

LCAO-based theoretical study of PbTiO₃ crystal to search for parity and time reversal violating interaction in solids

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An experiment towards the search for the interaction of the Schiff moment (S) of the ²⁰⁷Pb nuclei with electrons in PbTiO₃ crystal which violates the time reversal (T) and space parity (P) symmetries was proposed by Mukhamedjanov and Sushkov [Phys. Rev. A **72**, 034501 (2005)]. The interpretation of the experiment in terms of the Schiff moment requires knowledge of an electronic density gradient parameter (usually designated as X) on the Pb nucleus in the crystal, which is determined by the electronic structure of the crystal. Here we propose a theoretical approach to calculate the properties in solids which are directly sensitive to the changes of valence electron densities in atomic cores but not in the valence spatial regions (Mössbauer parameters, hyperfine structure (HFS) constants, parameters of T,P-odd Hamiltonians, etc. [L. V. Skripnikov and A. V. Titov, Phys. Rev. A **91**, 042504 (2015)]). It involves constructing the crystalline orbitals via the linear combination of atomic orbitals and employs a two-step concept of calculating such properties that was earlier proposed by us for the case of heavy-atom molecules. The application of the method to the PbTiO₃ crystal results in the energy shift, $\Delta\varepsilon = 0.82 \times 10^6 \frac{S(^{207}\text{Pb})}{ea_B^3}$ eV, due to the T,P-odd interactions. The value is compared to the corresponding parameter in diatomic molecules (TlF, RaO, PbO), which have been proposed and used in the past decades in the search for the nuclear Schiff moment. We also present the calculation of the electric field gradient at the Pb nucleus in PbTiO₃ for the comparison with other solid-state electronic structure approaches. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4959973>]

I. INTRODUCTION

A search for the effects of simultaneous nonconservation of time-reversal (T) invariance and space parity (P)^{1,2} symmetries, that leads to the existence of the permanent electric dipole moment of electron (e EDM), nuclear Schiff moment (NSM), scalar-pseudoscalar nucleus-electron interactions, nuclear magnetic quadrupole moment etc., is presently considered to be one of the most intriguing problems of modern physics. The existence of e EDM³ within the Standard Model (SM) even for the point (bare) electron model can be explained by considering the effects of vacuum polarization which involve P-odd weak interaction and empirically introduced the imaginary parameter in the Kobayashi-Maskawa matrix as a CP-violating phase (C means charge conjugation; the CP-violation according to CPT-theorem is equivalent to T-violation).^{1,2} Although the possible T violation mechanism within the SM induces too small effect, many of its extensions give rise to such T,P-odd effects which are already within the reach of modern experiments, e.g., the SM value of e EDM is estimated to be lower than 10^{-38} e-cm, while the SM extensions give values in the range 10^{-25} – 10^{-31} e-cm.² It was realized half a century ago^{1,2,4–8} that very promising experiments on search for the violation of fundamental symmetries could be performed on

atoms, molecules, and solids containing heavy elements. The electron EDM can induce EDM of the whole open-shell system (where electron angular momentum is not zero). Another possible source of T,P-odd effects is the nuclear Schiff moment. The electrostatic interaction of the nuclear Schiff moment with electrons can produce a net EDM of the closed-shell systems. The effects of T,P-violating interactions can be considerably enhanced in heavy-atom systems with a large nuclear charge (see Ref. 2 and references therein). However, some electronic structure parameters which are required to evaluate the cumulative (EDM) effect induced by a “bare” T,P-odd source (e EDM, Schiff and magnetic quadrupole moments, scalar-pseudoscalar nucleus-electron interactions, etc.) cannot be measured and can only be calculated within some theoretical models.

