Quantum-chemical studies of free and potassium-bound hole polarons in $SrTiO_3$ cubic lattice

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Abstract

Quantum-chemical computations based on the Hartree-Fock theory have been carried out for a free and impurity-bound hole polarons in $SrTiO_3$ crystal. Comparing hole localization energy versus lattice relaxation energy, the estimation of spontaneous hole self-trapping in the cubic lattice of pure $SrTiO_3$ has been made. The one-site hole spatial configuration has been found to be the only feasible hole geometry in both pure and potassium-doped $SrTiO_3$ crystals after carefully carried out automated geometry optimization. The ΔSCF calculated absorption energy for the potassium-bound hole polaron was found to be equal to 0.35 eV.

Keywords: Electronic structure; Point defects; Hole polarons; Oxides

1. Introduction

Strontium titanate is a widely used electronic ceramic material. Its typical application is use as a grain-boundary barrier layer capacitor [1,2], oxygen-gas sensor [3], and epitaxial growth substrate of the high temperature superconductor thin films [4] as well as catalytic material [5]. Despite the technological importance of the $SrTiO_3$ crystal, our understandings of structural and electronic properties of this crystal is not sufficient. For instance, phenomenological theory of Landau [6] fails to explain satisfactory structural phase transition of the $SrTiO_3$, which demonstrates the important role of critical fluctuations close to the transition temperature [7]. The explication of superconductivity phenomenon in the ceramic materials is not done as well. The $SrTiO_3$ crystal has been found to become superconducting when a little amount of electron carriers are introduced by oxygen vacancy, Nb substitution for Ti, or La substitution for Sr [8,9].

The above mentioned examples of unexplained phenomena and high technological importance are the reasons why the $SrTiO_3$ is under intensive investigation by both experimentalists [10-15] and theoreticians [16-18]. One of the interesting areas of research in titanates is carrier self-trapping study in the perfect lattice of these materials. Light-induced polarons and excitons like a pair of Jahn-Teller electron and hole has attracted growing interest among the scientists [17,19,20]. However, to our knowledge no attempts had been done so far to study the self-trapping possibilities of holes in the pure strontium titanate lattice.

We have used modified for crystals quantum-chemical intermediate neglect of differential overlap (INDO) method which was successfully exploited before to calculate different oxides and to study point defects therein [21-26] as well as to investigate crystals with simpler electronic band structures. Due to its semi-empirical character this method, as implemented into the CLUSTERD computer code [27], allows one to study very extended and complex systems, usually not available by non-empirical (*ab initio*) methods. In particular, the computer code has the important advantage of geometry prediction for crystals doped with impurity atoms [21,28]. Thanks to the very precise geometry reproduction some fundamental problems concerning the Li intercalation in the TiO_2 crystals were successfully resolved [23]. We have to note that within our method no *a priori* assumption is made upon the pattern of the electronic density distribution in the vicinity of the defect under study, i.e., it is obtained in the self-consistent-field (SCF) manner. This leads to a reliable information about the defect influence upon the electronic band structure properties. The method also allows one to calculate with a reasonable precision the excited state of the system thus giving the data about defect contribution into the absorption spectra of the crystal (ΔSCF method).

The method was found to be especially reliable in studies of free and impurity-bound hole polarons in α-Al_2O_3 [21,26,28,29] and TiO_2 [23] crystals. This is the first reason why we have chosen to apply CLUSTERD computer code to study similar defects in the strontium titanate. The second reason is that the computer program has already been used to compute perovskite-type materials, in particular, the phase transition phenomenon in $KNbO_3$ crystal [30] has been investigated giving very encouraging results. We have also successfully studied free and acceptor-impurity-bound hole polarons in the $BaTiO_3$ crystal [31,32], which has very similar structure to the $SrTiO_3$ crystal.

The main goals of this work are the following: (i) to determine theoretically whether a hole self-trapping can occur in a pure $SrTiO_3$ spontaneously under irradiation by estimating the energetical favourability of this process; (ii) to find out the possible spatial configurations of the free and potassium-bound hole polarons as well as the distortion of the crystalline lattice in the defective region; and finally (iii) to estimate hole polaron absorption energy using the ΔSCF method and its possible contribution into the absorption spectra of the $SrTiO_3$ crystal.

