the long-ranged physical effects, but a *multiscale approach* that seamlessly connects the different length scales is needed to develop a material-specific predictive approach and enable the rational design of defect-engineered 2D materials.

Density-functional theory (DFT) [7] is a powerful approach for studying the properties of defects in 2D materials from first-principles, i.e. without empirical parameters. DFT calculations often yield accurate defect geometries and formation energies. However, the results can be sensitive to the choice of exchange-correlation functional. In particular, hybrid functionals or DFT+U calculations can be required to accurately describe defects with highly localized electronic states [8, 9]. Moreover, the vast majority of defect calculations using DFT are carried out using a supercell approach. In this approach, a period arrangement of defects is simulated and properties of isolated defects are obtained in the limit of large defect separations. However, the numerical cost of DFT calculations increases rapidly with supercell size and the removal of finite-size effects, which are particularly important for charged defects, is notoriously difficult [10].

Another well-known problem in DFT calculations is the determination of the amount of charge which is transferred between the defect and the 2D host materials. Usually, a charge partitioning scheme is used to calculate the charge of the defect, but different approaches, such as Loewdin or Mulliken schemes, can yield significantly different results [11]. This uncertainty poses a significant challenge for the parametrization of coarse-grained approaches that describe the long-ranged dielectric response of the 2D host material.

Finally, DFT is a ground-state theory and as such cannot be used to calculate excited-state properties of impurities in 2D materials. Charged quasiparticle excitations, which are measured in photoemission, tunnelling or transport experiments, are accurately described using the *GW* approach [12, 13]. This technique yields the one-electron Green's function, whose poles are located are the excitation energies, by solving a Dyson equation.

Electron-electron interaction effects are described by the electron self-energy, which is calculated as the product (in a real-space and real-time representation) of the Green's function G and the screened Coulomb interaction W . Optical spectra including excitonic effects are obtained by solving the Bethe-Salpeter equation (BSE) for the electron-hole Green's function [14]. While the GW/BSE approach gives accurate quasiparticle energies and lifetimes, band gaps and absorption spectra, its numerical cost is significantly larger than that of DFT calculations and as a consequence it is rarely applied to defect systems [15, 16, 17].

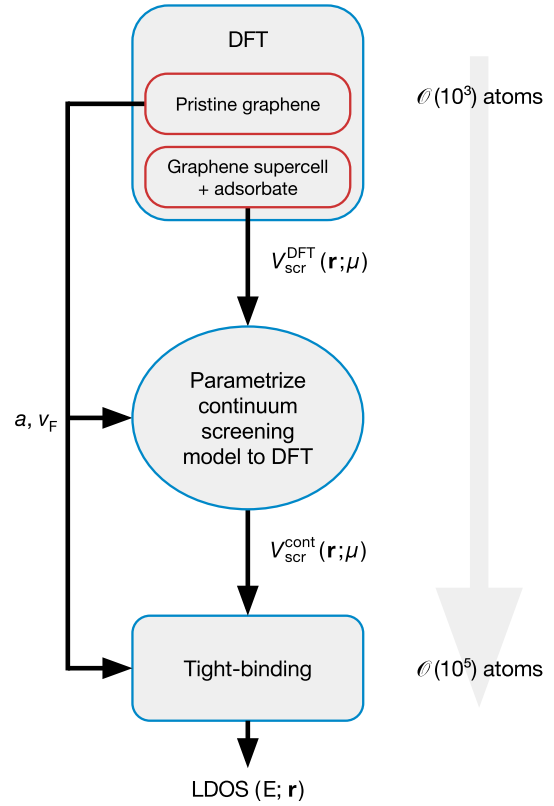


Figure 1: Workflow of the multiscale approach for modelling charged impurities in graphene. The graphene lattice constant a and Fermi velocity v_F are obtained from DFT calculations of pristine graphene. The screened impurity potential $V_{scr}^{DFT}(\mathbf{r};\mu)$ is then found using a DFT supercell calculation. This DFT impurity potential is used to parametrize a continuum screening model. Once the parameters are determined, the model can be used to calculate the screened impurity potential in significantly larger supercells. The resulting potential $V_{scr}^{cont}(\mathbf{r};\mu)$ is then used in large-scale tight-binding calculations of the local density of states (LDOS). From Ref. [11].

