Application of relativistic coupled-cluster theory to heavy atomic systems with strongly interacting configurations: Hyperfine interactions in $^{207}Pb^+$

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We report the results of our calculations of the magnetic dipole hyperfine constants for the ground and low-lying excited states of Pb^+ using the relativistic coupled-cluster theory. The spectacular role of correlation effects particularly for the $6p_{3/2}$ state is highlighted. The relative importance of core polarization and pair correlation effects have been studied and the result obtained for the ground state is different from that of Ba^+, which has a single s valence electron.

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Coupled-cluster theory has been used to study a wide range of many-body systems and has been referred to as the universal many-body theory [1–3]. It has recently been applied to calculate ground- and excited-state properties of nuclei [4]. Although the nonrelativistic version of this theory has been applied to a variety of light atoms and molecules [5], its extension to the relativistic regime is rather recent [6,7]. There have been relatively few theoretical studies of properties of heavy atomic systems based on the relativistic coupled-cluster (RCC) theory. $Pb^+(Z=82)$ is the heaviest atomic ion that has been trapped and cooled so far [8,9]. The magnetic dipole hyperfine constants have been measured for the $6p(^2P_{1/2})$ and $6p(^2P_{3/2})$ states of this ion [10], and these data can be compared with calculations of the corresponding quantities using RCC theory. Such comparisons would indeed constitute an important test of this theory. The nonlinear RCC in the singles and doubles approximation with partial triples added in some cases has yielded results to an accuracy of about 1% for atoms and ions with a single s valence electron [13,14]. However, the correlation effects in Pb^+ are expected to be much stronger as it has a $6p$ valence electron and two $6s$ electrons in its outermost core orbital.

The hyperfine structure constant (A) for the atomic state $|JM\rangle$ can be expressed in terms of a reduced expectation value

$$A = \mu_N \left[\frac{\mu_I}{I}\right] \frac{\langle J||T^{(1)}||J\rangle}{\sqrt{J(J+1)(2J+1)}}, \tag{1}$$

with μ_N being the nuclear magnetic moment and $[\mu_I/I]$ the Lande's nuclear g-factor (g_I). $T^{(1)}$ can be written as [15]

$$T^{(1)} = \sum_q t_q^{(1)} = \sum_{qj} -ie\sqrt{8\pi/3}\, r_j^{-2} \alpha_j \cdot \mathbf{Y}_{10}^{(q)}, \tag{2}$$

where r_j is the radial position of the jth electron, α_j is the Dirac matrix, and $\mathbf{Y}_{10}^{(q)}$ is a vector spherical harmonic.

We have used the RCC theory to obtain the atomic wave functions. In the open-shell coupled-cluster theory [17,18] the many-body wave function for a system with single valence electron can be written as

$$|\Psi_v\rangle = e^T\{1 + S_v\} a_v^\dagger |\Phi_0\rangle, \tag{3}$$

where $a_v^\dagger$ is the creation operator corresponding to a valence orbital v and $|\Phi_0\rangle$ is a closed-shell determinantal state built from occupied Dirac-Fock (DF) orbitals. T and S_v are the closed- and open-shell particle-hole excitation operators, respectively. The curly bracket represents normal ordered form of the operators. In this work both T and S_v operators are considered at the level of single and double excitations and effects from leading-order triple excitations are incorporated partially, as has been considered in our earlier work [13].

Explicitly, the T operator is defined as

$$T = T_1 + T_2 = \sum_{a,p} a_p^\dagger a_a t_a^p + \frac{1}{4} \sum_{ab,pq} a_p^\dagger a_q^\dagger a_b a_a t_{ab}^{pq}, \tag{4}$$

where t_a^p and t_{ab}^{pq} are the amplitudes of the single and double excitations, respectively, from the closed-shell core. Similarly, the open-shell excitation operator (S_v) is defined as,

$$S_v = S_{1v} + S_{2v} = \sum_{p\neq v} a_p^\dagger a_v s_v^p + \frac{1}{2} \sum_{a,pq} a_p^\dagger a_q^\dagger a_a a_v s_{va}^{pq}, \tag{5}$$

with s_v^p and s_{va}^{pq} being the single and double excitation amplitudes involving the valence electron.

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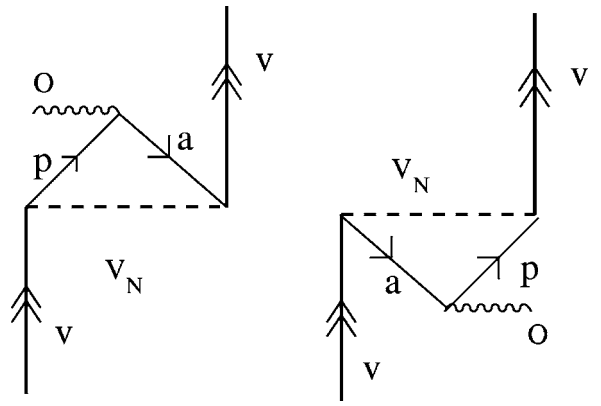

FIG. 1. Goldstone diagrams representing core polarization in MBPT.