2. Outline of the method and INDO parametrization for $SrTiO_3$ crystal

The structure of a strontium titanate has simple cubic symmetry, which at around 105 K transforms to the tetragonal one. This corresponds to the transition: paraelectric phase → ferroelectric phase. The primitive unit cell of the $SrTiO_3$ contains five atoms [33] like in the case of another perovskite-type ceramic materials. Since the chemical bonding in strontium titanate has both ionic and covalent contributions, special attention has to be paid to the correct choice of the size of defective region and the interaction between this region and the residual part of a crystal. The most correct way to incorporate the interaction of the defective region with the surrounding crystalline lattice is to utilize one of the available periodic models. However, since the hole is a *charged* intrinsic defect, its simulation by periodic models is not feasible without the inclusion of some compensating charge [34]. That was the reason why we have chosen to use the *embedded molecular cluster* (EMC) model [35] with the cluster consisting of 90 atoms to study a free hole and a hole trapped by the potassium impurity. The 90-atom cluster was chosen due to the following considerations. $SrTiO_3$ belongs to a large group of perovskite-type compounds. Many of the crystals with this arrangement (see Figure 1) give exceedingly simple diffraction pattern that can be accounted for in terms of a cubic cell containing one molecule. Therefore, we have chosen to use 90-atom cluster, which (i) has cubic form and (ii) is stoichiometric. Usually even smaller clusters describe reliably band structure changes due to the defect presence. In order to optimize the INDO parameter set, the electronic structure of the pure $SrTiO_3$ crystal was computed using the *large unit cell* (LUC) model [36]. This approach is more precise than the EMC model because of the two reasons: (i) it takes into account explicitly the periodic nature of a crystal under study and (ii) it treats more carefully the exchange interaction.

In the LUC **k**=**0** approximation, the Fock matrix elements are made self-consistent through terms of the form

$$\frac{1}{\mathrm{N}}\sum_{k}\mathrm{P}_{\mathrm{pq}}(k)\exp(\mathrm{i}kR_{v}) \qquad (1)$$

where the summation is carried out over the values **k** in the reduced Brillouin zone (RBZ) of the LUC. Actually, the model is not fully self-consistent because of the nature of the approach: we can obtain information about the density matrices $\mathrm{P}_{\mathrm{pq}}(k)$ only at the center of the BZ. However, it has been proved that the computation of the electronic structure of the unit cell at **k**=**0** in the RBZ is equivalent to a band structure calculation at those BZ **k** points which transform to the RBZ center on extending the unit cell [37]. As indicated by numerous studies [21,28,38-40], a fourfold- or eigthfold-symmetric extension of the primitive unit cell proves to be completely sufficient to reproduce correctly the electronic band structure of the crystal. We have used eigthfold (2x2x2) extended LUC to parametrize the $SrTiO_3$ crystal. The INDO parameter sets for the O and Ti atoms were taken from Refs. 27 and 41, respectively. The parameter set for the Sr atom was optimized by calculating the following properties and comparing them to the experimental results: (i) the main features of the strontium titanate crystal (width of the forbidden energy gap, widths of the upper and lower valence bands, composition of the valence bands, cubic lattice constant of the crystal), (ii) the inter-atomic distance and the ground state of the SrO molecule, and (iii) the first two ionization potentials for the Sr atom.

We reproduced quite well the ionization potentials for the Sr atom (Table 1) as well as the ground state of this atom. The obtained inter-atomic distance of 1.92 Å and the ground state symmetry ${}^1\Sigma^+$ for the SrO molecule match exactly the experimental data [45]. The main electronic and spatial structure properties of the $SrTiO_3$ are given in the Table 2. The widths and compositions of the valence bands are in a very good agreement with the X-ray photoelectron spectra measurements [46]. The lower valence band is composed mainly of O 2s states while the upper valence band predominantly is O 2p in nature (Figure 2). A considerable admixture of Ti 3d states was found in the upper valence band, which testifies the importance of the covalent bonding in the $SrTiO_3$ crystal. In addition, as it follows from the Figure 2, the subband of Sr 4p states is found to lie between the upper and lower valence bands. This energy band is very narrow having the width of only 0.2 eV. We considered essential to include the Sr 4p states as the basis atomic orbitals (AO´s) within the valence basis set since their overlap with AO´s of the other atoms is not negligible.

