

Accurate description of the van der Waals interaction of an electron-positron pair with the surface of a topological insulator

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Abstract. Positrons can be trapped in localized states at the surface of a material, and thus quite selectively interact with core or valence surface electrons. Hence, advanced surface positron spectroscopy techniques can present the ideal tools to study a topological insulator, where surface states play a fundamental role. We analyze the problem of a positron at a TI surface, assuming that it is a weakly physisorbed positronium (Ps) atom. To determine if the surface of interest in a material can sustain such a physisorption, an accurate description of the underlying van der Waals (vdW) interaction is essential. We have developed a first-principles parameter-free method, based on the density functional theory, to extract key parameters determining the vdW interaction potential between a Ps atom and the surface of a given material. The method has been successfully applied to quartz and preliminary results on Bi₂Te₂Se indicate the existence of a positron surface state. We discuss the robustness of our predictions versus the most relevant approximations involved in our approach.

Topological insulators (TIs) are materials with a bulk electronic structure that is insulating, but which possess at their surface “protected” conducting states. These surface states result, remarkably, from the time-reversal symmetry and topology of the bulk electronic structure, and are protected in the sense that they cannot be altered by impurities or defects if these do not break the time-reversal symmetry. Quite crucially, the surface states of a TI have their spin and momentum coupled [1]. To further our understanding of TIs, there is great interest in probing directly these surface states, and positron spectroscopy offers the ideal tools for this purpose. Indeed, it is known that after irradiation of a material with a positron beam, positrons can diffuse to the surface and may be momentarily trapped, or bound to it, if such a surface state exists [2]. More recently, a method based on an Auger process was devised to directly deposit positrons at a surface bound state using slow positron beams [3]. The signals from the subsequent positron annihilation with core or valence electrons are collected in experiment with various techniques, such as positron annihilation lifetime, Doppler broadening of annihilation radiation, two-dimensional angular correlation of annihilation radiation, or positron annihilation-induced Auger electron spectroscopy [2, 4, 5, 6]. If the annihilating positron is at the surface, the collected signals contain crucial information about the electronic properties, structure, and composition of the surface. Moreover, since spin-polarized positron beams can be used and annihilation occurs only with electrons of opposite spin, the spin of the probed states can be known.

Thus, to study the surface states of a TI with positron spectroscopy, it is of the greatest interest to determine whether positrons can be bound to its surface. In this regard, an important



model for positron-surface interactions was advanced by Platzman and Tzoar [7]. These authors viewed a positron in a low density electron gas as a weakly physisorbed positronium (Ps) atom (i.e, an electron-positron bound state). A few years ago, this idea was applied with success to the Ps-quartz surface interaction. Indeed, using essentially a first-principles approach, Saniz *et al.* [8] found a bound state for Ps on quartz with an energy close to the experimental value[9], solving a long standing disagreement between theory and experiment [10].

Current state-of-the-art *ab initio* techniques, based on density functional theory (DFT) [11], allow an accurate determination of the structural and electronic properties of narrow band gap semiconductors, such as the TIs. This means that one can theoretically determine with reliability the potential seen by an atom at their surface and, thus, whether Ps can be bound to it and what its binding energy would be [12]. In the following we describe how this is achieved. As an example, we consider Bi₂Te₂Se, a well known tetradymite TI [13, 14]. Our preliminary results indicate that Ps should have a bound state on the (111) surface. In this respect, we note that very recently the group of A. Weiss has produced very encouraging evidence for the presence of a positron surface state on the surface of Bi₂Te₂Se [15].

The interaction between a physisorbed atom and a crystal surface is given by an attractive van der Waals potential away from the surface, and a short-ranged repulsive potential close to it. If z denotes the coordinate of the atom with respect to the crystal surface, the interaction is given by [10, 16, 17, 18]

$$\begin{aligned} v(z) &= v_R(z) + v_{\text{vdW}}(z). \\ &= V_0 e^{-(z-z_0)/\lambda} - \frac{C}{(z-z_0)^3} F_3((z-z_0)/\lambda). \end{aligned} \quad (1)$$

The repulsive part is proportional to the valence electron density near the surface of the crystal. Specifically, define $\langle \rho \rangle_z$ as the electron density at coordinate z , averaged over the section of the unit cell perpendicular to the z axis. $\langle \rho \rangle_z$ will decay exponentially away from the point at which the contribution of the core electrons to the density vanishes. This point, z_0 , defines the “background edge”. λ is the exponential decay length. The amplitude of V_0 is given by the negative of the Ps work function [10]. The latter is given by $\epsilon_{\text{Ps}} = -A^+ - 6.8$ eV, with A^+ the positron affinity given by $A^+ = \mu^- + \mu^+$, where μ^- and μ^+ are the electron and positron chemical potentials, respectively [19].