Numerous experiments searching for T,P-odd effects were performed during the last decades and the experiment on ThO molecular beam has recently succeeded in obtaining a very rigid upper bound on e EDM,^{9–11} $9 \cdot 10^{-29}$ e-cm. This is already at the level predicted by the mainstream of SM extensions.⁹ The best limit on the nuclear T,P-odd interactions was obtained in atomic Hg experiments.¹² The Hg EDM measurements give a limit on the neutron EDM, which is comparable with one from the direct neutron EDM measurements.¹³ Numerous studies on the search for NSM have been performed for diatomics, e.g., TlF.^{14–17} Although the use of solids in search for T,P-violation effects was proposed by Shapiro many years ago,⁷ the experiments for

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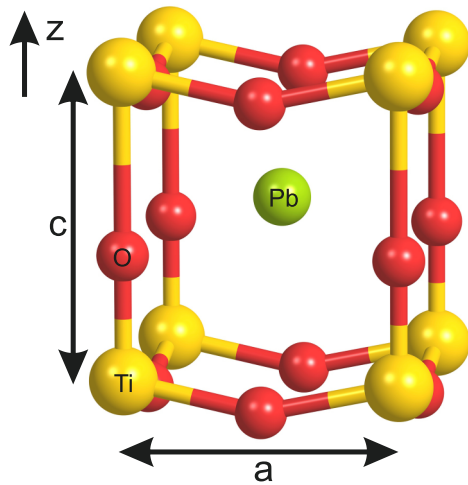


FIG. 1. Structure of PbTiO_3 crystal in the ferroelectric phase.

e EDM detection in solids became attractive only during the past decade due to the suggestions of Lamoreaux¹⁸ followed by other investigations^{19,20} to utilize gadolinium garnets. The main idea of the experiments in solids is based on the collinearity of e EDM with the direction of its spin (magnetic moment).²¹ Therefore, when applying some external electric field to a sample, one can observe macroscopic magnetization of the sample. A series of theoretical studies followed by an experimental searching for e EDM were performed on the $\text{Eu}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$ crystal^{22–25} and gadolinium gallium garnet.²⁶ The obtained limit on the e EDM in the solid-state experiment²⁵ is $6.05 \times 10^{-25} e\cdot\text{cm}$.

The use of PbTiO_3 crystal to search for the Schiff moment of the ^{207}Pb nucleus has recently been suggested by Mukhamedjanov and Sushkov.²⁷ According to the authors, one can attain a sensitivity to NSM up to ten orders of magnitude higher than the current limit obtained on the Hg nuclei using a beam of Hg atoms.¹² At 763 K, the PbTiO_3 crystal undergoes ferroelectric phase transition from the cubic to tetragonal symmetry. In the ferroelectric phase of PbTiO_3 , the Pb and Ti atoms are displaced along the tetragonal axis (“z” on Fig. 1) with respect to their non-ferroelectric positions (in cubic phase) that can induce rather strong T,P-odd effect on Pb.²⁷

Two types of NSM measurements were proposed in Ref. 27. The first one is similar to those proposed by Lamoreaux¹⁸ for gadolinium garnets, i.e., to measure macroscopic magnetization induced by an electric field due to T,P-odd interactions. The second is the nuclear magnetic resonance experiment (see Ref. 27 for details). Another interesting application of PbTiO_3 is using it as an axion dark matter detector.²⁸

A. The Schiff moment interaction and properties of “atoms in compounds”

As was pointed out by Schiff, a finite size nucleus will possess a nonzero T,P-odd (Schiff) moment if the charge and nucleon EDM distributions are different.²⁹ This is the so-called volume effect. The main contribution comes from the valence

unpaired nucleon. The Schiff moment, S , is collinear to the nuclear spin and it can induce electrostatic potential φ ,¹

$$\varphi(\mathbf{r}) = 4\pi(\mathbf{S} \cdot \nabla)\delta(\mathbf{r}). \quad (1)$$

Then the energy of the effective T,P-odd interaction between the nuclear Schiff moment and electrons of the system can be written in the form^{8,16}

$$\Delta\varepsilon = 6SX\vec{\sigma}_N \cdot \vec{\lambda}, \quad (2)$$

where $\vec{\sigma}_N$ is a unit vector directed along the nuclear spin of ^{207}Pb , $\vec{\lambda}$ is a unit vector along the tetragonal axis of PbTiO_3 , S is the Schiff moment of the ^{207}Pb nucleus, X is determined by the electronic structure close to the Pb nucleus,^{16,17}

$$X = \frac{2\pi}{3} \left[\frac{\partial}{\partial z} \rho_\psi(\mathbf{r}) \right]_{x,y,z=0}, \quad (3)$$

where $\rho_\psi(\mathbf{r})$ is the electronic density calculated from the relativistic wave function ψ of the system under consideration.