The most obvious discrepancy between the INDO calculated electronic band structure results and the experimental data is found to be for the value of the forbidden energy gap width. The reason of this disagreement is the omission of long-range correlation effects (only the short-range correlation corrections are accounted through the use of atomic parameters) which is the common fault of the methods based on the Hartree-Fock Molecular Orbital theory [42]. Long-range correlation between valence electrons is known to raise the upper valence band and to lower the bottom of the conduction band leading to a reduction of the bandgap width for oxide crystals by approximately 3-4 eV [21,43]. This estimated quantity falls between our "errors" of 1.3 eV and 5.7 eV obtained by the ΔSCF method and as a difference between HOMO and LUMO states, respectively. It has to be stressed once more that within the current method one should keep the forbidden energy gap considerably larger than the known experimental value in order to *reproduce correctly* the electronic band structure of the system under study. Thereby optimized parameters are given in Tables 3 and 4. In order to calculate K impurity, we had to use K parameter set, which was taken from Ref. 27. Generally speaking, the parameter set for each type of atoms consists of the following semi-empirical parameters: ζ, E_{neg}, P^0, β and α. The orbital exponent ζ enters the radial part of the Slater-type atomic orbitals. A valence basis set including 5s and 4p AOs on Sr, 4s, 4p and 3d AOs on Ti, 2s and 2p AOs on O and 4s AO on K was used. The parameters E_{neg} (AO electronegativity) and P^0 (AO population) enter the diagonal matrix elements of the Fock matrix. The so-called resonant integral parameter β enters the non-diagonal Fock matrix. Finally, the parameter α characterizes the non-point nature of the atomic core and enters the matrix elements describing electron-core interaction.

3. Results and discussion

In this section, first, the estimation of hole self-trapped energy is given for the cubic lattice of the $SrTiO_3$ crystal. This is followed by results obtained for hole spatial configurations and lattice distortion for both pure and potassium-doped strontium titanate. The absorption energy is calculated for potassium-bound polaron using the ΔSCF method.

3.1 Estimation of hole self-trapping energy in the $SrTiO_3$ cubic lattice

"Hole" means the absence of one electron. This point defect can appear in a crystal under irradiation. To decide whether the self-trapped hole (STH) is energetically preferred to a free-hole state in a given material, it is necessary to calculate the so-called self-trapping energy [47,48], i.e., the energy difference:

$$\Delta \mathrm{E} = \mathrm{E}_{\mathrm{ST}} - \mathrm{E}_{\mathrm{F}}^{(k)} \qquad (2)$$

where E_{ST} is the hole energy for the fully relaxed ST state and $\mathrm{E}_{\mathrm{F}}^{(k)}$ is the energy of the free-hole state at the bottom of the free hole band. If ΔE_{ST} is positive, the self-trapping does not occur, but if it is negative, the hole can be trapped spontaneously. The larger the absolute value of the negative ST energy, the larger the lifetime of the hole in the ST state rather than in a free-hole state.

To realize in practice the calculation of the ST energy, we have used the old idea of Gilbert [49] who considered the hole self-trapping as a hypothetical two-stage procedure. The localization of a free hole in a local perfect crystal region in the first stage, and the subsequent relaxation of the lattice with accompanying electronic charge redistribution in a local region in the second stage, until the ST state is formed. In the first stage, the hole acquires a positive contribution to its energy due to the loss of kinetic energy in the local state. In the second stage, however, the hole acquires a negative energy due to the atomic displacements around the localized hole. A competition between the positive localization energy, E_{loc}, associated with the first stage, and the negative relaxation energy, E_{rel}, obtained in the second stage, results in the actual sign of the ST energy,

$$\Delta E_{ST} = E_{loc} + E_{rel} \qquad (3)$$

and leads to a final conclusion about the possibility of finding stable hole polarons in a given crystal.

