In search of the electron dipole moment: *Ab initio* calculations on ^{207}PbO excited states

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We report *ab initio* correlated relativistic calculations of the effective electric field W_d acting on the electron in two excited electronic states of PbO, required for extracting the electric dipole moment of the electron from an ongoing experiment at Yale, which has the potential of improving accuracy for this elusive property by several orders of magnitude. The generalized relativistic effective core potential and relativistic coupled cluster methods are used, followed by nonvariational one-center restoration of the four-component wave function in the heavy atom core. W_d is -3.2×10^{24} Hz/(e cm) for the $a(1)$ state and -9.7×10^{24} Hz/(e cm) for the $B(1)$ state. Comparison of calculated and experimental values of the hyperfine constant $A_\parallel$ provides an accuracy check for the calculation.

I. INTRODUCTION

Following the discovery of the combined *CP*-parity violation in K_0-meson decay [1], the search for the electric dipole moment (EDM) of the electron, d_e, has become one of the most fundamental problems in physics [2]. Considerable experimental effort has been invested in measuring atomic EDMs induced by the electron EDM. The best available results for the electron EDM were obtained in the atomic Tl experiment [3], which established an upper limit of $|d_e| < 1.6 \times 10^{-27} e$ cm. It is expected that diatomic molecules containing a heavy atom can yield more definite results. Modern experiments searching for d_e in these molecules exploit the fact that the effective electric field seen by an unpaired electron, W_d, is greatly enhanced by the relativistic effects relative to the external field [4,5] reachable in a laboratory. The value of W_d is necessary to extract d_e from experimental measurements. For diatomic molecules with one unpaired electron, such as YbF and BaF, semiempirical estimates or *ab initio* calculations with approximate accounting for correlation and relativity provide reasonably reliable W_d values (see Refs. [6–8]). These molecules are, however, chemical radicals, posing experimental problems. It was pointed out recently that the excited $a(1)$ [5] or $B(1)$ [9] states of PbO can be used effectively in the search for d_e. An experiment, using a vapor cell to study excited PbO, has been started at Yale University. The unique suitability of PbO for searching the elusive d_e is demonstrated by the very high statistical sensitivity of the Yale experiment to the electron EDM, allowing detection of d_e of order $10^{-31} e$ cm [5], four orders of magnitude lower than the current limit quoted above. While semiempirical calculations [10] may be valuable, the authors of Ref. [10] stressed that "more elaborate calculations were highly desirable". High-order *ab initio* correlated relativistic calculations of the type developed recently

[11] are required to give accurate values of W_d acting on the unpaired PbO electrons. An accuracy check is provided by calculating experimentally known properties which also depend on the electron-spin density near the heavy nucleus, such as hyperfine constants.

The terms of interest for PbO in the effective spin-rotational Hamiltonian may be written following Ref. [12]. The P,T-odd interaction of d_e with W_d is

$$H_{\text{edm}} = W_d d_e (\boldsymbol{J} \cdot \boldsymbol{n}), \tag{1}$$

where $\boldsymbol{J}$ is the total electron moment and $\boldsymbol{n}$ is the unit vector along the axis from Pb to O. The hyperfine interaction of the electrons with the ^{207}Pb nucleus is

$$H_{\text{hfs}} = \boldsymbol{J} \cdot \hat{A} \cdot \boldsymbol{I}, \tag{2}$$

where $\hat{A}$ is the hyperfine tensor, characterized for a linear molecule by the constants $A_\parallel$ and $A_\perp$, and $\boldsymbol{I}$ is the spin of the ^{207}Pb nucleus ($I = 1/2$).

In practice, the effective operator

$$H_d = 2d_e \begin{pmatrix} 0 & 0 \\ 0 & \boldsymbol{\sigma E} \end{pmatrix} \tag{3}$$

is used to express the interaction of d_e with the inner molecular electric field $\boldsymbol{E}$ ($\boldsymbol{\sigma}$ are the Pauli matrices), to avoid the large terms which cancel each other [13] because of Schiff's theorem. After averaging over the electronic coordinates in the molecular wave function, one obtains

$$W_d = \frac{1}{\Omega d_e} \langle \Psi_\Omega | \sum_i H_d(i) | \Psi_\Omega \rangle, \tag{4}$$

where Ψ_Ω is the wave function for either $a(1)$ or $B(1)$, and $\Omega = \langle \Psi_\Omega | \boldsymbol{J} \cdot \boldsymbol{n} | \Psi_\Omega \rangle$. The hyperfine constant $A_\parallel$ is determined by the expression

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$$A_\parallel = \frac{1}{\Omega}\frac{\mu_{Pb}}{I}\langle\Psi_\Omega|\sum_i\left(\frac{\boldsymbol{\alpha}_i\times\boldsymbol{r}_i}{r_i^3}\right)_Z|\Psi_\Omega\rangle, \qquad (5)$$

where μ_{Pb} is the magnetic moment of ^{207}Pb, $\boldsymbol{\alpha}_i$ are the Dirac matrices for the ith electron, and $\boldsymbol{r}_i$ is its radius vector in a coordinate system centered on the Pb atom [14].

