Enhancement of the Electric Dipole Moment of the Electron in PbO

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The a(1) state of PbO can be used to measure the electric dipole moment of the electron d_e. We discuss a semiempirical model for this state, which yields an estimate of the effective electric field on the valence electrons in PbO. Our final result is a lower limit on the measurable energy shift, which is significantly larger than was anticipated earlier: \[ |W_{d_e}d_e| \approx 2.4 \times 10^{15}\text{ Hz}\left[ \frac{\text{cm}}{e}\right].\]

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In his pioneering work, Sandars pointed out that the effective electric field on a valence electron in a heavy atom is enhanced by a factor \( -\alpha Z \) relative to the applied laboratory field [1]. That started a long search for the electric dipole moment (EDM) of the electron in PbO. Since the excited state of PbO can be used to measure the electric dipole moment of the electron \( d_e \), we can estimate the effective internal field for the state \( a(1) \).

Even larger enhancement is present in heavy polar diatomic molecules [2,4,5]. The heavy atom there is subjected to an internal \( E \) field of \( \approx 10^9 \) V/cm, which is further enhanced by the relativistic factor \( \alpha^2 Z \). This effective field is many orders of magnitude larger than available laboratory fields; this makes diatomic molecules very attractive systems to look for \( d_e \).

Since \( d_e \) is linked to the electron spin, one must work either with radicals, which have an unpaired electron in the ground state, or with excited states of "normal" molecules. Diatomic radicals with the ground state \( \Sigma_1/2 \) have large enhancement factors which can be relatively easily calculated [6,7]. The first results of an EDM measurement in such a molecule (YbF) were recently published [8]. The molecule PbO is a favorable candidate for a search for \( d_e \), in the excited state \( a(1) \) [4,9], and the group at Yale has begun EDM experiments on PbO [10]. It is therefore timely to estimate the effective internal field for the state \( a(1) \) of PbO.

The interaction of \( d_e \) with an electric field \( E \) can be written in four-component Dirac notation as [11]

\[
H_d = 2d_e \begin{pmatrix} 0 & 0 \\ 0 & \alpha E \end{pmatrix}
\]

After averaging over the electronic wave function, this interaction can be expressed in terms of an effective spin-rotational Hamiltonian [5,6], \( H_d^{\text{eff}} = W_d d_e (J_e \cdot n) \), where \( J_e \) is the electronic angular momentum and \( n \) is the unit vector along the molecular axis. In this paper we estimate \( W_d \) for the molecular state \( a(1) \):

\[
W_d \equiv |d_e|^2 \langle a(1)|H_d|a(1)\rangle.
\]

TABLE I. Atomic parameters \( h_{\kappa \ell} \) (GHz), \( w_{sp} \) (a.u.), and \( \xi \) (cm\(^{-1}\)), calculated in the Dirac-Fock approximation for Pb and for Pb\(^+\). The relativistic quantum number \( \kappa \) is equal to \( -1, 1 \), and \(-2\) for \( s_{1/2}, p_{1/2}, \) and \( p_{3/2} \), correspondingly.

<table>
<thead>
<tr>
<th>( h_{-1,-1} )</th>
<th>( h_{1,1} )</th>
<th>( h_{1,-2} )</th>
<th>( h_{2,-2} )</th>
<th>( w_{sp} )</th>
<th>( w_{sp} \sqrt{-h_{-1,-1}h_{1,1}} )</th>
<th>( \xi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(^+)</td>
<td>45.5</td>
<td>-8.9</td>
<td>-1.1</td>
<td>1.8</td>
<td>-34.1</td>
<td>-1.7</td>
</tr>
<tr>
<td>Pb</td>
<td>42.3</td>
<td>-7.5</td>
<td>-0.9</td>
<td>1.4</td>
<td>-30.0</td>
<td>-1.7</td>
</tr>
<tr>
<td>Ratio</td>
<td>1.08</td>
<td>1.20</td>
<td>1.25</td>
<td>1.30</td>
<td>1.14</td>
<td>1.0</td>
</tr>
</tbody>
</table>
the orbitals $6s$ and $6p_j$. For the HFS operator we calculate
the parameters $h_{k,k'}$ as defined in [5] [we use atomic units
(a.u.) unless otherwise noted]:

$$h_{k,k'} = -\frac{g_n \alpha}{2m_p} \int_0^\infty (f_k g_{k'} + g_k f_{k'}) dr,$$