The stoichiometric molecular cluster consisting of 90 atoms $[Sr_{18}Ti_{18}O_{54}]^{+}$ has been used throughout the polaron calculations. When a hole was inserted into the molecular cluster, its spin density was mainly found localized on one of the O atoms. For a one-site Wannier-type localized state of the hole one can use Fowler estimate [50] as E_{loc} being equal to the half width of the upper valence band. However, this approximation is valid only for very diffuse and smooth energy bands, which is not our case because we have considerable admixture of Ti 3d states in the O 2p valence band.

In other words, the "center of gravity" of the O 2p band is not located at the exact middle of the band. Considering the Wannier representation of localized states and Fourier transform of the valence band energies (see Ref. 29 for more details) one can obtain the "center of gravity" of the corresponding occupied valence band in the following manner:

$$\varepsilon^{(W)} = \int \varepsilon \mathrm{N}_{\mathrm{j}}(\varepsilon) \mathrm{d}\varepsilon \qquad (4)$$

where $N_j(\varepsilon)$ is the density of states (DOS) of the valence band *j* normalized to unity and the integration is performed over the whole bandwidth. Using this approach we obtained the value of 2.85 eV for the hole localization energy E_{loc}.

In order to estimate the relaxation energy term, E_{rel}, we allowed to make displacements to twenty-seven atoms situated around the oxygen, which receives a hole. E_{rel} was computed as a difference of the total energies of the EMC in the relaxed and unrelaxed states, giving the value of 2.90 eV. So, using the equation (3) we obtained -0.05 eV as a value for the hole self-trapping energy. Since this magnitude is almost equal to zero we can conclude that the spontaneous occurrence of polarons in the pure strontium titanate cubic lattice with a considerable lifetime is practically impossible. In general, the larger the absolute value of the negative self-trapping energy, the larger the lifetime of the hole in the ST states rather in a free hole state. In accordance to our previous studies [21, 26, 29] and experimental expectations, the value of the ΔE_{ST} has to be at least few electronvolts if one wants to find the stable polarons in a given material.

3.2 Lattice distortion due to the hole polarons

In a pure $SrTiO_3$ cubic lattice the hole spin density finds itself on one of the O atoms, denoted hereafter as O_p. Some 90% of the spin density are located on the O_p atom, which is situated practically in the center of the molecular cluster, so any influence of the cluster border effects on the outcome of computations is excluded. The automated geometry optimization was carried out using the downhill simplex method in multidimensions [51]. During the geometry optimization twenty-seven polaron-nearest atoms were allowed to move from their regular lattice sites. As a result it was found that only two closest Ti atoms and four closest O atoms have noticeable displacements of the order of 0.1 Å. The negatively charged O atoms in the defective region move towards while the positively charged Ti atoms move outwards the O_p atom. This is in accordance with the expectations since the O_p has positive effective charge with respect to the perfect crystalline lattice after it receives a hole.

The same stoichiometric molecular cluster has been utilized to study K-bound polaron. The potassium atom was substituted for one of the Sr atoms situated in the center of $[Sr_{18}Ti_{18}O_{54}]^0$ cluster. The potassium has an effective negative charge with respect to the perfect $SrTiO_3$ crystalline lattice. So, one can easily foresee that the impurity will attract the positively charged hole. That was indeed observed in our computer simulations, i.e., the hole localized on one of the K-nearest O atoms, denoted hereafter as the O_k atom. Then the automated geometry optimization has been carried out, which showed 0.07 Å displacement of the O_k atom towards the potassium impurity. The movements of another atoms in the defective region were smaller as 0.04 Å. In our mind, the diminutive atomic displacements might be explained by the rigid crystalline lattice and the cubic close packing of atoms in the $SrTiO_3$ structure.