To access longer length scales and capture the dielectric response of the 2D host material to the charged defect, atomistic tight-binding (TB) approaches and non-atomistic continuum methods, such as effective mass or

Dirac theories, have been used [18, 19]. In the TB approach, non-interacting electrons hop between atomic sites which are characterized by their onsite energies. Hopping integrals and onsite energies can be obtained either by fitting to measured or calculated band structures or via a Wannier-transformation of the DFT Hamiltonian [20]. Continuum theories, such as the effective mass approach, have been successfully used to describe the electronic properties of defects in 3D semiconductors [21], but require values of effective masses and charge transfer parameters from experiment or first-principles calculations. Such theories are particularly useful when electron-electron interactions are included. The resulting effective-mass Thomas-Fermi approach can be used to investigate the non-linear response of 2D materials to charged defects and also to study complex defect assemblies [22, 23].

To combine first-principles theories for charged impurities in 2D materials with methods for studying the long-range dielectric response, we have developed several multiscale approaches. These approaches combine large-scale atomistic TB models with first-principles defect potentials. Importantly, electron-electron interactions, which are not captured by the TB approach, are included by replacing the bare Coulomb potential of the defect by its screened counterpart. The screened potential has been obtained via two routes: (i) linear response theory and (ii) direct extraction from DFT calculations. In route (i), the static dielectric function $\epsilon(q)$ of the (defect-free) 2D material is calculated from first-principles using the random-phase approximation (RPA) and the screened defect potential is then obtained via [24, 25]

$$V_{\text{scr}}(q) = \frac{2\pi Z}{\epsilon(q)q}, \quad (1)$$

where $2\pi/q$ denotes the 2D Fourier transform of the bare Coulomb interaction and Z denotes the transferred charge and atomic units have been used.

Alternatively, the screened potential can be directly extracted from the DFT calculations that include the charged defect. Specifically, the screened defect potential is simply equal to the effective Kohn-Sham potential experienced by the electrons in the 2D host material [11]. As discussed above, the screened defect potential in 2D systems decays slowly with a spatial extent of up to ten nanometres or more. Capturing this decay in simulations requires supercells containing tens of thousands of atoms. DFT calculations for such systems are extremely demanding and often not feasible.

To overcome this challenge, we have developed the following multiscale approach [11], see Fig. 1. First,

linear-scaling DFT calculations are carried out for supercells containing several thousand atoms. In these calculations, the effect of an applied gate voltage is captured by explicitly adding or removing electrons from the supercell. Next, the screened defect potential from the DFT calculation is used to parametrize an interacting continuum model in which the charged defect is modelled as a point charge Z and the effect of the gate voltage is captured by the chemical potential μ of the 2D material. Specifically, we carry out continuum model calculations for different values of Z and μ for the same supercell as in the DFT calculation and compute the screened defect potential for each combination of parameters. By comparing the continuum model results with the DFT screened defect potential, the optimal parameters are determined. Using these parameters, we proceed to evaluate the screened defect potential in much larger supercells which are required to describe its decay accurately. Finally, the converged screened potential is employed as an onsite energy in large-scale tight-binding calculations that yield observables, such as the local density of states.

The presented multi-scale theory of charged impurities in 2D materials is ideally suited to describe charged adsorbates. For physisorbed atoms and molecules, it is usually possible to use tight-binding models of the defect-free 2D material in the calculation of the local density of states. Other types of impurities, such as chemisorbed species, vacancies or substitutional atoms, can significantly modify the chemical bonding in the vicinity of the impurity. Such effects can sometimes be described by locally modifying the onsite and hopping energies of the pristine 2D material. Importantly, these chemical effects are usually short-ranged in comparison to the extent of the screened Coulomb potential and therefore simple tight-binding models of the defect-free 2D material often give accurate results for distances larger than 1-2 nanometers from the impurity.

