Investigating the nuclear Schiff moment of $^{207}$Pb in ferroelectric PbTiO$_3$

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Received 17 November 2012, in final form 6 March 2013
Published 27 March 2013
Online at stacks.iop.org/JPhysB/46/085001

Abstract
A positive experimental measurement of the nuclear Schiff moment would have important implications for physics beyond the standard model. To aid in the interpretation of a proposed experiment to measure the nuclear Schiff moment of $^{207}$Pb in the ferroelectric PbTiO$_3$, three-dimensional Hartree–Fock calculations have been performed to model the local electronic structure in the vicinity of the Pb nucleus. The energy shift due to the Schiff moment is found to be a factor of 2 smaller in comparison to existing estimates.

1. Introduction
The search for the permanent electric-dipole moment (EDM) of quantum particles has been of continued interest for over 40 years since the discovery of the violation of the combined symmetry of charge conjugation ($C$) and parity ($P$) in the decay of the $K^0$ meson [1]. By the $CPT$ theorem, the existence of $CP$-violation also implies that time-reversal ($T$) symmetry is violated [2]. $P$-violation, together with $T$-reversal asymmetry gives rise to a permanent EDM of a quantum system in a stationary state. Therefore ongoing searches for EDMs of elementary particles, nuclei, atoms and molecules are important for studies of fundamental symmetries [3] and they provide important constraints on theories that attempt to go beyond the standard model [4].

Currently, no EDM has been experimentally observed. Experiments on paramagnetic atoms provide the best upper limit on the electron dipole moment, with the most stringent limitation coming from experiments with atomic thallium [5] and the YbF molecule [6].

\begin{align}
\text{TI} & : \ d_e < 1.6 \times 10^{-27} \, e \text{ cm}.
\text{YbF} & : \ d_e < 1.05 \times 10^{-27} \, e \text{ cm}.
\end{align}

(1)

For diamagnetic atoms, the major contribution to the electron dipole moment is from the nuclear Schiff moment (NSM), $S$. The NSM can be defined by the $P$- and $T$-odd electrostatic potential [8],

\begin{equation}
\varphi(\mathbf{r}) = 4\pi (\mathbf{S} \cdot \nabla)\delta(\mathbf{r}).
\end{equation}

(3)

The result of [7] has been interpreted with the aid of calculations [9, 10] to yield an upper limit of the Schiff moment of the $^{199}$Hg nucleus of,

\begin{equation}
S^{(199)}_{\text{Hg}} < 0.8 \times 10^{-26} \, e \text{ a}_B^3,
\end{equation}

(4)

where $a_B$ is the Bohr radius.

Currently, there is intense interest in exploring physical systems that potentially can provide orders of magnitude increases in sensitivity to $CP$ violating effects. As first discussed by Shapiro [11], condensed matter systems are particularly promising in this regard. The electron’s EDM is aligned with the spin of the electron, and therefore its magnetic moment. It follows that in a compound with uncompensated spins, the application of an external electric field will align the EDMs and thus align the magnetic moments, giving rise to a macroscopic magnetization. Experiments then aim to measure the reversal of the magnetization by reversing the direction of the external electric field. Recent efforts have focused on gadolinium garnets [12–15] and more recently on the ceramic Eu$_{0.5}$Ba$_{0.5}$TiO$_3$ [16–19].

Similarly to the atomic case, condensed matter systems without unpaired electrons should also be sensitive to the NSM. Ferroelectric PbTiO$_3$ has a huge effective internal electric field and therefore it has been suggested for searches of parity and time reversal symmetry violations [20]. The
material was proposed for measuring the NSM in [21] where
the first estimate of the expected effect was also performed.
Experiments with this compound offer the possibility of an
improvement in sensitivity to the NSM by several orders of
magnitude in comparison with existing results [21–25].

There has been a recent suggestion to detect axion dark
matter with cold molecules [26]. It is possible that usage of
PbTiO3 as the dark matter detector has advantages compared
to molecules [27]. On the theoretical side the solid state part
of the calculation of the axion sensitivity is exactly similar
to that of the NSM. Actually the axion effect can be directly
recalculated from the NSM. Here, we will only consider the
NSM, but it is important to note the importance of this problem
to axions as well.