It follows from Eq. (2) that in order to interpret the measured value ($\Delta\varepsilon$) in terms of NSM, one should know the X parameter. Up to now, only a few models for calculating X were considered in crystals. In these models, a local electronic structure in the vicinity of a heavy-atom nucleus was simulated by a cluster of the nearest atoms and a system of point charges³⁰ or by considering an effective state of Pb in the oxygen environment.^{19,27} The periodic properties of the crystal were not accurately taken into account in these estimations as well as the finite nuclear size of Pb and correlation effects.

One can see from Eq. (3) that X is an example of the so-called *atoms in compounds* (AiC) characteristics,^{31–33} i.e., measurable electronic properties or just some electronic structure parameters, which are sensitive to the changes of the densities of *valence* electrons in the *core region* of an atom of interest.³⁴ Other examples are hyperfine magnetic dipole and electric quadruple constants (electric field gradients (EFGs)), chemical shifts of x-ray emission lines, volume isotope and Mössbauer shifts, etc.^{33,35} The common feature of the AiC properties is that in a very good approximation they are localized on an atom and do not depend on the bonding density in contrast to some other properties,^{36–39} etc. In the present paper the X parameter is evaluated using a new approach to the studies of the AiC characteristics in *solids*. The approach takes an account of relativistic and correlation effects and is valid for periodic structures; thus, our earlier developments directed on the investigation of the AiC characteristics in heavy-atom molecules^{15,32,35,40–42} and applied to different systems^{31,33,43–49} are extended to solids.

It is not possible to make a direct comparison of molecular or crystalline T,P-odd constants such as X or effective electric field acting on e EDM with the experiment.³⁴ It has become a common practice in numerous investigations of T,P-odd effects in molecules to compute other AiC properties like hyperfine structure (HFS) constant for which experimental data can be obtained.³² To our knowledge, up to now there are no experimental data about the electric quadrupole hyperfine coupling constant at Pb in the PbTiO_3 crystal. However, there are all-electron four-component calculations of the electric field gradient (EFG) at Pb nucleus which determines the hyperfine quadrupole coupling constant. The EFG tensor is

defined as (we assume that Pb atom is at the origin)

$$V_{ij} = \lim_{r \rightarrow 0} \left(\frac{\partial^2 V(\mathbf{r})}{\partial r_i \partial r_j} - \frac{1}{3} \delta_{ij} \nabla^2 V(\mathbf{r}) \right), \quad (4)$$

where $V(\mathbf{r})$ is the Coulomb potential. We have applied the proposed method to compute the EFG parameter at Pb in PbTiO_3 and compare it with the traditional methods of calculating such properties in solids, e.g., linearized augmented plane waves (LAPWs).⁵⁰

For the comparison and accuracy estimation, the value of the X parameter for the ground $^1\Sigma^+$ state of the ^{207}PbO molecule has also been calculated using the same approximations made in solid state calculations. We have also applied the relativistic coupled cluster approach with single and double cluster amplitudes, CCSD, as well as the relativistic coupled cluster approach with single, double, and perturbative triple cluster amplitudes, CCSD(T), which have not been routinely available for solid state calculations up to now.

II. METHOD OF CALCULATION OF AiC CHARACTERISTICS

Solid state calculations are usually performed within the Hartree-Fock method or density functional theory (DFT). In these approaches the wave function of a crystal is built as a Slater determinant of one-electron crystalline orbitals (COs) $\psi_i(\mathbf{r}, \mathbf{k})$.⁵¹ COs are formed as linear combinations of Bloch functions $\varphi_\mu(\mathbf{r}, \mathbf{k})$. In the approximation of linear combination of atomic orbitals (LCAO), Bloch functions are written as (e.g., see Ref. 52)

$$\varphi_\mu(\mathbf{r}, \mathbf{k}) = \sum_{\mathbf{g}} \chi_\mu(\mathbf{r} - \mathbf{A}_\mu - \mathbf{g}) e^{i\mathbf{k} \cdot \mathbf{g}}, \quad (5)$$

where \mathbf{g} runs over all the lattice vectors and \mathbf{A}_μ is an atomic coordinate in a zero reference cell, on which the atomic basis function χ_μ is centered. By solving Hartree-Fock or Kohn-Sham equations, one can obtain CO-LCAO expansion coefficients $C_{\mu i}(\mathbf{k})$ for the one-electron eigenstates $\psi_i(\mathbf{r}, \mathbf{k})$,

$$\psi_i(\mathbf{r}, \mathbf{k}) = \sum_{\mu} C_{\mu i}(\mathbf{k}) \varphi_\mu(\mathbf{r}, \mathbf{k}). \quad (6)$$