3. Results

3.1. Charged impurities in graphene

Alkali and alkaline-earth adatoms typically donate electrons to a graphene substrate and act as charged defects. We have studied the electronic structure of calcium adatoms on doped graphene [24, 11]. Initially, we employed linear response theory within the random-phase approximation to calculate the screened defect potential. In particular, the analytically known dielectric function of the Dirac model was used [26, 27] and the defect charge Z was kept as an adjustable parameter. To capture the slow decay of the screened defect

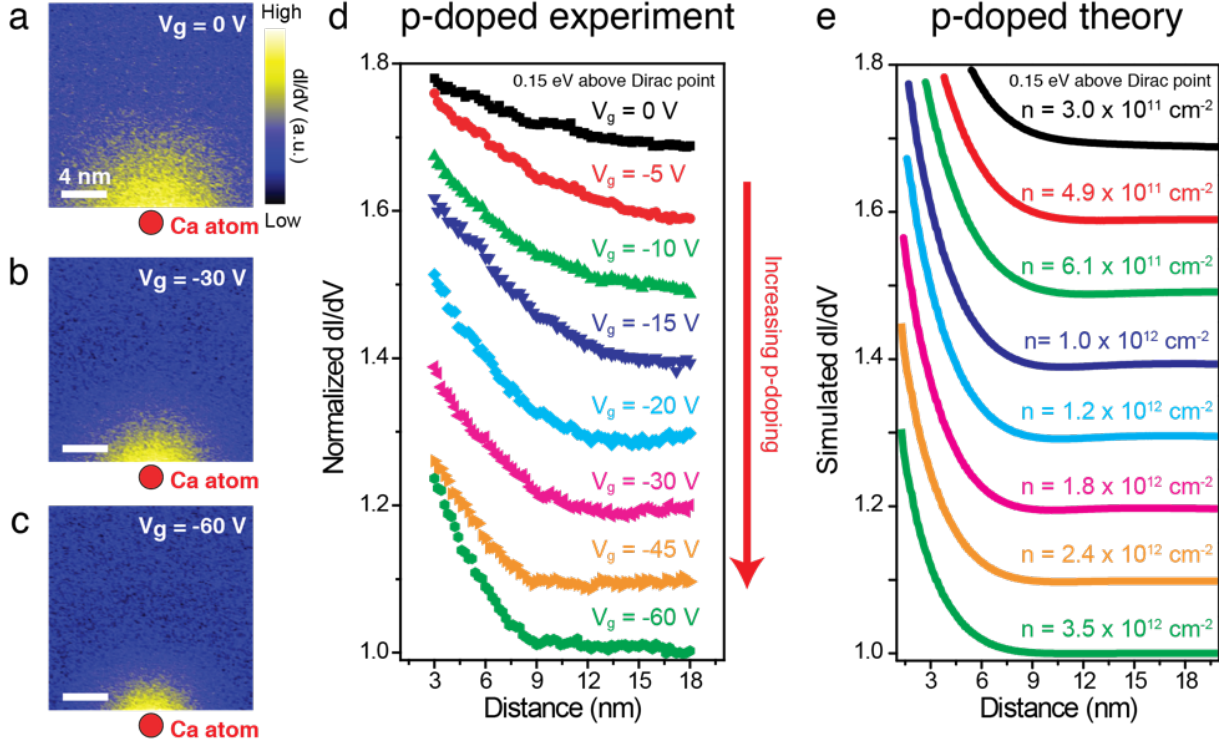


Figure 2: Comparison of theory and STM experiment for a single calcium adatom on p-doped graphene. Experimental dI/dV maps of states with energy 0.15 eV above the Dirac point are shown for different gate voltages V_g : (a) $V_g = 0$ V, (b) $V_g = -30$ V and (c) $V_g = -60$ V. (d) Experimental dI/dV curves as function of distance from the calcium adatom for different gate voltages. Note that the curves are vertically offset for clarity. (e) Calculated dI/dV curves as function of distance from the calcium adatom. The electron density in the calculations was chosen to correspond to the experimental gate voltage. From Ref. [24].