Both $A_\parallel$ and W_d depend strongly on the electronic spin density near the heavy nucleus, while the molecular bonds are formed in the valence region. As shown previously ([6,11,15] and references therein), it is possible to evaluate the electronic wave function near the heavy nucleus in two steps. Using this strategy here, a high-accuracy relativistic coupled cluster (RCC) calculation [16] of the molecular electronic structure with the generalized relativistic effective core potential (GRECP) is carried out, providing proper electronic density in the valence and outer core regions. This is followed by restoration of the proper shape of the four-component molecular spinors in the inner-core region of the heavy atom.

II. METHODS AND CALCULATIONS

A 22-electron GRECP for Pb [17] is used in the first stage of the two-step calculations of PbO: the inner shells of the Pb atom ($1s$ to $4f$) are absorbed into the GRECP, and the $5s5p5d6s6p$ electrons and all the oxygen electrons are treated explicitly. Two series of calculations are carried out, denoted as (a) and (b): calculation (a) correlates ten electrons, freezing the $5s5p5d$ shells of Pb and the $1s$ shell of O; (b) correlates all 30 electrons treated explicitly. States with the leading configurations $\sigma_1^2\sigma_2^2\pi_1^4$, $\sigma_1^2\sigma_2^2\pi_1^3\pi_2^1$, and $\sigma_1^2\sigma_2^1\pi_1^4\pi_2^1$ are calculated. Here $\sigma_{1,2}$ and $\pi_{1,2}$ are molecular valence orbitals, with the subscript enumerating them in order of increasing energy. For each series of calculations, correlation spin-orbital basis sets are optimized in atomic two-component GRECP/RCC calculations of Pb. The four $6s$ and $6p$ electrons are correlated in the basis set optimization stage of calculation (a), and 22 electrons ($5s$ to $6p$) are correlated in the optimization of the basis set used in series (b). Correlation is taken into account at this stage by the RCC method with single and double excitations (RCC-SD) [18]; the average energy of the five lowest states of Pb is minimized. The detailed description of the basis set generation procedure may be found in Refs. [19,20]. A $[4s3p2d]$ basis, obtained by omitting the f function from Dunning's correlation-consistent $(10s5p2d1f)/[4s3p2d1f]$ basis listed MOLCAS 4.1 library [21], is used for oxygen. We found that the f orbital has little effect on the core properties calculated here. Previous calculations show that these basis sets are adequate for our purpose.

PbO calculations start with a one-component self-consistent field (SCF) computation of the molecular ground state, using the spin-averaged GRECP (AGREP). The Pb spinors $5s5p5d$ are frozen in the (a) series, using the level-shift technique [22]. An AGREP/RASSCF (restricted active space SCF) calculation [21,23] of the lowest $^3\Sigma^+$ state of PbO is then performed. In the RASSCF method, orbitals are divided into three active subspaces: RAS1, with a restricted number of holes allowed; RAS2, where all possible occupations are included; and RAS3, with an upper limit on the number of electrons.

Different distributions of electrons in these active subspaces are used (details may be found in Ref. [24]) to estimate the different correlation contributions to the RASSCF values of $A_\parallel$ and W_d. Two-component RCC-SD molecular calculations are then performed. The AGREP/RASSCF calculations include only the most important correlation and scalar-relativistic effects, while the GRECP/RCC-SD calculations also account for spin-orbit interaction. The Fock-space RCC calculations start from the ground state of PbO and use the scheme

$$\begin{array}{ccccc} PbO^+ & \leftarrow & PbO & \rightarrow & PbO^- \\ & \searrow & & \swarrow & \\ & & PbO^* & & \end{array} \qquad (6)$$
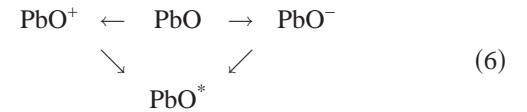
Details on the model spaces used may be found in Ref. [24].

Only valence and outer-core electrons have been treated so far. Since we are interested in properties near the Pb nucleus, the shape of the four-component molecular spinors has to be restored in the inner-core region. All molecular spinors are restored using the nonvariational one-center restoration scheme (see Refs. [6,11,22,25] and references therein). This is done in two steps.