The one-electron reduced density matrix in a direct lattice takes the following form:

$$\tilde{P}_{\mu\nu}^{\mathbf{g}-\mathbf{g}'} = \sum_{\mathbf{k}} \tilde{P}_{\mu\nu}(\mathbf{k}) e^{i\mathbf{k} \cdot (\mathbf{g}-\mathbf{g}')}, \quad (7)$$

where $\tilde{P}_{\mu\nu}(\mathbf{k})$ is the density matrix in a reciprocal lattice that is determined by coefficients $C_{\mu i}(\mathbf{k})$.

All-electron relativistic approaches on the basis of the Dirac-Coulomb-(Breit) Hamiltonian would have been formally optimal for the calculations of AiC characteristics in a heavy-element compound; however, the four-component calculations are already difficult for diatomics and they are a lot harder for solids (note, however, about some promising all-electron developments on the basis of LAPW method,⁵⁰ etc.).

In our study, we have extended the molecular two-step approach developed by our group earlier^{35,42} to periodic

structures (solids). The new implementation of the concept is as follows. First, an electronic calculation for valence and outer-core electrons is performed using the Density Functional Theory or Hartree-Fock method for a given crystal. The inner-core electrons of heavy atoms are excluded from the calculations using a generalized relativistic effective core potential, GRECP, method.^{53,54} Second, since the inner-core parts of the valence one-electron ‘‘pseudo-wavefunctions’’ are smoothed in the GRECP calculations, they have to be recovered using the core-restoration method^{32,35} before they can be used to evaluate the AiC characteristics. The non-variational restoration, which is based on the proportionality of valence and virtual spinors in the inner-core spatial region of heavy atoms,⁵⁵ is used presently, in which one generates the *equivalent* basis sets of one-center four-component spinors

$$\begin{pmatrix} f_{nlj}(r)\theta_{ljm} \\ g_{nlj}(r)\theta_{2j-l,jm} \end{pmatrix}$$

and smoothed two-component pseudospinors

$$\tilde{f}_{nlj}(r)\theta_{ljm}$$

via atomic all-electron finite-difference Dirac-Fock-Breit and GRECP/SCF_{jj} (where SCF_{jj} means self-consistent field calculations employing the jj -coupling scheme) of the same configurations of a considered atom and its ions.⁵⁶⁻⁵⁹ Here n is the principal quantum number, j is the total electronic momentum, m is its projection, and l is the orbital momentum. These basis sets, describing mainly the given atomic core region, are independently generated of the basis set used for the crystalline (GRECP) calculations.

In addition, a set of spin-orbitals (and not complex spin-orbit-mixed spinors) $\tilde{\xi}_p$ is generated; $\tilde{\xi}_p$ are then expanded in the basis set of one-center two-component atomic pseudospinors,

$$\tilde{\xi}_p \approx \sum_{l=0}^{L_{\max}} \sum_{j=|l-1/2|}^{j=|l+1/2|} \sum_{n,m} T_{nljm}^p \tilde{f}_{nlj}(r)\theta_{ljm}. \quad (8)$$

The atomic two-component pseudospinors are replaced by the equivalent four-component spinors while the expansion coefficients from Eq. (8) are preserved,

$$\xi_p = \sum_{l=0}^{L_{\max}} \sum_{j=|l-1/2|}^{j=|l+1/2|} \sum_{n,m} T_{nljm}^p \begin{pmatrix} f_{nlj}(r)\theta_{ljm} \\ g_{nlj}(r)\theta_{2j-l,jm} \end{pmatrix}. \quad (9)$$

Thus, one obtains the ‘‘restored’’ four-component function ξ_p which we call the ‘‘equivalent’’ one to the two-component pseudofunction $\tilde{\xi}_p$.

Crystalline spin-orbitals with the spatial part $\chi_\mu(\mathbf{r} - \mathbf{A}_\mu - \mathbf{g})$ can be expanded in the basis of $\tilde{\xi}_p$ functions. This operation corresponds to a similarity transformation of the density matrix,

$$\|\tilde{P}_{\mu\nu}^{\mathbf{g}}\| \longrightarrow \|\tilde{D}_{pq}\|, \quad (10)$$

where $\|\tilde{D}_{pq}\|$ is a density matrix in the basis of $\tilde{\xi}_p$ functions.