potential and the local density of states (LDOS), large-scale tight-binding simulations with up to 50,000 carbon atoms in the supercell were carried out. The resulting LDOS decays to its bulk value over several nanometers with a decay length depending sensitively on the applied gate voltage, see Figs. 2 and 3. In particular, for low gate voltages (corresponding to undoped graphene) the change in the LDOS induced by the charged defect decays over ten nanometers or more. The dependence of the LDOS and the screened potential on the chemical potential is a consequence of the linear dispersion relation of the graphene electrons near the Fermi level which gives rise to a density of states varying linearly with the chemical potential for a wide range of doping levels. For comparison, no such dependence is observed for a standard 2D electron gas which exhibits a *constant* density of states.

It can also be observed that the LDOS is enhanced in the vicinity of the defect when states above the Dirac point are probed, while there is a reduction for states below the Dirac point. This is a consequence of band

bending. To a good approximation, the screened potential of the positively charged defect rigidly shifts the LDOS to lower energies resulting in an LDOS enhancement above and an LDOS reduction below the Dirac point, see Fig. 4. Note, however, that the simple band bending picture breaks down for energies very close to the Dirac point whose energy is not changed in the presence of the defect potential.

To overcome the limitations of the linear response framework, we also extracted the screened defect potential directly from DFT calculations, see Methods section. For this, we first determine the structure of the Ca adatom using standard plane-wave/pseudopotential DFT calculations [11]. We find that the Ca atom sits about 2 Å above the hollow position, i.e. the centre of the graphene hexagon. Next, we carry out linear-scaling DFT calculations [28] on supercells containing more than 6,000 atom and extracted the screened defect potential. We then use this result to determine the charge Z and the chemical potential μ using various interacting continuum approaches. Specifically, we employ both