3.3 Calculation of absorption energy for the potassium-bound hole polaron

When the geometry of the EMC containing the point defect was optimized, we calculated the absorption energy for the potassium-bound polaron. This corresponds to the hole transition $2p_y \rightarrow 2p_x$ (or electron transition $2p_x \rightarrow 2p_y$), where $2p_y$ and $2p_x$ are hole polaron wavefunctions corresponding to the ground and excited states, respectively. The one-electron level of the hole polaron ground state, which is described by the wavefunction $2p_y$, lies in the forbidden energy gap while the one of the excited state, which is mainly described by the wavefunction $2p_x$ lies within the upper valence band. We have to note that the hole polaron wavefunctions in the ground and excited states were obtained in the SCF manner, i.e., without any *a priori* assumption on this matter. The absorption energy was computed using the ΔSCF method, i.e., as a difference of the EMC total energies in the relaxed ground state and the excited state having identical atomic configuration with the ground state (the vertical optical transition). Thus calculated absorption energy was found to be equal to 0.35 eV. We have to note that besides p_y and p_x AOs, the wavefunctions of the hole polaron ground and excited states have considerable another non p-type contributions.

4. Conclusions

This paper describes the first attempt to estimate theoretically the polaron self-trapping possibilities in the cubic lattice of pure $SrTiO_3$ crystal. The positive hole localization energy is computed versus the negative atomic relaxation energy. The obtained resultant hole polaron self-trapping energy is close to the zero. Thus our studies point out that the stable hole polarons will not occur in the cubic $SrTiO_3$ lattice unless the acceptor impurities are present in the material. In the latter case, the impurity may act as a trap of hole polarons since it has a negative effective charge with respect to the perfect crystal.

It was found that the potassium atom substituting for one of the Sr atoms indeed acts as a trap. The polaron is trapped at one of the potassium-nearest oxygen atom. The calculated absorption energy, which results from the presence of the potassium-trapped hole polaron, is found to be equal to 0.35 eV using the ΔSCF method.

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Table 1.

Calculated ionization potentials of the Sr atom (in eV) in comparison to the experimental data [44].

	INDO results	Exp. data
1st IP	5.60	5.692
2nd IP	12.89	11.027

Table 2.

Basic properties of the $SrTiO_3$ crystal obtained by the INDO method in comparison to the available experimental results: ΔE_{g1}, width of the forbidden energy gap obtained by the ΔSCF method (in eV); ΔE_{g2}, width of the forbidden energy gap obtained as a difference between HOMO and LUMO states (in eV); E_{v1}, the upper valence band width (in eV); E_{v2}, the lower valence band width (in eV); *a*, lattice constant (in Å); q(Sr), q(Ti) and q(O), charges on Sr, Ti and O atoms, respectively, (in *e*).

Property	INDO results	Exp. data[a]
ΔE_{g1}	4.5	3.2
ΔE_{g2}	8.9	3.2
E_{v1}	6.7	5.0
E_{v2}	3.0	1.5
a	3.90	3.90
q(Sr)	1.88	
q(Ti)	2.23	
q(O)	-1.37	

[a] The experimental values the of band structure properties are taken from [46] while the lattice constant is taken from [33].

Table 3.

Semi-empirical INDO parameter sets used in the present work: ζ (in au), E_{neg} (in eV), P^0 (in *e*) and β (in eV).

Atom	AO	ζ	E_{neg}	P^0	β
Sr	5s	1.59	11.15	0.18	-0.4
	4p	2.80	37.5	2.00	-4.5
Ti	4s	1.4	3.7	0.65	-0.5
	4p	1.1	-15.0	0.04	-0.5
	3d	1.93	7.2	0.55	-9.0
O	2s	2.27	4.5	1.974	-16.0
	2p	1.86	-12.6	1.96	-16.0
K	4s	1.1	1.8	0.10	-0.1

Table 4.

