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Many-body effects in hyperfine interactions in ^{205}Pb$^+$

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Abstract. Ab initio calculations have been carried out to study the magnetic dipole and electric quadrupole hyperfine structure constants of ^{205}Pb$^+$. Many-body effects have been considered to all orders using the relativistic coupled-cluster theory in the singles, doubles and partial triples approximation. The trends of these effects are found to be different from atomic systems that have been studied earlier.

1 Introduction

With the advent of ion trapping techniques, it has become possible to perform high precision measurements of different atomic properties; including hyperfine structure constants for the ground and low-lying excited states of stable isotopes [1,2]. Studies of these interactions have served as stringent tests of relativistic many-body theories. It has been found that the behavior of electron correlation in the hyperfine interactions in the d-states is substantially different from those of s- and p-states [3]. The underlying reason for this is the strong and unusual core-polarization effects associated with the former.

The work presented in this paper is carried out using the relativistic coupled-cluster (RCC) theory. It is equivalent to all orders relativistic many-body perturbation theory. Core-polarization and pair-correlation effects which are important for such calculations are computed to all orders in this theory. It has been successfully applied to heavy atomic systems with a single valence electron [4,5].

^{205}Pb is one of the stable isotopes of lead which has a lifetime about 1.5×10^7 years. The nuclear structure of this isotope is different from the other stable isotope, ^{207}Pb. It's nuclear magnetic moment and electric quadrupole moment are non-zero. Theoretical studies of the magnetic dipole and electric quadrupole hyperfine structure constants of ^{205}Pb$^+$ are the focus of the present work.

There are relatively few measurements of the hyperfine structure constants for the excited states of heavy atoms and ions. It is certainly worthwhile to perform highly correlated calculations of these quantities for Pb$^+$ as it could be a promising candidate for the observation of parity non-conservation [6]. This theoretical effort could motivate experimentalists to carry out high precision measurements of ^{205}Pb$^+$.

In Section 2 of this paper, we give an outline of the RCC theory and in Section 3 we discuss the pertinent details of the calculation. The results of our calculations are presented and discussed in Section 3 and finally we make some concluding remarks in Section 4.

2 Theory

In order to obtain the RCC wavefunction for Pb$^+$, we require the closed-shell Pb^{++} wavefunction, which is given in terms of the lowest order Dirac-Fock (DF) wavefunction $|\Phi_{DF}\rangle$, as

$$|\Psi\rangle = \Omega|\Phi_{DF}\rangle, \qquad (2.1)$$

where in conventional many-body perturbation theory, the wave operator, Ω is expressed in powers of the residual interaction, $V_{es} = \sum_{i<j} \frac{1}{r_{ij}} - \sum_i U_{DF}(r_i)$. This results in a hierarchy of approximations for the correlation energy and the wavefunction.

The coupled cluster theory is based on the following exponential ansatz for the closed-shell wave operator [7]

$$\Omega = N[\exp(T)], \qquad (2.2)$$

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where the cluster operator T is expressed in terms of the connected diagrams of the wave operator. The operator T also can be expressed in terms of the cluster operators T_n corresponding to different orders of excitations n of the core electrons from the DF state, $|\Phi_{DF}\rangle$, explicitly defined by,

$$T = T_1 + T_2 + ...$$
$$= \sum_{ap} a_p^\dagger a_a t_a^p + \frac{1}{4} \sum_{abpq} a_p^+ a_q^+ a_b a_a t_{ab}^{pq} + ..., \quad (2.3)$$

with $a, b, c, ...$ $(p, q, r, ...)$ representing occupied (unoccupied) orbitals. t_a^p is the cluster amplitude corresponding to the single excitation from the orbital a to p and so on. Termination of the series at T_2, results in the coupled cluster theory with single and double excitations (CCSD). The Breit interaction [8] which is four orders of magnitude smaller than the Coulomb interaction has been neglected in the present work.

For a single valence atomic system the wavefunction in the RCC method can be written as [7,9]

$$|\Psi_v\rangle = e^T \{1 + S_v\}|\Phi_v\rangle, \quad (2.4)$$

with the new reference state

$$|\Phi_v\rangle = a_v^\dagger |\Phi_{DF}\rangle, \quad (2.5)$$

for the given valence electron v; S_v represents excitation operators which excite at least the valence electron. The explicit form of this operator can be written as

$$S_v = S_{1v} + S_{2v} + ...$$
$$= \sum_{p \neq v} a_p^+ a_v s_v^p + \frac{1}{2} \sum_{bpq} a_p^+ a_q^+ a_b a_v s_{vb}^{pq} + ... \quad (2.6)$$

An approximate treatment of the triple excitations to the CCSD method is included by contracting the residual Coulomb operator, which effectively forms a two-body operator, and the double-excitation operators T_2 and S_{2v} [10], thereby defining the CCSD(T) approximation

$$S_{vbc}^{pqr} = \frac{\widehat{V_{es}T_2} + \widehat{V_{es}S_{2v}}}{\epsilon_v + \epsilon_b + \epsilon_c - \epsilon_p - \epsilon_q - \epsilon_r}, \quad (2.7)$$

where ϵ_i is the orbital energy of the corresponding ith electron.