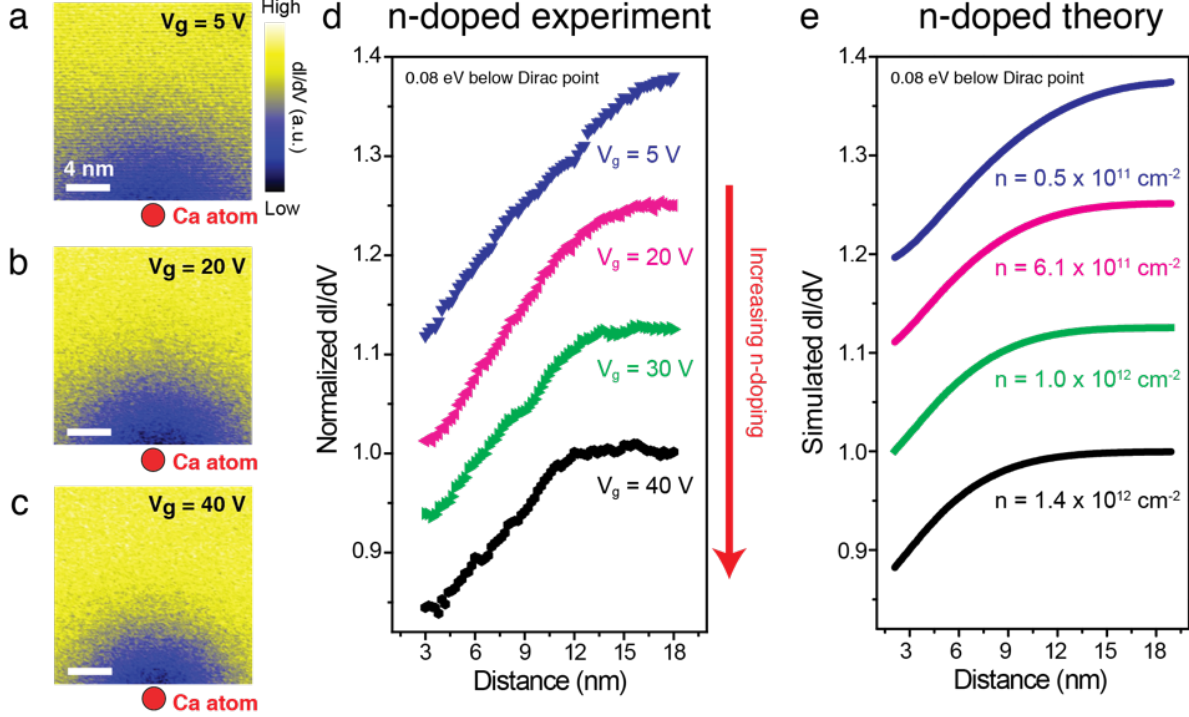


Figure 3: Comparison of theory and STM experiment for a single calcium adatom on n-doped graphene. Experimental dI/dV maps of states with energy 0.08 eV below the Dirac point are shown for different gate voltages V_g : (a) $V_g = 5$ V, (b) $V_g = 20$ V and (c) $V_g = 40$ V. (d) Experimental dI/dV curves as function of distance from the calcium adatom for different gate voltages. Note that the curves are vertically offset for clarity. (e) Calculated dI/dV curves as function of distance from the calcium adatom. The electron density in the calculations was chosen to correspond to the experimental gate voltage. From Ref. [24].

Table 1: Impurity charge Z of a calcium atom adsorbed on graphene. Here, Z is obtained by fitting the screened impurity potential of a continuum model to the DFT potential. The quality of the fit is described by the fitness metric $\mathcal{F}$. Here, LTF and NTLF denotes the linear and nonlinear Thomas-Fermi model, respectively. If screening by interband transitions is included, we add “+inter” to the model.

Model	Z [e]	$\mathcal{F}$ [eV]
LTF	0.3	8.9×10^{-3}
LTF+inter	1.3	8.4×10^{-3}
NLTF	1.6	9.3×10^{-3}
NLTF+inter	1.6	7.4×10^{-3}

the linear and non-linear Thomas-Fermi approach and also include the effect of interband transitions.

Table 1 shows our results for the defect charge Z . We find that Z depends sensitively on the description of electron-electron interactions in the continuum model [11]. Inclusion of nonlinearity and interband transitions both result in a significant increase of Z from the linear Thomas-Fermi (LTF) result $Z = 0.3$. The most accurate continuum model which includes both nonlinearity

and interband transition (denoted NLTF+inter) yields $Z = 1.6$. This is in good agreement with the chemical intuition which suggests that calcium donates its two valence electrons to reach a closed-shell configuration.

Adsorbed organic molecules are another interesting class of graphene impurities. We have studied the properties of tetrafluorotetracyanoquinodimethane (F4-TCNQ) molecules on doped graphene [29]. This molecule with chemical formula $C_{12}F_4N_4$ has been suggested as a promising acceptor molecule because of the high electronegativity of the fluorine atoms. In fact, we have found using GW calculations that the lowest unoccupied molecular orbital (LUMO) of F4-TCNQ is very close in energy to graphene’s Dirac point. By tuning the graphene chemical potential via the gate voltage, it is therefore possible to reversibly charge and discharge the F4-TCNQ molecule. Moreover, we have found that image charge interactions between adsorbates and graphene depend sensitively on the graphene chemical potential resulting in gate-voltage dependent molecular energy levels. These predictions are in excellent agreement with recent experimental scanning tun-