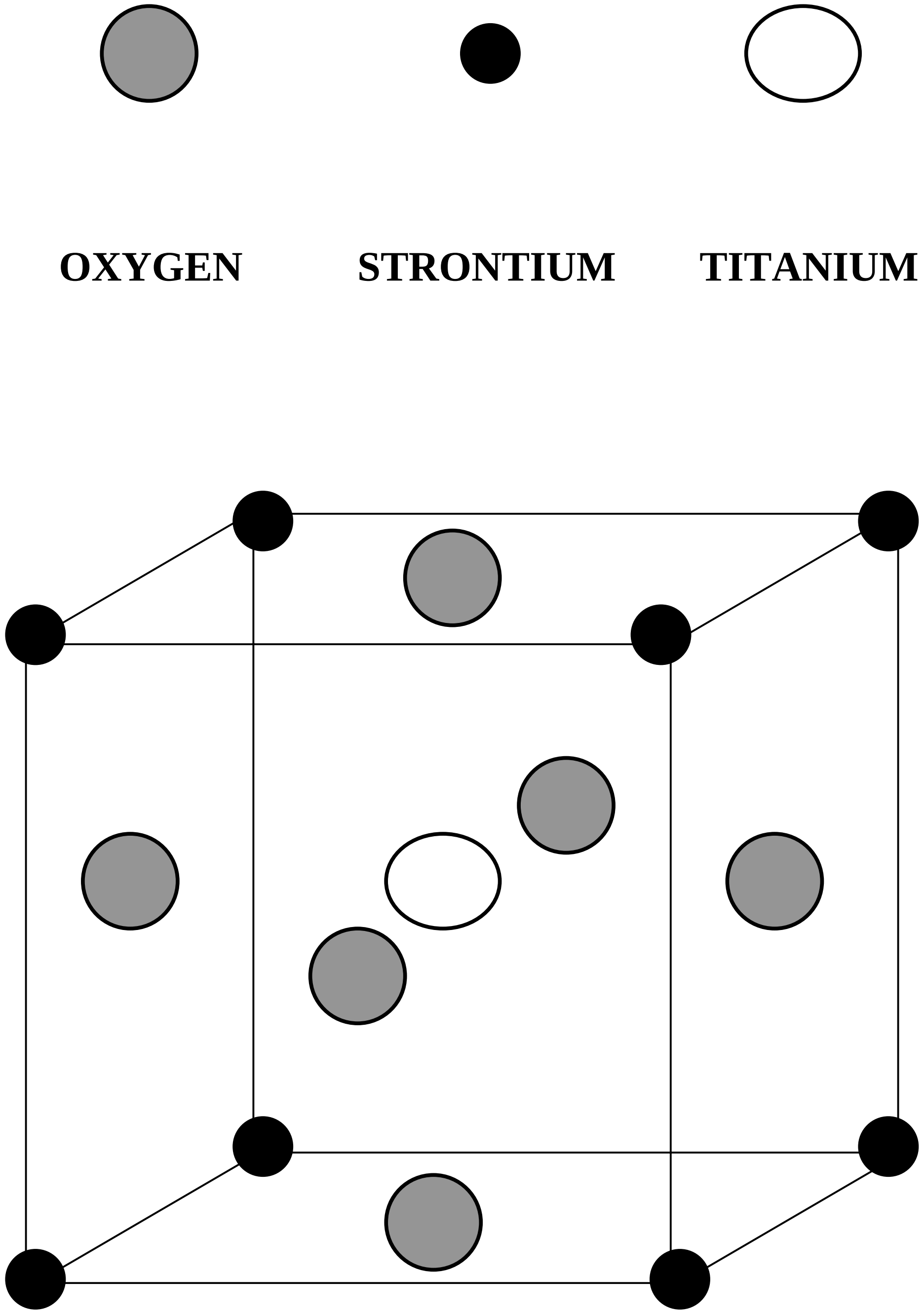
Semi-empirical INDO two-center parameters $\alpha_{\mu B}$ (au^{-1}) optimized during the calculations; μth AO belongs to the atom A, where A≠B.

A	B			
	Sr	Ti	O	K
Sr	0.15	0.55	0.25	0.00
Ti	0.09	0.13	0.10	0.00
O	0.59	0.38	0.15	0.26
K	0.00	0.00	0.05	0.00

FIGURE CAPTIONS

Fig. 1. A fragment of the $SrTiO_3$ cubic lattice. Black balls situated in the vertices of the cube denote Sr atoms. White atom in the center of the cube denotes Ti atom. Grey atoms centered at the faces of the cube denote O atoms.