First, equivalent numerical one-center basis sets of four-component spinors and two-component pseudospinors are generated by the finite-difference all-electron Dirac-Hartree-Fock (DHF) and GRECP/SCF calculations, respectively, of the same valence configurations of Pb and its ions. In the DHF calculations the inner-core spinors ($1s$ to $4f$) are frozen after the calculation of Pb^{2+}, and the nucleus is modeled by a uniform charge distribution within a sphere of radius $r_{nucl} = 7.12$ fm$=1.35\times10^{-4}$ a.u. The root-mean-square radius of the nucleus is 5.52 fm, in accord with the parametrization of Johnson and Soff [26], and agrees with the ^{207}Pb nucleus experimental value of 5.497 fm [27]. Taking the experimental value for the root-mean-square radius and a Fermi distribution for the nuclear charge changes $A_\parallel$ and W_d by 0.1 % or less. The all-electron four-component HFD [28] and two-component GRECP/HFJ [17,29] codes are employed for the basis generation, using the procedure developed in Refs. [19,20]. The basis sets generated are $[9s14p7d]$ for series (a) and $[6s7p5d]$ for series (b), with the latter carefully optimized. These sets are orthogonal to the inner core (see above). They describe mainly the core region, and are generated independently of the basis set for the molecular GRECP calculations discussed earlier.

In the second step, the basis of one-center two-component atomic pseudospinors is used to expand the molecular pseudospinorbitals; these two-component pseudospinors are then replaced by the equivalent four-component spinors, retaining the expansion coefficients. A very good description of the wave function in the core region is obtained.

The RCC-SD calculation of W_d and $A_\parallel$ employs the finite field method [30,31]. The operator corresponding to the desired property [Eq. (1) and (2)] is multiplied by a parameter λ and added to the Hamiltonian. The first derivative of the

TABLE I. Calculated parameters $A_\parallel$ (in MHz) and W_d (in 10^{24} Hz/$(e$ cm)) for the $a(1)$ and $B(1)$ states of ^{207}PbO. The experimental value of $A_\parallel$ in $a(1)$ is -4113 MHz. The preliminary value of $A_\parallel$ is $B(1)$ is 5000 ± 200 MHz (Ref. [35]).

State	$a(1)\sigma_1^2\sigma_2^2\pi_1^3\pi_2^1\,{}^3\Sigma_1$					$B(1)\sigma_1^2\sigma_2^1\pi_1^4\pi_2^1\,{}^3\Pi_1$				
Parameters	$A_\parallel$			W_d		$A_\parallel$			W_d	
Expansion	s	s,p	s,p,d	s,p	s,p,d	s	s,p	s,p,d	s,p	s,p,d
10e-RASSCF	−759	−1705	−1699	0.96	0.91			1900	0.0	0.0
10e-RCC-SD			−2635	−2.93				3878	−11.1	
30e-RCC-SD			−2698		−4.1			4081		−9.1

calculated energy with respect to λ gives the evaluated property. This is strictly correct only at the limit of vanishing λ, but it is usually possible to find a range of λ where the energy is linear in λ and the energy changes are large enough to attain the required precision. The quadratic dependence of the energy on λ is eliminated here by averaging the components of a given term, $a(1)$ or $B(1)$, with opposite signs of λ.

III. RESULTS AND DISCUSSION

Calculated results for the (a) and (b) series are presented in Table I. The internuclear distance is 2.0 Å. The RASSCF calculations use the 22-electron GRECP for Pb. Twenty of the 30 electrons treated were in the inactive space, and only 10 were correlated. Using the C_{2V} classification scheme, 2 A_1 orbitals are in RAS1, 6 orbitals (2 A_1, 2B_1, and 2B_2) in RAS2, and 41 (16 A_1, 5 A_2, 10 B_1, and 10 B_2) in RAS3. No more than two holes in RAS1 and two particles in RAS3 are allowed. The basis sets on Pb are $(16s18p16d8f)/[6s7p5d3f]$ for the RASSCF and 30-electron RCC-SD calculations and $(15s16p12d9f)/[5s7p4d2f]$ for ten-electron RCC-SD. A $(10s5p2d)/[4s3p2d]$ basis is put on O in all calculations.

We discuss mainly the results for the $a(1)$ state (leading configuration $\sigma_1^2\sigma_2^2\pi_1^3\pi_2^1$), for which the reliable experimental value of $A_\parallel$ is available (-4113 MHz) [32] and a semiempirical estimate of $|W_d|\geq12\times10^{24}$ Hz/$(e$ cm) was made recently [10]. There are several points to note.