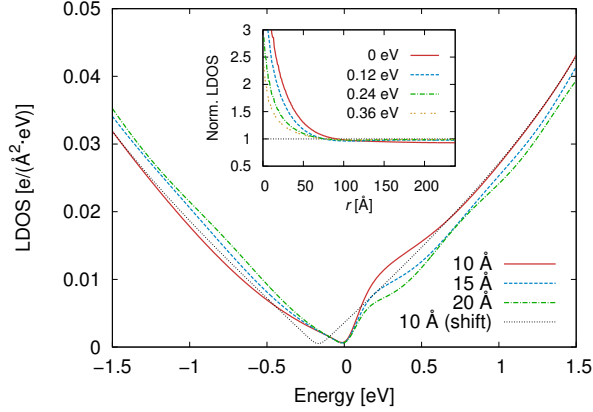


Figure 4: Local density of states (LDOS) of doped graphene with a single calcium adatom as function of energy for different distances from the adatom. The black dotted line denotes the LDOS of defect-free graphene which has been shifted by the local value of the screened impurity potential. The inset shows the LDOS as function of distance from the impurity for different chemical potentials. From Ref. [11].

nelling spectroscopy results [29].

3.2. Charged impurities in transition-metal dichalcogenide monolayers

In contrast to graphene, many monolayers of the transition-metal dichalcogenide (TMD) family, such as MoS₂, MoSe₂, WS₂ and WSe₂, possess a band gap which makes them useful for a wide range of applications. Similar to charged defects in 3D semiconductors, charged impurities in these 2D semiconductors give rise to a series of bound states which can be probed using various experimental techniques, including scanning tunnelling microscopy (STM) or optical spectroscopy.

We have studied charged impurities in MoS₂ using linear-response theory [25]. Specifically, we carried out first-principles DFT calculations on defect-free monolayers and calculated the RPA dielectric function which was then used to determine the screened defect potential, see Fig. 5. Next, large-scale tight-binding calculations on 51×51 supercells using the three-band model proposed by Liu [30] and coworkers were carried out to calculate the energies and wavefunctions of the impurity states.

Figure 6 shows the most strongly bound states for a negatively charged acceptor impurity and compares them to the eigenstates of the hydrogen atom in two dimensions. It can be seen that the wavefunctions look qualitatively similar and we can label the defect states using hydrogenic quantum numbers. Interestingly, we find *two* states with *1s* symmetry. This is a consequence

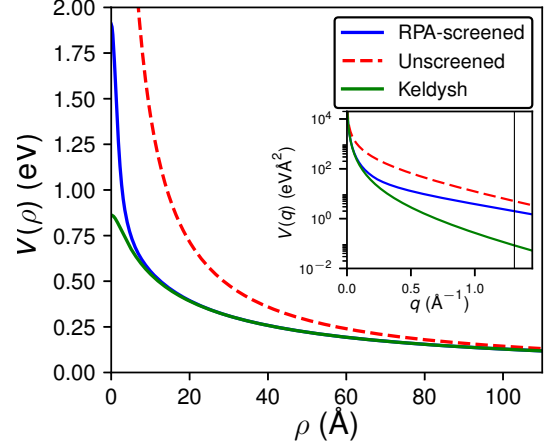


Figure 5: Screened impurity potential of a charged adatom on MoS₂ obtained using the random-phase approximation (RPA) and the Keldysh model. For comparison, the unscreened impurity potential is also shown. The adatom is located 2 Å above the molybdenum atom and has a charge $Z = 1$. The inset shows the Fourier transform of the screened impurity potential. The vertical line indicates the wave vector which connects the K and K' points of the first Brillouin zone. From Ref. [25].

of the special valence bandstructure of MoS₂ which exhibits three valleys, see Fig. 7(b): the two degenerate K and K' valleys and the Γ valley which is slightly lower in energy, but has a bigger effective mass than the K and K' valleys. Each valley acts as an effective 2D hydrogen atom and contributes a series of hydrogenic defect states explaining the occurrence of multiple *1s* states.