Due to the ‘‘equivalence’’ of $\tilde{\xi}_p$ and ξ_p functions (see Eqs. (8) and (9)) based on the appropriate properties of the hard-core shape-consistent (G)RECP versions,⁶⁰ one can write

$$\|D_{pq}\| \approx \|\tilde{D}_{pq}\|, \quad (11)$$

where D_{pq} are elements of the density matrix in the basis of four-component ξ_p functions (9). Thus, as an approximation, we can equate the D_{pq} elements to \tilde{D}_{pq} and interpret this as the restoration of the “true” four-component density matrix structure, which is important, above all, for the inner-core spatial region and consequently for the AiC characteristics.

The mean value of some one-electron operator A corresponding to an AiC property of a given atom in the zero reference cell can be evaluated as follows:

$$\langle A \rangle = \sum_{pq} D_{pq} A_{pq}, \quad (12)$$

where A_{pq} are the matrix elements of the operator A in the basis of four-component functions ξ_p .

In the current implementation of restoration procedure, the $\tilde{\xi}_p$ spin-orbitals are taken in the form of contracted Gaussians thus enabling analytical integration at step (10).

The developed code was interfaced to the CRYSTAL09 code⁶¹ to use the periodic density matrix (7).

To perform a GRECP/restoration calculation of AiC characteristics in *molecules* with the spin-orbit effects taken into account at the GRECP calculation stage, the code is also developed for the case when *two-component* molecular spinors φ_μ are used.³² The code is interfaced to use the two-component density matrices obtained in the GRECP calculations using the molecular DIRAC12⁶² and MRCC⁶³ codes.

It should be emphasized that the computation of the X parameter, Eq. (3), is not a trivial task even for the diatomic molecules using the highly elaborate four-component Dirac-Coulomb codes such as DIRAC⁶² with the Gaussian basis sets. The problem is in the strong (about two orders of magnitude) cancellation of large- and small-component contributions¹⁷ in the calculation of the density gradient. The authors of Ref. 17 concluded that very large even-tempered basis sets are required even for simple diatomic molecules to achieve a numerical stability whereas popular energy optimized basis sets cannot be used. In the present method, the four-component functions ξ_p used to evaluate the matrix elements of the operator A are taken in a numerical (finite-difference) form. Moreover, the wavefunctions are represented by power series of the electronic radius-vector in the spatial region very close to the nucleus. This allows one to eliminate complications in reproducing the asymptotic wavefunction behavior in the region near the nucleus. Another required condition for the relativistic four-component computation of the X parameter is the use of the finite nuclear size model due to a wavefunction singularity in the point-nucleus case. The requirement is not always satisfied in four-component codes. In the present work, we use the Fermi model of nuclear density. One should note that the computation of such AiC properties as HFS constants are easier and can be successfully performed in four-component approaches using available gaussian basis sets⁴⁷ since there are no such cancellations as in the case of the X parameter.

III. RESULTS AND DISCUSSIONS

It was shown in a number of papers^{64–66} that commonly used density functionals, such as PBE (proposed

by Perdew, Burke, and Ernzerhof)⁶⁷ and PW91,⁶⁸ give extremely poor predictions of the volume and strain of ferroelectrics such as PbTiO₃ and BaTiO₃. A modified exchange density functional, WC, exploiting the generalized gradient approximation was proposed in Ref. 64 and predicts the structural properties much better. Later, a hybrid B1-WC functional was suggested that gives a good description of both structural and electronic properties of ferroelectric oxides.⁶⁶ The latter functional was applied in the present paper for the calculation of valence electronic structure of tetragonal PbTiO₃, while the *1s–4f* inner-core electrons of Pb were excluded from the calculation using the valence (semi-local) version of GRECP operator⁵³ taken from our previous studies.^{69,70} To describe the Pb atom in PbTiO₃ crystal, a new basis set consisting of six *s*-type, seven *p*-type, and four *d*-type segmentally contracted Gaussian functions was generated with the code developed in Ref. 71 and extended here. For Ti and O atoms, the basis sets of triple-zeta valence with polarization quality, TZVP, from Ref. 72 were used. All the electrons of Ti and O were treated explicitly. Table I lists the calculated bulk properties of PbTiO₃ tetragonal phase in comparison with the experimental data.⁷³ The calculated band gap, 2.7 eV, is in good agreement with the previous calculation utilizing the same functional (2.7 eV in Ref. 66) and experiment (3.4 eV in Ref. 74).