The van der Waals attraction decreases essentially as the inverse cubic power of the “distance” of the atom to the surface. This distance is measured from the background edge, z_0 [17]. The proportionality constant (van der Waals constant), C , is given by

$$C = \frac{\hbar}{4\pi} \int_0^\infty d\xi \alpha(i\xi) \left(\frac{\epsilon(i\xi) - 1}{\epsilon(i\xi) + 1} \right), \quad (2)$$

with ϵ the dielectric function of the material and α the polarizability of the adatom [17]. F_3 is the damping, or regularization function, introduced by Patil and co-workers [18], ensuring that the adatom-surface interaction does not diverge at the reference position, z_0 .

Except for the Ps polarizability, all the above quantities can be calculated with first-principles methods, as already indicated. The polarizability of Ps is most easily determined by rescaling the polarizability of the H atom, which is well parametrized [20]. We discuss the calculation of the other quantities here. The most common exchange-correlation functionals used in DFT based calculations, such as the local-density approximation (LDA) or the Perdew-Burke-Ernzerhof approximation (PBE), are typically able to describe with good accuracy the structural properties of surfaces. However, it is important to realize that these functionals suffer from the well-known band gap problem. That is, the band gap and energies of the excited states of semiconductors and insulators are seriously underestimated when using these functionals. In the case of narrow

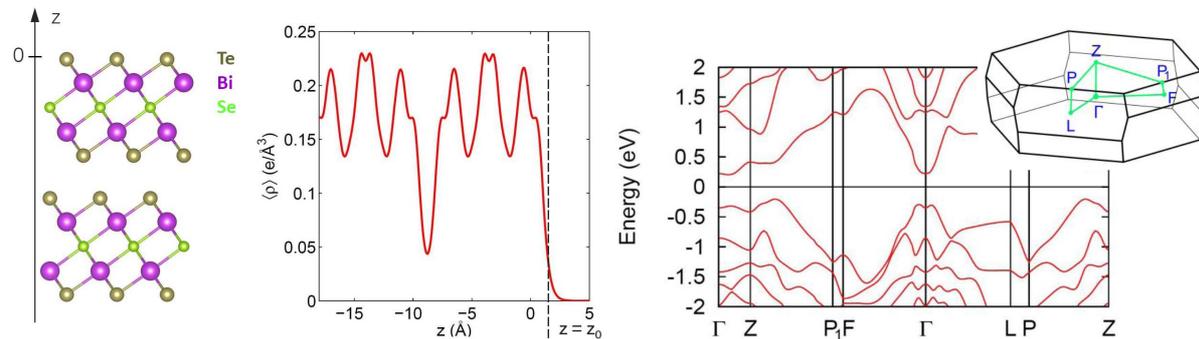


Figure 1. (a) Partial side view of the Bi₂Te₂Se slab and average electron density as a function of z . (b) Bulk band structure of Bi₂Te₂Se (HSE06 hybrid functional), including spin-orbit coupling.

gap semiconductors, such an error can lead to their erroneous description as metals. Given that incorrect gap and excited state values can lead to an incorrect dielectric function, it is important to follow a calculation scheme that does not present this problem. One can obtain a much better description of the electronic structure of semiconductors and insulators within the GW approximation [21, 22]. However, this approximation is computationally very expensive, and an accurate calculation of the dielectric function over sufficiently large frequency range is prohibitive. A less expensive approximation is provided by hybrid functionals, such as the HSE06 [23]. In essence, the latter combines the PBE exchange functional at long range, with Hartree-Fock exchange at short range. This is because the PBE (or the LDA) is known to overscreen the exchange interaction. The HSE06 hybrid functional has proven to provide accurate structural and electronic properties. In most *ab initio* codes, the imaginary part of the dielectric tensor is calculated through [26]

$$\text{Im } \varepsilon_{ij}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q \rightarrow 0} \frac{1}{q^2} \sum_{c,v} \sum_{\mathbf{k}} 2w_{\mathbf{k}} \delta(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}} - \omega) \langle u_{c\mathbf{k}+\hat{e}_i q} | u_{v\mathbf{k}} \rangle \langle u_{c\mathbf{k}+\hat{e}_j q} | u_{v\mathbf{k}} \rangle^*, \quad (3)$$

where Ω is the unit cell volume, and $\epsilon_{c\mathbf{k}}$ is the energy of conduction band state c with momentum \mathbf{k} , $w_{\mathbf{k}}$ denoting the cell-periodic part of the corresponding wavefunction ($u_{\mathbf{k}}$ is the \mathbf{k} -point weight). The real part, $\text{Re } \varepsilon_{ij}(\omega)$, is obtained with the Kramers-Kronig relation (see Ref. [26] for details). One final point is that in materials with heavy ions, spin-orbit interactions can contribute importantly to the properties of materials. This is the case of TIs, in which spin-orbit coupling leads to the band inversion that is responsible for the existence of the topologically protected surface states which give the Dirac cone. Thus, it is important to include spin-orbit coupling in *ab initio* studies of topological insulators. Such computations are considerably more expensive, but are still tractable on large parallel computers.