The dependence of the defect state binding energy, defined as the difference of the defect state energy and the valence band edge, on the defect charge Z is shown in Fig. 7(a). Importantly, we discovered that the character of the most strongly bound state depends on the defect charge. For small defect charges the *1s* state from the K and K' valleys is the most strongly bound state, but at a critical defect charge $Z = -0.32$ the *1s* state originating from the Γ valley becomes more strongly bound. This is a consequence of the larger effective mass at Γ . The tunability of the electronic structure of defective TMDs via the defect charge opens up new avenues for controlling functional properties in these systems. It is also worth pointing out that the defect energies cannot be described by the solutions of the 2D hydrogen atom because the spatial dependence of the screened defect potential is qualitatively different from the unscreened Coulomb potential, see Fig. 5.

We have also studied the properties of positively charged donor impurities. Again, the presence of multiple valleys in the conduction band structure, see

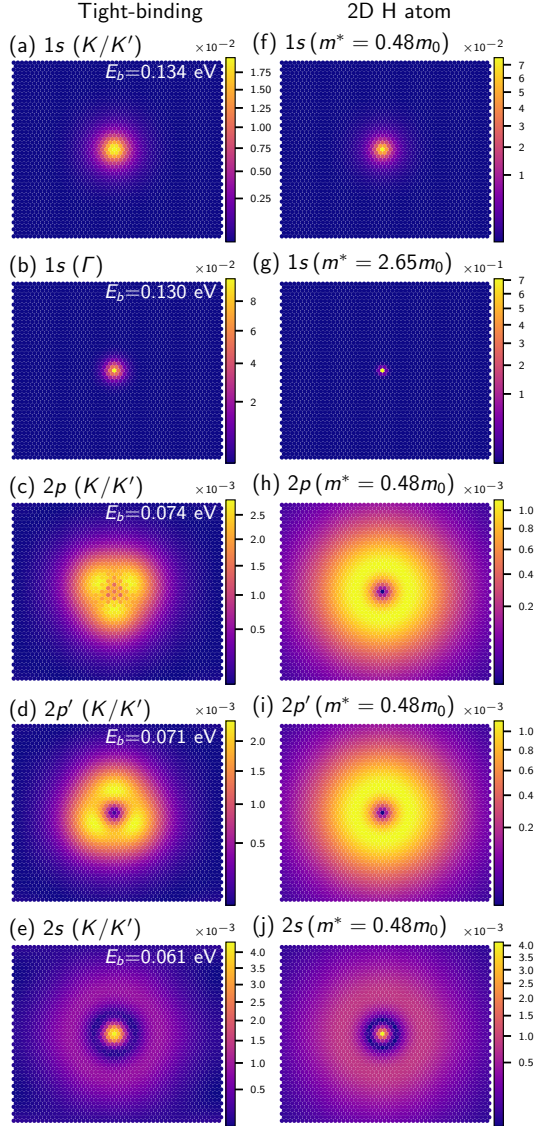


Figure 6: (a)-(e) Wavefunctions (squared) of the bound impurity states for a charged adatom on MoS₂. The adatom is located 2 Angstrom above the molybdenum atom and has a charge $Z = -0.3$. The binding energies of the states (measured with respect to the valence band maximum) are also shown. (f)-(j) Bound states of the two-dimensional hydrogen atom with nuclear charge $Z = -0.3\zeta$. Here, ζ denotes the ratio of the screened and unscreened impurity potentials directly underneath the adatom. From Ref. [25].