The NSM can be detected experimentally either by a
measurement of the macroscopic magnetization induced by
an electric field or by nuclear magnetic resonance. The lead
nuclei will interact with the large internal electric field in
the ferroelectric leading to a P, T-odd energy shift. Here, we
perform three-dimensional Hartree–Fock calculations in order
to model the local electronic structure of PbTiO3 around the
Pb nucleus and determine the energy shift caused by the NSM
of the 207Pb nucleus.

2. Model calculations

PbTiO3 is an ionic crystal made up of Pb5+, Ti4+ and
O2− ions. In the ferroelectric phase, PbTiO3 is tetragonal with
c/a = 1.065, a = 3.902 Å, c = 4.156 Å [28], with Pb5+
and Ti4+ displacements of 0.47 and 0.30 Å with respect to
their non-ferroelectric positions [29]. The ion displacements
are in accordance with the Schiff theorem [30]. The lattice
relaxes so as to screen the strong internal ferroelectric field
such that the average field that acts on each charged particle
in the compound is zero. However, the finite size of the ions
plays an important role, with oxygen electrons (s and p-wave)
penetrating into the core of the Pb ion creating, due to the Pb
displacement, a gradient of electron density at the Pb nucleus.
The NSM interacts with this gradient, leading to an energy
shift. The electron density gradient can be expressed in terms
of the mixing of s- and p-electron orbitals at the Pb nucleus.
In the semiclassical approximation this leads to the following
formula for the NSM energy shift Δε [13],

\[
\Delta \varepsilon / E_0 \simeq \frac{16 \beta}{\sqrt{3}} \frac{Z^2}{(\nu_1 \nu_p)^{3/2}} \left( \frac{1}{3} R_{1/2} + \frac{2}{3} R_{3/2} \right) \frac{(X \cdot S)}{\alpha \beta \gamma \delta}, \tag{5}
\]

Here X is the ferroelectric Pb ion displacement with respect
to the oxygen coordination sphere, \( E_0 = 27.2 \text{ eV} \), \( e = |e| \)
is the charge of the electron, \( Z = 82 \) is the nuclear charge
of Pb, \( \nu_1 \) and \( \nu_p \) are effective principal quantum numbers and \( \beta \) is a parameter describing lead orbitals partially occupied
by oxygen electrons, see below. \( R_{1/2} \) and \( R_{3/2} \) are relativistic enhancement factors [3, 13] given by,

\[
R_{1/2} = \frac{4 \gamma_{1/2} \beta_{2/0}^{2\pi_{1/2}/2}}{\Gamma(2\gamma_{1/2} + 1)} \frac{2^{2\pi_{1/2}/2}}{(2\pi_{1/2} + 1)},
\]

\[
R_{3/2} = \frac{48 \gamma_{3/2} \beta_{2/0}^{2\pi_{1/2}/2}}{\Gamma(2\gamma_{1/2} + 1)} \frac{2^{2\pi_{1/2}/2}}{(2\pi_{1/2} + 1)}, \tag{6}
\]

where \( \gamma_{1/2} = \sqrt{1 - Z^2 \alpha^2} \), \( \gamma_{3/2} = \sqrt{4 - Z^2 \alpha^2} \), \( \alpha \) is the
fine structure constant, \( \Gamma(x) \) is the gamma function and \( x_0 = (2Zr_0/eB) \), with \( r_0 \) the nuclear radius. Note that in
the present work we follow the definition of the NSM in
equation (3) that differs by a factor of 4\pi from that used in
[13].

An understanding of the order of magnitude of the energy
shift (5) can be gained by considering that the energy shift can
be approximated by the product of the internal electric field in
ferroelectric PbTiO3, \( E_{int} \approx 10^5 \text{ V cm}^{-1} \), and the EDM
of the Pb5+ ion, \( d(Pb^{5+})/(e \text{ cm}) \approx 10^{-2} S/(e\alpha^2) \), where we have
assumed that the EDM of the Pb5+ ion is similar to that of
the Hg atom. This gives, \( \Delta \varepsilon \simeq E_{int} d(Pb^{5+}) \approx 10^6 \frac{s}{e\alpha^2} \text{ eV} \) [22].