3 Method of calculation

For computational simplicity, the T amplitudes are solved first for the closed-shell Pb^{++} and then the valence electron is attached to calculate the open-shell wavefunctions. The matrix equations for solving the correlation energy and the T amplitudes are given by

$$\langle \Phi_{DF}|\overline{H_N}|\Phi_{DF}\rangle = \Delta E_{corr} \quad (3.1)$$
$$\langle \Phi_{DF}^*|\overline{H_N}|\Phi_{DF}\rangle = 0, \quad (3.2)$$

where H_N is the normal ordering Hamiltonian which can be written as $H_N = f_N + V_N$, sum of one-body and two-body terms. In the above equation, $\overline{H_N}$ is defined as $\overline{H_N} = e^{-T}H_N e^T$, ΔE_{corr} is the correlation energy and $|\Phi_{DF}^*\rangle$ corresponds to excited states from $|\Phi_{DF}\rangle$.

For the open-shell RCC calculations, the S_v operators are solved using the following equations

$$\langle \Phi_v|\overline{H_N}\{1 + S_v\}|\Phi_v\rangle = -\Delta E_v \quad (3.3)$$
$$\langle \Phi_v^*|\overline{H_N}\{1 + S_v\}|\Phi_v\rangle = -\langle \Phi_v^*|\{S_v\}|\Phi_v\rangle \Delta E_v, \quad (3.4)$$

where ΔE_v is the ionization potential (IP) energy of the corresponding valence electron v. Similarly $|\Phi_v^*\rangle$ are the excited states from $|\Phi_v\rangle$.

The relativistic hyperfine Hamiltonian is given by [11]

$$H_{hfs} = \sum_k \mathbf{M}^{(k)} \cdot \mathbf{T}^{(k)}, \quad (3.5)$$

where $\mathbf{M}^{(k)}$ and $\mathbf{T}^{(k)}$ are spherical tensor operators of rank k. In first-order perturbation theory, hyperfine energies $E_{hfs}(J)$ of the fine-structure state $|JM_J\rangle$ are expectation values of the hyperfine interaction Hamiltonian. Details of the expression are given by Cheng and Childs [11]. The magnetic dipole and electric quadrupole hyperfine energies are defined by

$$E_{M1} = AK/2 \quad (3.6)$$

and

$$E_{Q2} = \frac{B}{2} \frac{3K(K+1) - 4I(I+1)J(J+1)}{2I(2I-1)2J(2J-1)}, \quad (3.7)$$

respectively. Here I and J being the total angular momentum of the nucleus and the electron state, respectively, and $K = 2\langle I \cdot J \rangle$. The magnetic dipole hyperfine constant A and electric quadrupole hyperfine constant B are defined as

$$A = \mu_N g_I \frac{\langle J||T^{(1)}||J\rangle}{\sqrt{J(J+1)(2J+1)}} \quad (3.8)$$
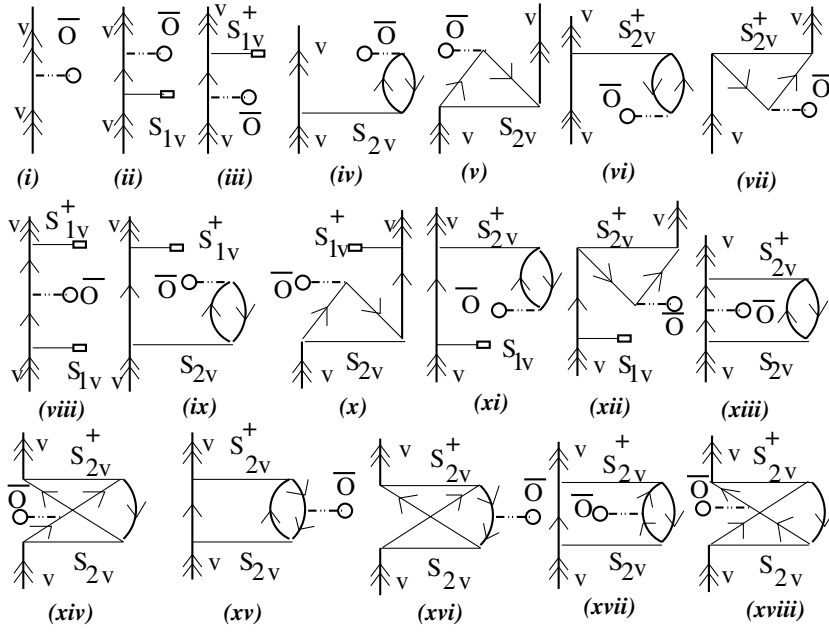
and