(5)

where $g_n = 0.59$ is the nuclear $g$ factor of $^{207}$Pb, $m_p$ is the
proton mass, $f_k$ and $g_k$ are upper and lower components of
the Dirac orbitals, and $k = (l - j)(2j + 1)$ is the relativis-
tic quantum number. For the EDM operator (1) in our
minimal basis set there is only one nonzero radial integral,
between $6s_{1/2}$ and $6p_{1/2}$ orbitals:

$$w_{sp} = -\int_0^\infty g_{-1} g_1 \frac{d\phi}{dr} r^2 dr,$$

(6)

where $\phi$ is the atomic electrostatic potential. Finally, we
also need the atomic SO constant $\xi$ for the $6p$ shell:

$$H_{SO} = \xi \mathbf{l} \cdot \mathbf{s} \quad \Rightarrow \quad \xi = \frac{3}{2} (e_{6p_{1/2}} - e_{6p_{3/2}}).$$

(7)

Note that the ratio of the radial integrals for the ion and
for the atom are similar for all relevant integrals (see the
last row of Table I). A simple relation between $w_{sp}$ and
HFS constants holds for both cases: $w_{sp} = -1.7 \sqrt{\hbar_{-1,1}} h_{1,1}$. This relation also holds for other
principal quantum numbers $n$, e.g., for $7s$ and $7p_j$. This fact
is critical for semiempirical models of the EDM enhance-
ment: it implies that the value of $W_d$ does not depend
strongly on what set of radial integrals is used. (The particu-
lar choice of the radial integrals does enter the final
result, through the normalization of the wave function.)
Since the Pb atom in PbO is positively charged, we have
chosen to use the ionic set of integrals from Table I.

In order to develop a semiempirical model for the state
$a(1)$, we have found it necessary to also consider the wave
functions of several low-lying states of PbO. Previous work
has shown that these states correspond to the configura-
tions and nominal $\Lambda$, $\Sigma$-coupling terms as follows [12,13]:

$$|a(1)|^3\Sigma^+\rangle = \frac{1}{\sqrt{2}} (|\pi_{1,\lambda=1} \pi_{2,\lambda=-1}\rangle + |\pi_{1,\lambda=-1} \pi_{2,\lambda=1}\rangle)$$

$$|a(1)|^3\Pi\rangle = \frac{1}{\sqrt{2}} (|\sigma_{\pi_{2,\lambda=1}}\rangle \| + |\sigma_{\pi_{2,\lambda=-1}}\rangle \|)$$

(12a)

$$|A(0^+)\|^3\Pi\rangle = \frac{1}{\sqrt{2}} (|\sigma_{\pi_{2,\lambda=1}}\rangle \| - |\sigma_{\pi_{2,\lambda=-1}}\rangle \|) = \frac{1}{\sqrt{2}} (|\sigma_{\pi_{2,\lambda=1}}\rangle \| - |\sigma_{\pi_{2,\lambda=-1}}\rangle \|)$$

etc. (12b)

We have transformed each wave function from $\lambda - \sigma$ to
$\omega - \omega$ representation for convenience.

The rules for calculating hole matrix elements follow
from the fact that the hole in the state $|\omega\rangle$ actually means
the absence of the electron in the state $|-\omega\rangle$. Thus, the
expectation value for an electronic operator $\hat{P}$ over the hole
state $|\omega\rangle$ can be written as

$$\langle \omega | \hat{P} | \omega \rangle = -\langle -\omega | \hat{P} | -\omega \rangle_e = T \mp \langle \omega | \hat{P} | \omega \rangle_e,$$

(13)

where we applied the time-reversal operation $T$. Thus the
final sign depends on the time-reversal symmetry of $\hat{P}$,
with the minus sign corresponding to a $T$-even electron
operator. For example, the HFS interaction is given by the
product of the $T$-odd electronic vector $\hat{A} \mathbf{J}$, and the nuclear
spin $\mathbf{I}$. Thus, for the HFS interaction the plus sign in
Eq. (13) is correct. A similar argument shows that the SO
constant $\xi$ for a hole has the opposite sign as for an
electron.

From Eqs. (12), the first-order SO splitting $\Delta_{AB}$ between
states $A(0^+)$ and $B(1)$ is

$$\Delta_{AB} = \frac{\xi}{2} (\langle \pi_{2,3/2} | \pi_{2,3/2} \rangle - \langle \pi_{2,1/2} | \pi_{2,1/2} \rangle) = \frac{\xi P_0^2}{2},$$

(14)
Using the experimental value of this splitting [14] and the ionic value for $\xi$ from Table I, we estimate $P_2$:

$$P_2 = \frac{2 \Delta_{AB}}{\xi} = \frac{2 \cdot 2420}{9450} = 0.51.$$  

(15)

We see that the orbital $\pi_2$ has a large contribution from the Pb orbital $6p$. The data on energy levels [14] show that for all levels with one electron in the $\pi_2$ orbital, the SO interaction is comparable to the splittings between these levels. Therefore, there must be significant SO mixing between such states.