Fig. 7(b), gives rise to multiple defect states whose binding energies and relative ordering depend sensitively on the defect charge. In particular, states from the Q valley become more strongly bound than states from the K and K' valleys at a critical defect charge $Z = 0.6$. In contrast to the valence bands, spin-orbit coupling is very weak in the conduction bands at K and K' . As a conse-

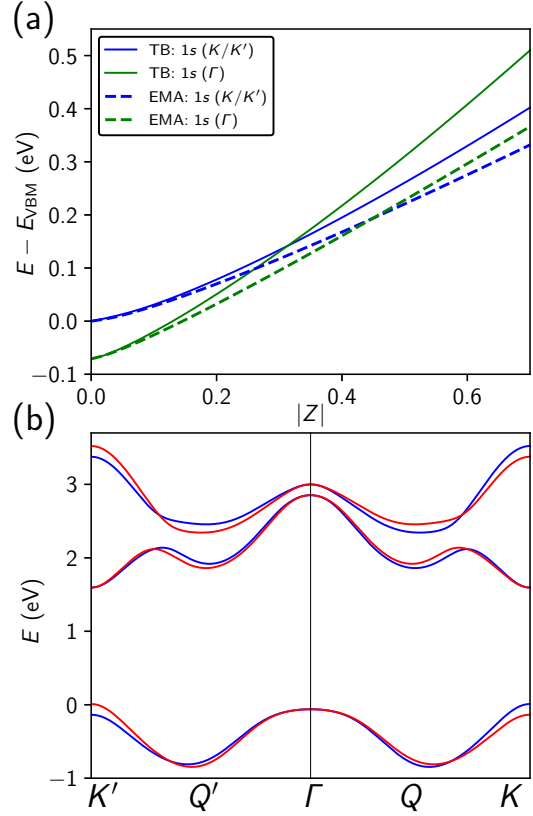


Figure 7: (a) Binding energies of bound impurity states of a negatively charged adatom on MoS₂ from tight-binding (TB) calculations. For comparison, results from the effective mass approximation (EMA) with a Keldysh potential are also shown. (b) Band structure of MoS₂ obtained from tight-binding calculations. Bands with spin-up character are red and bands with spin-down character are blue. From Ref. [25].

quence, impurity states originating from K and K' can hybridize with each other and the resulting defect eigenstates are linear combinations of states from K and K' . The splitting of the hybridized states is determined by the value of the screened defect potential at $\mathbf{q} = \mathbf{K} - \mathbf{K}'$. For defect charges larger than $Z \approx 0.5$, the splitting of the hybridized states is about 0.1 eV and should therefore be measurable in STM experiments. Interestingly, the splitting predicted by the frequently used Keldysh potential which is derived from macroscopic electrostatic considerations [31] is several orders of magnitude smaller than the RPA result. This is a consequence of the unphysically rapid decay of the Keldysh potential in Fourier space, see Fig. 5.

4. Conclusions

I have reviewed the work of my research team on modelling charged impurities in two-dimensional materials. To capture the complex interplay of chemical effects that occur at short atomistic length scales and physical effects on longer mesoscopic length scales, we have developed multiscale approaches that combine atomistic first-principles calculations with coarse-grained electronic structure methods. This allows us to model supercells with 100,000 atoms and more which are required to converge the slow decay of the screened impurity potential in these systems. We have applied this computational framework to charged adsorbates on doped graphene and impurities in transition-metal dichalcogenide monolayers. For the adsorbates on doped graphene, we have found that the spatial extent of the impurity-induced change in the graphene local density of states depends sensitively on the graphene chemical potential which can be controlled via a gate voltage. For charged impurities in TMD monolayers, our calculations have revealed a complex interplay between the TMD bandstructure, spin-orbit coupling and unconventional screening in 2D semiconductors. Moreover, defects properties in these systems can be tuned via the defect charge which opens up new pathways for a rational design of defect-engineered 2D materials with applications to ultrathin devices for energy, information and medical technology.

Future work will focus on studying optical properties of charged impurities in 2D materials, complex defect assemblies and charged impurities in emerging materials, such as monolayer black phosphorus and twisted bilayer graphene.

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