$$B = 2eQ \left[\frac{2J(2J-1)}{(2J+1)(2J+2)(2J+3)} \right]^{1/2} \langle J||T^{(2)}||J\rangle, \quad (3.9)$$

respectively, where μ_N is Bohr magneton, $g_I = \mu_I/I$ with μ_I and I are the nuclear dipole moment and spin, and Q is nuclear quadrupole moment.

The expectation value for a general one particle operator O in a given valence electron (v) state can be expressed in RCC theory as

$$\langle O \rangle_v = \frac{\langle \Psi_v|O|\Psi_v\rangle}{\langle \Psi_v|\Psi_v\rangle}$$
$$= \frac{\langle \Phi_v|\{1 + S_v^\dagger\}e^{T^\dagger}Oe^T\{1 + S_v\}|\Phi_v\rangle}{1 + N_v}$$
$$= \frac{\langle \Phi_v|\{1 + S_v^\dagger\}\overline{O}\{1 + S_v\}|\Phi_v\rangle}{1 + N_v}. \quad (3.10)$$

Fig. 1. Hyperfine constants evaluating Goldtone diagrams from $\overline{O}_{o.b.}$. Lines with double arrows represent valence orbital (v), lines with upward arrow and lines with downward arrow represent virtual orbitals ($p, q, r, ...$) and occupied orbitals ($a, b, c, ...$), respectively. Solid lines represent all order RCC operators and doted lines represent hyperfine operator dressed with T operators.

In the CCSD approximation, the above expression is given by

see equation (3.11) below.

We have defined in the above expressions

$$\overline{O} = e^{T^\dagger} O e^T \qquad (3.12)$$

and

$$N_v = \langle \Phi_v | S_v^\dagger [e^{T^\dagger} e^T] + S_v^\dagger [e^{T^\dagger} e^T] S_v + [e^{T^\dagger} e^T] S_v | \Phi_v \rangle$$
$$= \langle \Phi_v | S_v^\dagger \overline{n_v} + S_v^\dagger \overline{n_v} S_v + \overline{n_v} S_v^\dagger | \Phi_v \rangle. \qquad (3.13)$$

For computational simplicity we evaluate the matrix elements of any operator in two steps. We expand $\overline{O}$ using Wick's general theorem [7] as

$$\overline{O} = (e^{T^\dagger} O e^T)_{f.c.} + (e^{T^\dagger} O e^T)_{o.b.} + (e^{T^\dagger} O e^T)_{t.b.} + ..., \qquad (3.14)$$

where we have used the abbreviations *f.c.*, *o.b.* and *t.b.* for fully contracted, effective one-body and effective two-body terms respectively. In this expansion of $\overline{O}$, the effective one-body terms are computed keeping terms of the form of

$$\overline{O}_{o.b.} = O + T^\dagger O + OT + T^\dagger OT. \qquad (3.15)$$

We have shown the Goldstone diagram representation of the above expression in Figure 1. The calculation procedure for these terms are given by Geetha et al. [4]. They are finally connected with S_v and $S_v^\dagger$ operators in the evaluation of properties. Contributions due to the effective

two-body terms from $\overline{O}$ are constructed using the procedure shown diagrammatically in our earlier works [4,12] and computed directly during the calculation of properties. The following types of terms are considered for the construction of the effective two-body terms

$$\overline{O}_{t.b.} = OT_1 + T_1^\dagger O + OT_2 + T_2^\dagger O. \qquad (3.16)$$

Other effective terms correspond to higher orders in the residual Coulomb interaction and are neglected in the present calculation. A similar procedure has been followed to account for the normalization factor.

The contributions from the normalization factors for the corresponding valence electron v that are given in Tables 3 and 4, were obtained using the following relations:

$$Norm = \langle \Psi_v | O | \Psi_v \rangle \left\{ \frac{1}{1 + N_v} - 1 \right\}. \qquad (3.17)$$

4 Results and discussions

The starting point of our calculations is the generation of the DF orbitals for ^{205}Pb^{++}. These orbitals are constructed as linear combinations of Gaussian type orbitals (GTOs) as given by Chaudhuri et al. [13]. It has been found [6] that the RCC calculations based on this choice of GTOs provide accurate A-values for the low-lying states of ^{207}Pb$^+$. In the present work, we have used similar basis functions to calculate both A- and B-values of ground and some of the important excited states of ^{205}Pb$^+$.