In [21], equation (5) was applied to calculate the energy shift
using a value of \( \beta = -0.29 \) estimated previously for
GdO3 clusters [13]. This gave an estimate for the energy shift of,

\[
\Delta \varepsilon \simeq -1.1 \times 10^6 \frac{s}{e\alpha^2} \text{ eV}. \tag{7}
\]

The method used to estimate \( \beta \) involved matching a linear
combination of the electron wavefunctions of the 2p\( _{\sigma} \) electrons
of O2− possessing the correct cubic symmetry, with single
particle 6s and 6p states of the central Gd3+ ion that can be
thought of as being occupied by the oxygen electrons. The
matching is done at an intermediate distance in the cluster
between the O2− ions and the central Gd3+ ion.

In the present paper we perform a much more accurate
calculation as compared to the estimate of [21]. It is well
known that relativistic effects are very important for
the calculation of the NSM. Therefore in an ideal case one should
calculate the many-body relativistic electron wave function
of the material and then calculate the expectation value of
the operator (3) with this wave function. Certainly in this
case one has to use the relativistic version of the operator
(3) which is known [8]. There are the following complexities
in such a calculation (i) the multi-centre nature of the electron
wave function, (ii) electron correlations effects, (iii) relativistic
effects. Clearly the ideal calculation is impossible, one needs
to do simplifications.

Our first simplification concerns point (iii), relativistic
effects. This simplification is based on experience with the
calculation of the NSM in atoms. Since the NSM interaction
is a local operator the relativistic effects can be factorized
into relativistic factors as is done in equation (5). So, we
will use equation (5) instead of (3). This assumes that
the many-body electron wave function is factorized at the
nucleus. The factorization is certainly valid in the Hartree–
Fock approximation, however, it is much better than that. It is
known that all Brueckner type correlations can be re-absorbed
in the single particle orbitals, the wave function remains
factorized. Thus, we will use the non-relativistic Hamiltonian,

\[
H = \sum_{\text{electrons}} \frac{P_i^2}{2m} + \sum_{\text{electrons}} \frac{e^2}{|r_i - r_j|} - \sum_{\text{electrons, nuclei}} \frac{e^2 Z_a}{|r_i - R_a|}, \tag{8}
\]

in our calculations and account for relativistic effects via
equation (5). Based on experience with atoms we believe
that the account of relativistic effects via this procedure does not bring an inaccuracy higher than 10%, probably less. To confirm the accuracy of the account of relativistic effects in terms of relativistic factors introduced in the non-relativistic calculation one can compare the exact relativistic calculation of parity violation in the Cs atom [31] with effective non-relativistic calculations (with relativistic factors) [32, 33]. The difference is roughly 4%, with the major part of the difference arising from correlations accounted for in [31] and omitted in [32, 33].

The second simplification concerns point (ii), correlation effects. We disregard correlation effects and use the Hartree–Fock method. This simplification bothers us much more than relativistic effects. Even in atoms correlation effects can give up to ~50% correction to matrix elements of local operators. However, matrix elements of the NSM for systems without unpaired electrons are always more stable than say matrix elements of the usual weak interaction, see, e.g. [9, 32, 34, 10]. We hope that the inaccuracy due to unaccounted correlation effects does not exceed 30%. Direct account of the correlation effects computationally is hardly possible in this system.

A feasible way to estimate the effect of correlations is to perform a similar calculation using the density functional theory (DFT) method. The DFT effectively accounts for Brueckner correlations, and therefore a comparison between Hartree–Fock and DFT results would allow an estimate of the Brueckner correlations, and therefore a comparison between theory (DFT) method. The DFT effectively accounts for relativistic effects computationally is hardly possible in this system. A diffuse sp shell is also added to the Pb2+ ions present in this system. A diffuse sp shell is added to the Pb2+ and O2− orbitals in order to better represent the ion-radical present in this system. A trial wavefunction is built from Pb2+ and O2− Hartree–Fock wavefunctions, where in both cases the ions are enclosed by a cubical array of point charges. For O2− this is necessary in order to obtain a stable ground state in the Hartree–Fock approximation. This trial wavefunction is then used as a starting approximation to obtain a converged Hartree–Fock wavefunction for the PbO12 cluster. To check that the WTBS basis is sufficient for our purposes we first performed atomic calculations using this basis. By this, we mean atomic calculations of energy levels and NSM matrix elements for isolated Pb2+, Pb3+, ions and for the isolated Oxygen atom. Results of the calculations were compared with known atomic results obtained by different methods. Parameters of the WTBS basis were adjusted to provide the best possible agreement. This is especially important to describe correctly the Pb interior. All in all the inaccuracy related to the WTBS basis can hardly exceed 1% and is completely negligible compared to the balance of errors presented above. Using converged Hartree–Fock wavefunctions of the PbO12 cluster we calculate the electron energy levels and NSM matrix elements for isolated Pb2+, Pb3+, ions and for the isolated Oxygen atom. Results of the calculations were compared with known atomic results obtained by different methods.
density distribution around the Pb nucleus and then evaluate the
NSM energy shift (5) using the procedure described below.