The computed value of effective T,P-odd interaction of the ²⁰⁷Pb nuclear Schiff moment with electrons, $\Delta\varepsilon$, as a function of the Pb nucleus shift with respect to the O₁₂ frame (with appropriate shifts of other atoms) is shown in Fig. 2. At the experimental geometry, we obtain our final value, $\Delta\varepsilon = 0.82 \times 10^6 \frac{S}{ea_B^3}$ eV and $X = 5045$ a.u.

One should note that a similar calculation by the Hartree-Fock method gives 1.63 times larger values of $\Delta\varepsilon$ and X . Thus, the relative contribution of the correlation to $\Delta\varepsilon$ estimated as a difference between DFT and HF results with respect to DFT is very high: 63%. The obtained periodic structure Hartree-Fock result is 2.3 times greater in magnitude than the value obtained in Hartree-Fock calculations using a cluster model of PbTiO₃ crystal.³⁰ It is shown below that the Hartree-Fock approximation also significantly overestimates the X value in the molecular PbO case.

As another application of our method, we have calculated one more AiC property—the electric field gradient. The V_{zz} component of EFG tensor (see Eq. (4)) at Pb nucleus in the tetragonal phase of PbTiO₃ crystal has been previously

TABLE I. Equilibrium structural parameters for tetragonal $P4mm$ phase of PbTiO₃. Positions of atoms u_z are given in terms of the lattice constant “c.”

Property	Calc.	Experiment, room temperature
		data, see Ref. 73
a , Å	3.82	3.90
c/a	1.15	1.07
$u_z(\text{Pb})$	0.000	0.000
$u_z(\text{Ti})$	0.545	0.540
$u_z(\text{O1})$	0.649	0.612
$u_z(\text{O3})$	0.146	0.112

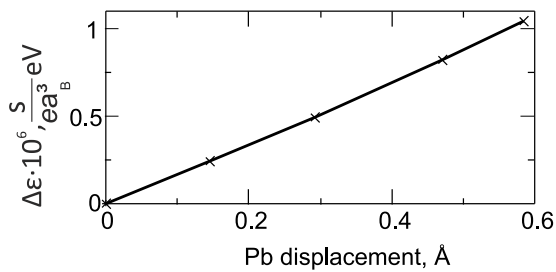


FIG. 2. $\Delta\epsilon$ as a function of the Pb displacement. The last point (0.58 Å) corresponds to $X = 6363$ a.u. and $\Delta\epsilon = 1.04 \times 10^6 \frac{S}{ea_B^3} \text{ eV}$.

calculated in Ref. 75 within all-electron linearized augmented plane wave plus local orbital, LAPW+lo, method.⁵⁰ Our value, calculated at the same experimental geometry as was used in Ref. 75, $V_{zz} = 0.43 \cdot 10^{22} \text{ V/m}^2$, is in good agreement with the all-electron calculation $V_{zz} = 0.36 \cdot 10^{22} \text{ V/m}^2$.⁷⁵

In our previous studies, the X parameter was evaluated for TIF¹⁵ and RaO⁷⁶ molecules using the above mentioned two-step procedure and the relativistic Fock-space coupled cluster method with single and double cluster amplitudes to treat the electron correlation effects. The influence of the “inner core–valence electron” correlations on the X value was estimated in Ref. 77 to be no more than 2% for the TIF molecule. We have recently considered a magnetic dipole HFS constant of the ground electronic state of ²⁰⁷PbF molecule within the two-step approach.⁷⁸ It was mentioned in the Introduction that HFS is another example of the AiC property, which means that the expectation value of the HFS operator is strongly dependent on the wavefunction in the region close to a heavy-atom nucleus (with non-zero spin) as in the case of the X parameter. The relative error of the computed HFS constant with respect to the experimental value^{69,79} is 2%.⁷⁸ As one more test of our restoration technique in the present paper, we have calculated EFG at Pb in PbO molecule at the Hartree-Fock level⁸⁰ using our GRECP/restoration approach and direct four-component one with CV4Z basis set⁸¹ for Pb and aug-cc-pV4Z for O.⁸² The results $V_{zz} = -19.5 \cdot 10^{22} \text{ V/m}^2$ and $V_{zz} = -19.4 \cdot 10^{22} \text{ V/m}^2$ are in excellent agreement.