In Table 1, we present A and B hyperfine structure constants of the low-lying states of Pb$^+$. We use the Landé

$$\langle O \rangle_v = \frac{\langle \Phi_v | \overline{O} + S_{1v}^\dagger \overline{O} + S_{2v}^\dagger \overline{O} + \overline{O} S_{1v} + \overline{O} S_{2v} + S_{1v}^\dagger \overline{O} S_{1v} + S_{2v}^\dagger \overline{O} S_{1v} + S_{1v}^\dagger \overline{O} S_{2v} + S_{2v}^\dagger \overline{O} S_{2v} | \Phi_v \rangle}{1 + N_v} \qquad (3.11)$$

Table 1. A and B results of ^{205}Pb$^+$ using DF and RCC methods.

	$6p_{1/2}$	$6p_{3/2}$	$7s_{1/2}$	$7p_{1/2}$	$7p_{3/2}$	$6d_{3/2}$	$6d_{5/2}$	$8s_{1/2}$
$\underline{A}$								
DF	2765.54	220.58	1879.06	476.34	43.84	19.05	7.53	687.77
RCC	3099.5	149.7	2680.3	543.7	74.8	−10.03	60.97	929.3
$\underline{B}$								
DF		377.81			75.09	11.08	13.07	
RCC		464.6			99.3	50.7	56.9	
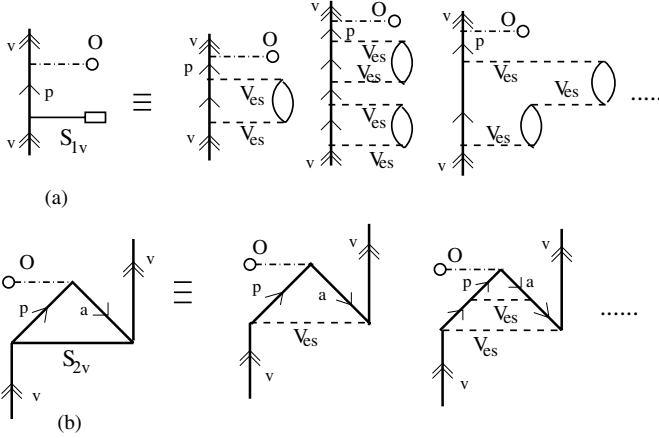
Fig. 2. Diagrammatic representation of the relation between pair-correlation (a) and core-polarization (b) effects from CC and MBPT methods. In the pair-correlation diagram $p \neq v$. All order RCC operators are shown with solid lines whereas residual interaction lines are shown with dashed lines. The pure hyperfine operator is shown by dashed line with single dots.

nuclear g-factor, $g_I = 0.28468$ to calculate A and nuclear quadrupole moment, $Q = 0.234$ to calculate B [14]. From the differences of the DF and RCC results given in Table 1, it is evident that for both the hyperfine constants A and B the electron correlation effects vary from (10–710)%.

All the core orbitals were excited in our calculations. The core-polarization effects, which are the largest contributors to the hyperfine constants of the $6p_{3/2}$ state of ^{207}Pb$^+$ [6] and the $d_{5/2}$ states of the alkaline earth ions [15], have been accounted to all orders through the OS_{2v} term. It was also found from the hyperfine structure studies of the $s_{1/2}$ and $p_{1/2}$ states in the alkaline earth ions that pair-correlation and core-polarization effects are important (see Figs. 2a and 2b for the definitions of all order pair-correlation and core-polarization effects, respectively). In order to appreciate the importance of these effects in Pb$^+$, we present their contributions in Table 2. Comparison of these results with their corresponding DF values from Table 1, brings out some distinct many-body features of the system. The most prominent among them is the size of the core-correlation and core-polarization effects for the d-states. As in the case of some of the alkaline earth ions, the sign of the core-polarization effect in the $d_{5/2}$ state is opposite that of the DF value and the net contribution is 710% of the corresponding DF value. However, unlike those alkaline earth ions [15] the final RCC result has the same sign as the DF result. This is due to the large

Table 2. The contributions of core-correlation, core-polarization and pair-correlation of A and B results in ^{205}Pb$^+$.