We start with the mixing within configuration $\sigma^2 \pi_1^2 \pi_2$. The mixing angle $\alpha$ between states $a(1)$ and $C'(1)$ is

$$\alpha = \frac{\langle \sum |H_{\text{so}}|^{2} \sum \rangle}{\Delta_{aC}} = \frac{\xi_1 + \xi_2}{2 \Delta_{aC}},$$

(16)

where $\Delta_{aC}$ is the energy splitting between $a(1)$ and $C'(1)$, and $\xi_1 = \xi_2 P_1^2$. If we assume that $P_1^2 \ll P_2^2$ (corresponding to the naive ionic model), we can estimate the value of $\alpha$:

$$\alpha = \frac{\xi_2}{2 \Delta_{aC}} = 0.3.$$  

(17)

and write the new wave function in the form:

$$\langle a(1)|H_{\text{hfs}}|a(1)\rangle = c_0^2\left[\langle \sigma |1/2\rangle |h_{\text{hfs}}|\pi_1 |1/2\rangle + s_1 |\pi_2 |3/2 \rangle - \langle \pi_2 |1/2\rangle |h_{\text{hfs}}|\pi_1 |1/2\rangle + s_1 |\pi_2 |3/2 \rangle \right].$$  

(20)

We use expressions from Ref. [5] for the one-electron matrix elements and numbers from Table I, combined with the measurement of the hyperfine constant for the state $a(1)$, $A_{12} = -4.1$ GHz [15], to find another equation relating the various coefficients of the model

$$30(c_0^2 s_1^2 + s_1^2 s_2^2 + 1.8(c_0^2 s_2^2 + s_1^2 s_1^2))s_1^2 + (4.6c_0^2 c_1^2 - 1.4c_0^2)P_1^2 + (4.6c_0^2 c_1^2 - 1.4c_0^2)P_2^2 - 4.7s_2^2 c_1 s_1 P_1 S_p - 4.7c_0^2 c_2 s_2 P_2 S_p = 4.1.$$  

(26)

(Note that the formulas of Ref. [5] are strictly applicable only for orbitals and states with $\omega = \Omega = 1/2$. Equation (26) takes into account simple modifications of these formulas for the present situation.)

Finally, we introduce two additional constraints, which account for normalization and the Pauli principle:

$$S_2^2 + S_3^2 \leq N_0, \quad P_1^2 + P_2^2 \leq N_0.$$  

(27)

We choose $N_0 = 1.2$ here in order to account for inaccuracy of the Hartree-Fock approximation used to determine the atomic parameters in Table I.

The parameters $\alpha$ and $P_2$ are unambiguously fixed by Eqs. (15) and (17). We choose $s_1$ and $P_1$ as free parameters and solve Eqs. (21), (24), and (26) for parameters $s_2$, $S_p$, and $S_z$. After that we reject solutions which do not meet the constraints (27). Only some of the parameters are well accounted for by substitution of the original orbitals $|\pi_{1/2}\rangle$ with the perturbed orbitals

$$|\pi_{1/2}\rangle = c_0 |\pi_{1/2}\rangle + s_1 |\pi_{1/2}\rangle.$$  

(20)

There is no experimental information about levels of the configuration $\sigma^2 \pi_1^2 \pi_2$, so we cannot reliably estimate the mixing parameter $s_2$. In contrast, both levels with $\Omega = 0$ of the configuration $\sigma^2 \pi_1^2 \pi_2$ are known [i.e., $B(1)$ and $D(1)$]. That allows us to write for $s_1$ the estimate

$$s_1 = 2.8s_2^2 P_1 S_p.$$  

(21)

These SO mixings then lead to the final form of the wave function of the state $a(1)$,

$$|a(1)| = c_0 |\pi_{1/2}| + s_1 |\pi_{1/2}|.$$  

(22)

The $G$ factor for the state (22) is given by

$$G_{12} = \langle a(1)|L_0 + 2S_0|a(1)\rangle = -s_2^2 s_1^2 + s_0^2.$$  

(23)

The measured value $G_{12} = 1.84(3)$ [15] corresponds to the following equation for mixing parameters:

$$s_2^2 s_1^2 + s_0^2 = 0.16(3).$$  

(24)

The signs of the parameters $s_{1,2}$ should be chosen so that the contribution of atomic orbital $6p_{1/2}$ to the molecular orbital $\sigma$ is increased: in this case relativistic corrections to the binding energy of the $\sigma$ orbital are positive.