Fig. 2. Total density of states (DOS) of the cubic $SrTiO_3$ crystal. The lower valence band is composed mainly of O 2s states while the upper valence band predominantly is O 2p in nature. A narrow subband of Sr 4p states lie between the upper and lower valence bands. The bottom of the conduction band is composed mainly of Ti 3d states.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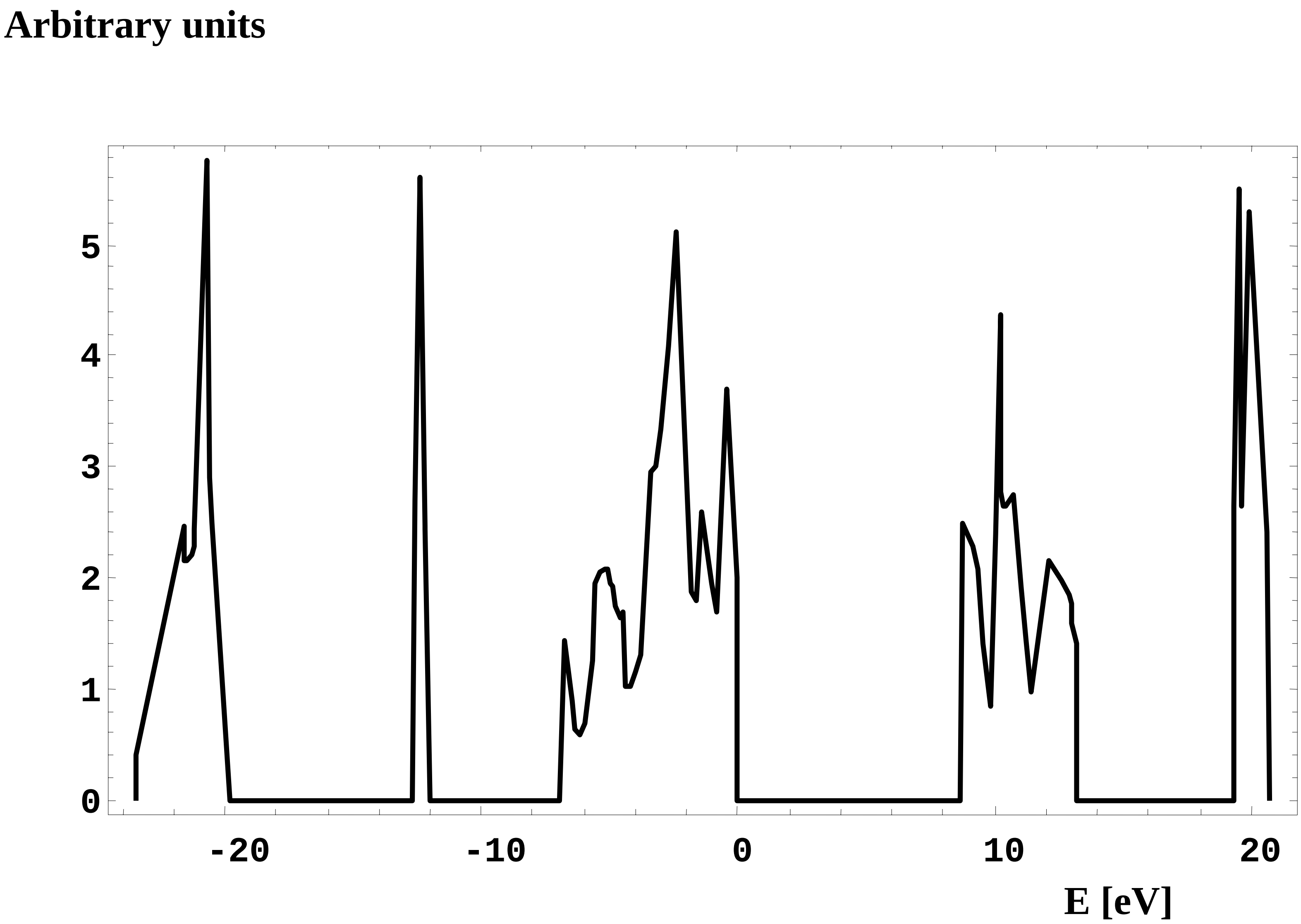
Arbitrary units
5
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