States	Core-corr.	Core-pol.	Pair-corr.
A			
$7p_{3/2}$	−0.68	15.17	6.01
$6d_{3/2}$	−1.02	11.13	9.30
$6d_{5/2}$	−0.48	−15.73	3.45
$8s$	70.29	144.23	139.92
B			
$6p_{3/2}$	29.26	79.19	35.55
$7p_{3/2}$	3.34	15.78	10.29
$6d_{3/2}$	−0.65	17.87	5.44
$6d_{5/2}$	−0.88	23.46	5.96

Table 3. Contributions of different coupled-cluster terms to the Pb$^+$ magnetic dipole hyperfine structure constant (A). cc stands for the complex conjugate part of the corresponding terms.

Terms	$6p_{3/2}$ state	$7p_{3/2}$ state	$6d_{3/2}$ state	$6d_{5/2}$ state	$8s_{1/2}$
O (DF)	220.58	43.84	19.05	7.53	687.77
$\overline{O}$	231.07	44.52	20.07	8.01	617.48
$\overline{O}S_{1v} + cc$	18.83	6.01	9.30	3.45	139.92
$\overline{O}S_{2v} + cc$	−141.96	15.17	11.13	−15.73	144.23
$S_{1v}^{\dagger}\overline{O}S_{1v}$	0.38	0.21	1.09	0.38	7.92
$S_{1v}^{\dagger}\overline{O}S_{2v} + cc$	0.14	−0.86	2.02	−2.08	4.85
$S_{2v}^{\dagger}\overline{O}S_{2v} + cc$	46.74	11.04	−54.93	68.91	29.74
Important effective two-body terms of $\overline{O}$					
$S_{2v}^{\dagger}OT_1 + cc$	0.48	−0.03	−0.03	−0.01	1.03
$S_{2v}^{\dagger}OT_2 + cc$	−3.03	−0.44	0.74	0.26	−3.61
$Norm$	−1.61	−0.69	0.39	−2.21	−10.06

positive contributions from the $S_{2v}^{\dagger}\overline{O}S_{2v}$ term, shown in Table 3. Therefore, it is imperative to consider such terms to obtain accurate results.

The role of electron correlation in the hyperfine interactions in ^{45}Sc and ^{89}Y has similarities [3] with Pb$^+$ even though those systems are neutral and have different electronic configurations. Another interesting feature of the present study on ^{205}Pb$^+$ is that the RCC result of the A-value of $6d_{3/2}$ is of opposite in sign than that of the DF result. This trend is different from the other $d_{3/2}$ states in alkaline earth ions [3,16]. The main reason for this behavior is due to another unusual contribution from $S_{2v}^{\dagger}\overline{O}S_{2v}$. The core correlation effect on B-values though reduces as higher excited states are considered, which is

Table 4. Contributions of different coupled-cluster terms to the Pb$^+$ electric quadrupole hyperfine structure constant (B).

Terms	$6p_{3/2}$ state	$7p_{3/2}$ state	$6d_{3/2}$ state	$6d_{5/2}$ state
O (DF)	377.81	75.09	11.08	13.07
$\overline{O}$	348.55	71.56	11.73	13.95
$\overline{O}S_{1v} + cc$	35.55	10.29	5.44	5.96
$\overline{O}S_{2v} + cc$	79.19	15.78	17.87	23.46
$S_{1v}^{\dagger}\overline{O}S_{1v}$	0.87	0.36	0.64	0.65
$S_{1v}^{\dagger}\overline{O}S_{2v} + cc$	2.18	0.62	2.27	2.75
$S_{2v}^{\dagger}\overline{O}S_{2v} + cc$	10.11	2.56	14.26	11.75
Important effective two-body terms of $\overline{O}$				
$S_{2v}^{\dagger}OT_1 + cc$	−0.72	−0.05	−0.02	−0.02
$S_{2v}^{\dagger}OT_2 + cc$	−5.19	−0.76	0.43	0.46
$Norm$	−4.89	−0.93	−2.02	−2.07

expected, but contributions to the d-states are not similar to the p-states. This is evident from the B-values given in Table 2.

Tables 3 and 4 present the important effective two-body terms obtained from $\overline{O} = e^{T^{\dagger}}Oe^{T}$, but they contribute very little. One can therefore justifiably ignore the higher order terms given in equation (3.15) and save computational time. The correlation effects of the A-values of other states presented in Table 1, behave the same way as in ^{207}Pb$^+$ [6].

5 Conclusion

The RCC theory has been employed to study the magnetic dipole and electric quadrupole hyperfine structure constants of the ^{205}Pb$^+$. Strong electron correlations effects are found in the d-states and their behavior is different from other systems studied earlier. Experiments to measure these quantities will constitute important tests of the relativistic coupled-cluster theory.

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