(1) Inclusion of the spin-orbit interaction changes $A_\parallel$ and W_d dramatically, as may be seen from the difference between the ten-electron RASSCF and RCC-SD results.

(2) The *ab initio* value of W_d is three times smaller than the semiempirical estimate [10].

(3) Accounting for outer core-valence correlation by 30-electron RCC-SD changes W_d by 40% and $A_\parallel$ by 3%, yet the error in the calculated $A_\parallel$ is 34%; calculations on BaF [7] and YbF [8] gave 10% accuracy.

(4) $A_\parallel$ is mainly determined by the p wave, whereas W_d mostly comes from s-p mixing.

The need for including correlation in the PbO molecule for the properties discussed here can be seen already in the semiempirical model [10]. The leading contribution to the highest occupied σ_2 orbital in this model comes from the Pb 6s atomic orbital, with a weight of ~0.5 (the corresponding coefficient in the molecular orbital expanded as a linear com-

bination of atomic orbitals is ~0.7). This contradicts the qualitative analysis of the chemical bond formation, which predicts that the σ_2 orbital is mainly formed from the oxygen $2p_\sigma$ and lead $6p_\sigma$ orbitals. The RASSCF calculations of the lowest ${}^3\Sigma^+$ state confirm this point, with the weight of the Pb 6s orbital varying between 0.04 for ten active electrons and 0.1 for 30 active electrons. The weight of the oxygen $2p_\sigma$ is ~0.5 and that of the lead $6p_\sigma$ is ~0.1, whereas σ_1 consists mainly of the lead 6s orbital, with negligible contribution from lead $6p_\sigma$. Note that the oxygen $2p_\sigma$ and lead $6p_\sigma$ orbitals are not orthogonal to each other; after one-center reexpansion of the oxygen basis functions on lead (see Ref. [15] and Eq. (6) in Ref. [11]), the weight of the $6p_\sigma$ orbital goes up to 0.3. We expect that such strong admixture of the s wave to the σ_2 orbital would not appear in the semiempirical model if configurations describing the correlation of the σ_2 electrons were included in the model space. It is important to add that the lowest virtual σ_3 orbital gets the main contribution from the lead $6p_\sigma$ (with a weight of about 0.5), and the configurations containing this orbital are first admixed into the leading configuration of the $a(1)$ state due to the spin-orbit interaction on Pb.

If the spin-orbit interaction is neglected, the s-wave contribution to $A_\parallel$ and the s,p-wave contributions to W_d are due primarily to correlation of the σ electrons. The RASSCF calculation indicates (see Table I) that such contributions increase $A_\parallel$ but decrease W_d, resulting in a sign change for W_d, in agreement with the final RCC-SD result (details may be found in Ref. [33]). Besides, as correlation is expected to have a strong influence on the values of $A_\parallel$ and W_d, introducing the SO interaction with the ${}^3\Pi$ and ${}^1\Pi$ states by just mixing the corresponding σ and π orbitals may not be satisfactory. All these conclusions could be reached only after extensive molecular calculations, and the estimates made in Ref. [10] were important at the first stage of the experimental effort.

As may be expected, the accuracy of the calculated $A_\parallel$ and W_d values is lower for such a complicated system as the excited states of the PbO molecule than for the ground states of BaF and YbF. The valence electron in the latter molecules is in a σ orbital, with much higher density near the heavy nucleus than the valence π electrons in PbO. Thus, the s,p,d waves on the Pb nucleus are affected more strongly by correlation, and higher-order inclusion of correlation (triple and quadruple amplitudes in the RCC method) as well as larger basis sets may be necessary. Our estimated error bounds put

the real W_d between 75% and 150% of the calculated value, which is quite satisfactory for the first stage of the EDM experiment on PbO. It should be noted that the estimate of statistical sensitivity to the electron EDM made in Ref. [5] is based on a W_d value close to that obtained here.

A detailed analysis of correlation and spin-orbital effects on $A_\parallel$ and W_d in PbO will be published elsewhere [33]. Unfortunately, the experimentally available $A_\parallel$ of the $a(1)$ and $B(1)$ states provides a check on the p wave only. It would be desirable to measure $A_\parallel$ in some state with an excited σ_1 electron, with the main contribution coming from the s wave. Another accuracy check, using $1/3\sqrt{(A_\parallel + 2A_\perp)(A_\parallel - A_\perp)}$, is not applicable here. Our estimate of the accuracy of the calculated W_d is therefore not as straightforward as for YbF and BaF [7,8].

Finally, we would like to note that we identified the lowest $^3\Pi_1$ state as $B(1)$ according to the ΛS classification given in Ref. [34]. Conclusive identification requires more extensive *ab initio* correlation calculations.

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