We have applied the above scheme to find out if Ps has a bound state on the surface of Bi₂Te₂Se. For this purpose we used the Vienna *ab initio* simulation package (VASP) [24]. The calculation of the structure and electron density at the surface of a slab were done using the PBE functional. Figure 1(a) shows a partial side view of the slab used for this calculation (the slab in the calculations is three quintuple layers thick), as well as the average electron density profile in the z -direction. The position of the background edge (which we find to be 1.55 Å) is also indicated. The electron density decay length is 0.35 Å. The calculations of the electronic structure were done with the experimental lattice structure parameters [25], and using the hybrid HSE06 exchange-correlation functional. The band structure along high symmetry lines is shown in Fig.1 (b). The dielectric function was calculated using a $12 \times 12 \times 12$ \mathbf{k} -point mesh, and up to 480 bands, resulting in a van der Waals constant $C = 15.95 \text{ eV } a_0^3$ ($a_0 = \text{Bohr radius}$). Finally,

our estimate of the Ps work function in BiTe₂Se₂ yields a value close to zero (-0.034 eV). This is based on calculations of the electron and positron chemical potentials with the Abinit code [27], using the functional of Puska *et al.* [28]. With these parameters we find a bound state with energy -0.27 eV. This is a preliminary result because of some of the simplifying assumptions in the calculations. Indeed, in this first study, spin-orbit coupling was not included [except for the band plot in Fig. 1(b)]. This represents heavier calculations, which we are currently performing. Also, we used an approximate value for the Ps work function in BiTe₂Se₂, whose small value has yet to be confirmed. It would be of great interest to have this value determined experimentally. Thus, the final theoretical binding energy may deviate somewhat from the value we report here, but our result is robust to small variations of the different parameters determining the physisorption potential, and we do not expect the main conclusion of our work to be different.

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References

- [1] Ando Y 2013 J. Phys. Soc. Jpn. **82** 102001.
- [2] Puska M J and Nieminen R M 1994 Rev. Mod. Phys. **66** 841.
- [3] Mukherjee S, Nadesalingam M P, Guagliardo P, Sergeant A D, Barbiellini B, Williams J F, Fazleev N G, and Weiss A H 2010 Phys. Rev. Lett. **104** 247403 (2010).
- [4] Weiss A H, Mayer R, Jibaly M, Lei C, Mehl D, and Lynn K G 1988 Phys. Rev. Lett. **61** 2245.
- [5] Barbiellini B 2001, in *New Directions in Antimatter Chemistry and Physics*, edited by Surko C M and Gianturco F A (The Netherlands: Kluwer Academic Publishers), p. 127.
- [6] Tuomisto F and Makkonen I 2013 Rev. Mod. Phys. (to appear).
- [7] Platzman P M and Tzoar N 1986 Phys. Rev. B **33** 5900.
- [8] Saniz R, Barbiellini B, Platzman P M and Freeman A J 2007 Phys. Rev. Lett. **99** 096101; *ibid.* 2008 **100** 019902.
- [9] Sferlazzo P, Berko S, and Canter K F 1985, Phys. Rev. B **32** 6067.
- [10] Ford G W, Sander L M, and Witten T A 1976 Phys. Rev. Lett. **36** 1269.
- [11] Martin R M 2008 *Density Functional Theory: Basic Theory and Practical Methods* (Cambridge: Cambridge University Press).
- [12] Knowing the Ps wavefunction, furthermore, can allow one to estimate the pick-off annihilation rates with valence and core electrons near the surface.
- [13] Ren Z, Taskin A A, Sasaki S, Segawa K, and Ando Y 2010 Phys. Rev. B **82** 241306.
- [14] Lin H, Das T, Wray L A, Xu S-Y, Hasan M Z, and Bansil A 2011 New J. Phys. **13** 095005.
- [15] A. Weiss *et al.*, to be published.
- [16] Nordlander P and Harris J 1984 J. Phys. C **17** 1141.
- [17] Zaremba E and Kohn W 1976 Phys. Rev. B **13** 2270.
- [18] Patil S H, Tang K T, and Toennies J P 2002 J. Chem. Phys. **116** 8118.
- [19] Puska M J, Lanki P, and Nieminen R M, J. Phys.: Condens. Matter **1**, 6081 (1989).
- [20] Dalgarno A and Victor G A 1966 Mol. Phys. **10** 333.
- [21] Aulbur W G, Jönsson L, and Wilkins J W 1999 Solid State Phys. **54**.
- [22] Onida G, Reining L, and Rubio A 2002 Rev. Mod. Phys. **74** 601.
- [23] Heyd J, Scuseria G E, Ernzerhof M 2003 J. Chem. Phys. **118** 8207.
- [24] See Kresse G and Joubert D 1999 Phys. Rev. B **59** 1758 and references therein.
- [25] Nakajima S 1963 J. Phys. Chem. Solids **24** 479.
- [26] Gajdoš M, Hummer K, Kresse G, Furthmüller J, and Bechstedt F 2006 Phys. Rev. B **73** 045112.
- [27] Gonze X *et al.* 2009 Comput. Phys. Commun. **180** 2582.
- [28] Puska M J, Seitsonen A P, and Nieminen R M 1994 Phys. Rev. B **52** 10947.