As it follows from the previous studies of PbTiO₃^{64–66} and other systems, there are no reliable *theoretical* criteria to choose the most appropriate DFT exchange-correlation functional; therefore, the error of the evaluated AiC characteristics can hardly be estimated on the basis of DFT studies alone. Another source of possible uncertainties of the present solid state calculations is the omission of spin-orbit effects for the valence and explicitly treated outer-core electrons of Pb at the GRECP calculation stage within the codes employed for the periodic structures; though, they are partly recovered at the restoration stage. A theoretical estimation of errors for the used approximations can be obtained by comparing them to the results of high-level correlation calculations with the explicit inclusion of spin-orbit effects which is done here. For this we have calculated the X parameter for the PbO molecule in its $^1\Sigma^+$ ground state at different levels of the correlation treatment. We have set Pb–O internuclear distance to 3.6 Bohrs which is

TABLE II. The values of X on Pb in PbO calculated using different popular exchange-correlation functionals in comparison with high-level coupled cluster calculations. GRECP calculations were performed with (SO) and without (SR) accounting for spin-orbit effects.

Method	$X(\text{SR})$ (a.u.)	$X(\text{SO})$ (a.u.)
Hartree-Fock	9324	9436
LDA	6688	7144
PBE ⁶⁷	6735	7184
B3LYP ⁸⁶	7316	7725
PBE0 ⁸⁷	7599	8020
WC ⁶⁴	6829	
B1-WC ⁶⁶	7400	
CCSD	7699	8076
CCSD(T)	7489	7875

close to the experimental value of 3.63 Bohrs⁸³ in all the calculations.⁸⁴ The molecular axis is directed from Pb to O in the calculations. Two series of calculations were performed: (i) without accounting for the spin-orbit term in the GRECP operator (see Ref. 53) and (ii) with this term (SO). The former corresponds to a scalar-relativistic (SR) approximation for the valence and outer core electrons,⁸⁵ the latter includes the spin-orbit terms and assumes the two-component description of one-electron functions. The results of calculations are listed in Table II.

It follows from Table II that the spin-orbit contribution to X at the CCSD(T) level is about 5%. The scalar-relativistic B1-WC calculation of X reproduces the scalar-relativistic CCSD(T) value almost exactly. Moreover, all of the DFT based calculations also reproduce spin-orbit contributions with good accuracy. In contrast, the Hartree-Fock method gives a rather poor prediction of both the spin-orbit contribution and total X value. The relative correlation contribution is considerably bigger for the solid state case (26% (PbO) vs. 63% (PbTiO₃), see above). This can shed light on the failure to describe other properties of PbTiO₃ ferroelectric phase by the most popular exchange-correlation functionals mentioned in Ref. 64. Note that in both cases, correlation *reduces* the considered interaction energy. Taking into account these results and a more complicated structure of the PbTiO₃ crystal, one can expect a theoretical uncertainty of 20% for the solid-state results.

From the experimental point of view, the larger the X (or $\Delta\epsilon$ shift), the better. One of the advantages of solid state experiments to search for T,P-odd interactions is many orders of magnitude larger density of atoms with respect to atomic or molecular beam experiments. However, in molecular experiments, one can use rather “exotic” systems (not stable in ordinary conditions) like ThF⁺ and HfF⁺ cations^{88,89} or ThO molecule in excited electronic state.⁹ In the case of solids, there are practical limitations in such a choice. In the recent solid state experiment to search for electron electric dipole moment with the Eu_{0.5}Ba_{0.5}TiO₃ crystal,²⁵ the enhancement factor of electron EDM is 2 orders of magnitude lower than in the Tl atom.²⁴ The present study demonstrates that the electronic structure parameter X in PbTiO₃ has the same order of magnitude as in the PbO molecule (5045 a.u. vs. 7400 a.u.).