\[ \Delta \rho(z) = \frac{\rho(z) - \rho(-z)}{2} \]  

(9)

On the one hand this asymmetry is directly calculated via the
Hartree–Fock procedure and on the other hand it can be re-
expressed in terms of Pb atomic orbitals. Near the Pb\(^{2+}\) ion
the electrostatic potential for electrons is dominated by that of
the central Pb\(^{2+}\) ion. Therefore the wavefunctions of electrons
in this region can be well described by partially occupied
Pb\(^{2+}\) orbitals. The interaction of electrons with the NSM of
lead ion along the \( z \) direction is then,

\[ |S \rangle \rightarrow \beta_s |7s \rangle \quad |P_i \rangle \rightarrow \beta_p |6p \rangle, \]

(10)

where \( i = x, y, z \). Note that the choice of 7s and 6p orbitals
of Pb is arbitrary, all external orbitals behave similarly close
to Pb nucleus. For example one can chose 8s orbital instead
of 7s and redefine \( \beta, \beta_s |7s \rangle = \beta |8s \rangle \). When the Pb ion
is shifted from the centre of the cluster, the \( |S \rangle \) and \( |P \rangle \) states
no longer have exact s and p-wave symmetries with respect to
the lead ion but are instead a mixture of the two. For a small
ferroelectric displacement \( X_i \) one always can use the linear
approximation

\[ |S \rangle \rightarrow \beta_x |7s \rangle + \sum_i \beta_{x,i} X_i |6p \rangle \]
\[ |P_i \rangle \rightarrow \beta_p |6p \rangle + \sum_i \beta_{p,i} X_i |7s \rangle. \]

(11)

The change in the density due to the displacement of the Pb\(^{2+}\)
ion along the \( z \) direction is then,

\[ \Delta \rho(z) = 4\beta X a_B \psi_7z(r) \psi_6p(z), \]

(12)

where \( \beta = (\beta_s + \beta_p) / 2 \) and a factor of 2 comes from the
double occupancy of each orbital. Atomic orbitals 7s and
6p are known from atomic calculations. Therefore comparing
(12) with (9) we find the coefficient \( \beta \) and hence we calculate
the NSM matrix element (5). Actually we even do not need to
know the effective principal quantum numbers \( \nu_s \) and \( \nu_p \) since
the matrix element (5) can be rewritten directly in terms of
\( \psi_7z(r \rightarrow 0) \) and \( \psi_6p(r \rightarrow 0) \) which are known numerically.

3. Results

In order to test the various assumptions made in the present
model, a number of calculations have been carried out. Firstly,
the point charges representing the Ti ions are treated here as an
adjustable parameter in order to assess the dependence of the
final result on the crystal structure, with calculations carried
out for a range of Ti charges. Secondly, the assumed linearity
of the density shift is tested by carrying out calculations for a
number of Pb displacements.

First, to illustrate how well equation (12) performs in
capturing the essential physics of the density shift, \( \Delta \rho \) as
a function of the distance from the Pb nucleus is plotted in
figure 2 for a Ti charge of +3.5. We match the numerical
density shift to the analytical expression of equation (12) using
atomic Hartree–Fock wavefunctions for the 6p and 7s states
of Pb\(^{2+}\), treating \( \beta \) as an adjustable parameter. The GAMESS-
US density is not reliable at very small distances because of
limitations of the WTBS basis. Therefore, the matching is done
at points above the first node at \( r > 0.02 a_B \), and then an average
value of \( \beta \) is taken. As is clear, the analytical expression agrees
well with the numerical results. The solid GAMESS-US line
is practically indistinguishable from the dashed line given by
equation (12).

Next, the validity of the linear approximation for the
density shift is investigated. Figure 3 plots \( \Delta \rho \) at distances
from the Pb nucleus corresponding to the first minimum and maximum of $\Delta \rho$, as a function of the Pb$^{2+}$ ion displacement. From the figure, it is seen that a Ti charge of 3.5 gives the best agreement with the linear approximation out to $X = 0.5 \, \AA$, with some deviation from linearity observed for charges of 3.0 and 4.0. Most likely these small deviations observed only at very small $z$ are due to limitations of the WTBS basis. In any case the deviations are insignificant.