The matrix element of the HFS interaction for the state $a(1)(22)$ has the form

$$\langle \pi_2 |1/2\rangle |h_{\text{hfs}}|\pi_1 |1/2\rangle.$$  

(25)

(25)

The parameter $P_1$ appears to be restricted only by the normalization condition (27).

It may be possible to add some restrictions to reduce the ranges of variation in Eq. (28). For example, the relatively large value of $s_2$ should require a large value of $S_p$. However, such additional restrictions would add arbitrariness to the model and may affect its reliability. We use only the minimal set of constraints to determine the range of possible values of $W_d$.

For the wave function (22), there are two contributions to the EDM parameter $W_d$ from each of the one-electron orbitals with $|\omega| = 1/2$.
TABLE II. Dependence of the EDM constant $W_d$ (in a.u.) on the parameters of the model.

| $A^\parallel$ (GHz) | $G^\parallel$ | $\alpha$ | $P_2^2$ | $|W_d|$ max | $|W_d|$ min |
|-------------------|-------------|----------|---------|-----------|-----------|
| -4.1              | 1.84        | 0.30     | 0.51    | 19.6      | 13.7      |
| -4.1              | 1.81        | 0.30     | 0.51    | 19.1      | 12.0      |
| -4.1              | 1.87        | 0.30     | 0.51    | 20.3      | 15.4      |
| -4.1              | 1.84        | 0.24     | 0.51    | 19.8      | 13.2      |
| -4.1              | 1.84        | 0.36     | 0.51    | 20.3      | 15.5      |
| -4.1              | 1.84        | 0.30     | 0.41    | 18.2      | 12.1      |
| -4.1              | 1.84        | 0.30     | 0.61    | 20.3      | 15.1      |
| -3.3              | 1.84        | 0.30     | 0.51    | 17.0      | 11.2      |
| -4.9              | 1.84        | 0.30     | 0.51    | 22.0      | 16.4      |

\[ W_d = -c^2_a W_d^\#z - s^2_a W_d^\#s \]
\[ = \frac{4\omega_{sp}}{\sqrt{3}} S_p (\sqrt{2}c^3_a c^2_s s^2_p - c^2_s s^2_a S_p) + \sqrt{2} c^2_s c^2_s s^2_s P - c^2_s s^2_a S_p \]  

(29a)

(29b)

We find that the first term in (29b) always dominates the sum. The second term is not negligible, but the final two terms contribute $\approx 10\%$. It is important that the leading contribution to $W_d$ is similar to the first term in Eq. (26), which dominates the HFS. This implies that the parameter $W_d$ is well constrained even though some of the parameters of the wave function are not. We obtain

\[ |W_d| = 16.6 \pm 3.0 \text{ a.u.}, \]  

(30)

where the uncertainty reflects the range of values found within the model just described.

It is also important to check how $W_d$ depends on the “fixed” parameters $\alpha$ and $P_2$, as well as on the input data for $A^\parallel$ and $G^\parallel$, since our model relating the MO LCAO coefficients to these parameters is rather crude. In Table II we solve the model equations for values of these quantities varying from the best values by $\pm 20\%$. We find that this variation of the input parameters widens the range for $W_d$ substantially (to $\pm 5.4 \text{ a.u.}$), but still does not allow dramatically smaller values of $W_d$.

It is known from previous calculations of $W_d$ for other diatomic molecules, that correlation corrections tend to decrease the result by 10%–20% from the Hartree-Fock level. Therefore, we state our final result as a conservative lower limit on $W_d$.

\[ |W_d| \geq 10 \text{ a.u.} = 12 \times 10^{26} \frac{\text{Hz}}{e \text{ cm}}. \]  

(31)

This lower bound is several times larger than earlier, naive estimates which did not consider the effect of SO mixing on the (nominally) $\pi$-type orbitals of the $a(1)$ state [5]. Our model shows significant similarity between the orbital $\pi_{2,1/2}$ in PbO and the single valence orbital in the ground state of the free radical PbF. It is thus natural that our bound is close to the value calculated for PbF [16]. (Coincidentally, our bound is also similar to the calculated value for YbF [17–20].) However, we stress that this first semiempirical estimate of the effective field in PbO has very limited accuracy. Thus, more elaborate calculations of the $a(1)$ state are highly desirable.

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