Other considered molecules, e.g., RaO have the similar value of X .⁷⁶ Thus, there are no advantages in using molecules with transition elements compared to the PbTiO_3 crystal to find the nuclear Schiff moment *from the point of view of the electronic structure enhancement factor*.

IV. CONCLUSION

A method of calculation of the AiC characteristics (such as hyperfine structure constants, chemical shifts, etc.) in solids is proposed and implemented. It is applied to the evaluation of T,P-odd interaction parameter X in a periodic model of the $^{207}\text{PbTiO}_3$ crystal. The calculated interaction energy in terms of the Schiff moment of ^{207}Pb nucleus is found to be $0.82 \times 10^6 \frac{S}{ea^3}$ eV. The uncertainty of the method for the case of the DFT treatment of electronic correlations is investigated and estimated as 20% for the considered system. The computational accuracy can be increased by an explicit treatment of correlation effects within the coupled cluster approach, though this method is not yet easily applicable for the periodic structure calculations.⁹⁰ It is shown that T,P-odd effect in $^{207}\text{PbTiO}_3$ due to the nuclear Schiff moment has the same order of magnitude as the popular diatomic molecules which have been proposed and experimentally used to search for the nuclear Schiff moment.

We have found a good agreement between the present results and previous available theoretical and experimental data for the band gap,⁷⁴ electric field gradient, and equilibrium geometry of the PbTiO_3 crystal in tetragonal phase. In particular, the ferroelectric displacement of Pb atom has been reproduced with a good accuracy. The main goal of the study was to evaluate the T,P-odd interaction energy in terms of the nuclear Schiff moment. For this quantity, we have presented not only the equilibrium-geometry value but also its dependence on the geometry of the crystal; almost a linear dependence of the considered energy shift with respect to the ferroelectric shift of Pb atom is found. Thus, if the geometry parameters of the crystal are corrected in further experiments, it will also be possible to refine the value of the energy shift in terms of the nuclear Schiff moment. The latter will be required to interpret the corresponding experiment in terms of the Schiff moment of ^{207}Pb nucleus.

The two-step approach to calculations of AiC properties is implemented within the linear combination of atomic orbitals, LCAO, paradigm which is the most popular concept in the *ab initio* atomic and molecular electronic structure quantum theory. We have been implementing and improving the method for more than 30 years (since 1985), applying it to the cases of molecules.^{32,35,42} Therefore, the present implementation can be considered as a generalization of the approach to a three-dimensional periodic case. The features of the approach are as follows: (i) the finite nuclear size model is used; (ii) the Breit interaction can be taken into account;⁵³ (iii) the applicability to atoms, molecules, and crystals is unified and flexible; (iv) even now for atoms and molecules (clusters), it is possible to employ such high-level methods as the coupled cluster with single, double, triple, and quadruple

cluster amplitudes;^{11,32,91} (v) simple extension to the different embedding approaches using existing codes; (vi) usage of a very accurate four-component wavefunction in the vicinity of a heavy atom (as a polynomial decomposition with correct asymptotic behavior) which is critically important in the considered case of electronic density gradient due to the strong cancellation of contributions from large and small components.¹⁷

Based on the properties of the approach, it is possible, e.g., to estimate an uncertainty of different density functional methods in calculations of atomic clusters by explicitly treating the correlation effects within the coupled cluster approaches followed by the periodic structure calculation of a crystal. Due to unified LCAO approach, one can use the same basis sets and other computational conditions for both the cluster and crystal.

One should note that for solid-state calculations, a number of restoration (reconstruction) techniques have been implemented and successfully used, e.g., more than 20 years ago, the Projector Augmented Wave, PAW, method was formulated.⁹² It is extensively used now for many problems.⁹³ The method is available for the plane-wave based representations of wavefunctions. However, up to now no such approach for LCAO-based representations has been formulated and implemented to our knowledge.

Further, we plan to extend the approach to the case of clusters with the crystalline potential embedded. It will allow us to take account of some high-level correlation effects, e.g., within the coupled cluster approaches. Furthermore, we plan to consider and investigate in detail (and enhance) different cluster models, e.g., the ones used in Ref. 30, as well as apply the method to other systems. In particular, one should note that there is a wide range of effects due to the violation of P symmetry (and conservation of T symmetry) of fundamental interactions in solids.⁹⁴ We plan to consider possible applications of the proposed method to these problems in further research.

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