Finally, $\beta$ as a function of the Ti charge is plotted in figure 4 for a Pb$^{2+}$ displacement of $X = 0.5 \, \AA$. It is seen that for Ti charges between +3 and +4, $\beta$ ranges from $-0.125$ to $-0.125$, demonstrating that $\beta$ does not depend strongly on the crystal structure. This compares to a previous estimate of $\beta \approx -0.29$ [21, 22] used for PbTiO$_3$ that was originally derived for the garnet structure of a Gd$^{3+}$ ion enclosed by eight O$^{2-}$ ions [13]. Taking a value of $\beta \approx -0.125$ for a Ti charge of +3.5 as an upper limit for $|\beta|$, equation (5) is evaluated for a Pb displacement of 0.47 $\, \AA$, with effective principal quantum numbers of the 6p and 7s states of Pb$^{2+}$, derived from Hartree–Fock energies of 1.028 and 1.417 respectively. The nuclear radius, $r_0$, of $^{207}$Pb is taken $r_0 \approx CA^{1/3} \approx 7.39 \times 10^{-15} \, \text{m}$, where $A = 207$ is the atomic mass number and $C = 1.25 \times 10^{-15} \, \text{m}$. The resulting energy shift is then found to be,

$$\Delta \epsilon \approx -0.66 \times 10^6 \frac{X \cdot S}{a_0 e a_0} \, \text{eV} = -0.59 \times 10^6 \frac{S}{e a_0} \, \text{eV}. \quad (13)$$

This is approximately two times lower than the previous estimate, see equation (7). We reiterate that expected uncertainty of this result is about 30–50%, see the discussion in section 2.

4. Conclusions

The work in this paper is part of a continuing theoretical and experimental programme in aid of experimental investigations of CP violating effects in condensed matter systems. In the present work we have calculated the energy shift caused by the nuclear Schiff moment of $^{207}$Pb in the ferroelectric PbTiO$_3$. A Hartree–Fock calculation of the PbO$_{12}$ cluster enabled the density asymmetry around the Pb nucleus due to the penetration of the oxygen electrons into the Pb ion to be calculated. From this an energy shift was calculated that is almost a factor of 2 lower than a previous estimate [21]. It is recommended that the present estimate of the energy shift in equation (13) supersede the earlier result of [21].

There are two areas in the current work that merit further investigation. Firstly, the effect of the potential due to the crystal field needs to be properly taken into account. A possible solution to this issue is via the CRYSTAL code [38, 39]. This particular code uses linear combinations of atom centred Gaussian functions to perform both Hartree–Fock and a variety of density functional theory calculations. This would allow a good description of both the crystal structure and also the penetration of the O electrons into the Pb ion. An existing calculation using the CRYSTAL code has provided accurate structural and electronic properties of PbTiO$_3$ [40]. As we discussed above the DFT calculation would also allow an estimate to be made of the magnitude of the correlation correction. Hopefully it would also allow an extension of the size of the dynamic cluster.

In the present work we account for relativistic effects via effective renormalization of non-relativistic matrix elements. According to previous calculations for heavy atoms this method works pretty well. However, this has never been checked for solids. Therefore the account of relativistic effects inside the Hartree–Fock or DFT method would be desirable. As a first step, this can be done by solving the Dirac–Fock equations for the PbO$_{12}$ cluster. A challenge here will be in converging the self-consistent four-component Dirac–Fock equations for such a large system. The BERTHA [41] or DIRAC codes [42] can be investigated for this purpose.

These two phenomena that must be included in any complete treatment of the problem, namely the potential due to the crystal lattice and relativistic effects due to the high nuclear charge of the Pb nucleus, make this a highly demanding theoretical and computational problem.

A positive experimental finding of the nuclear Schiff moment would be of great importance to the entire physics community. Theoretical input into the design and interpretation of future experiments will be crucial in this effort. As such, we hope that the present model calculations will prompt renewed theoretical interest in this field.

Acknowledgments

We are very grateful to H M Quiney, T N Mukhamedjanov and G F Gribakin for helpful advice and discussions. This work was supported by the Australian Research Council.

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