In coupled-cluster theory, the expectation value of any operator can be expressed as

$$\langle O\rangle = \frac{\langle\Psi_v|O|\Psi_v\rangle}{\langle\Psi_v|\Psi_v\rangle} = \frac{\langle\Phi_v|\{1+S_v^\dagger\}e^{T^\dagger}Oe^T\{1+S_v\}|\Phi_v\rangle}{\langle\Phi_v|\{1+S_v^\dagger\}e^{T^\dagger}e^T\{1+S_v\}|\Phi_v\rangle}. \quad (6)$$

The above expression was applied to compute the hyperfine structure constant A as given in Eq. (1). The details of the procedure for calculating this expression have been given by [11,12] and applied in [13,14,19].

The orbitals used in the present work were constructed as linear combinations of Gaussian type orbitals of the form [20]

$$F_{i,k}(r) = r^k e^{-\alpha_i r^2}, \quad (7)$$

where $k=0,1,\ldots$ for $s,p,\ldots$ type orbital symmetries, respectively. For the exponents, the even tempering condition

$$\alpha_i = \alpha_0 \beta^{i-1} \quad (8)$$

was used. The occupied orbitals are the DF single-particle states for closed-shell Pb^{++}. The occupied and virtual orbitals were constructed from the closed-shell potential of Pb^{++} using the same Fock operator. All orbitals were generated on a grid using a two-parameter Fermi nuclear distribution approximation given by

$$\rho = \frac{\rho_0}{1+e^{(r-c)/a}}, \quad (9)$$

where the parameter c is the *half-charge radius*, and a is related to the *skin thickness*, which is defined as the interval of the nuclear thickness in which the nuclear charge density falls from near 1 to near zero. Table I displays total number of basis functions used for the DF calculation, total number of occupied and virtual orbitals considered for the coupled-cluster calculations and the energy criteria in atomic unit for selecting virtual orbitals. We have chosen α_0 as 0.008 25 and β as 2.73 for all the symmetries. The DF energies for occupied orbitals obtained using these parameters are in good agreement with the corresponding values of the numerical DF orbitals. They have also been used in calculating excitation energies and the lifetime of the first excited state for Pb^+ in our earlier work [16].

In Table II we present the results for the hyperfine constants using the DF approximation with the Lande's nuclear g-factor, $g_I=1.185\,166$ and compare them with the experimental values for the $6p_{1/2}$ and $6p_{3/2}$ states—the only two states on which measurements have been made. The poor agreement of the results indicate the importance of correlation effects for these states (which were absent in the DF approximation).

It is interesting to note that the DF values for these two states deviate from their respective experimental values in opposite directions, so that the sign of the correlation contributions are opposite for the two cases. This is further supported by the results obtained from the leading diagrams based on second-order relativistic many-body perturbation theory [RMBPT(2)] that are given in Table II. Here the dominant contributions to RMBPT(2) are given explicitly. While electron correlation at this level is substantial for all the states, it is dramatic in the case of $6p_{3/2}$ state because of the unusually large and negative core polarization. We have also given the results of our effective valence shell Hamiltonian method (H^v), which is a variant of multireference many-body perturbation theory [21], for $6p_{1/2}$ and $6p_{3/2}$ states. In the same table we give the significant contributions to the core polarization using RMBPT(2) that arises from the interaction of the outermost core $6s$ and the valence $6p_{3/2}$ electrons (fourth and fifth columns, respectively). The sum of these individual contributions is −971.5 MHz, and after taking into account the polarization of all the other core electrons, a net contribution of −814.6 MHz is obtained. The corresponding H^v contribution is −791.9 MHz. Clearly, the H^v method is inadequate for obtaining an accurate value of the magnetic dipole hyperfine constant of the $6p_{3/2}$ state. The very large size of this second-order correction suggests that an all-order method like coupled-cluster theory is necessary for a correct quantitative description of the correlation, effects in Pb^+. This is indeed reflected in the results given in Table III. Again, the "bare" operator O represents the DF

TABLE I. Description of total number of basis functions, active holes, and active particles involved in this calculation.

	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$	$f_{5/2}$	$f_{7/2}$	$g_{7/2}$	$g_{9/2}$
	38	35	35	30	30	25	25	20	20
Active holes	6	4	4	3	3	1	1	0	0
Active particles	7	9	9	8	9	7	7	7	7
Upper energy limit (a.u.)	2800	2850	2850	510	510	22.6	22.6	22.6	22.6

TABLE II. Dirac-Fock values, second-order relativistic many-body polarization theory [RMBPT(2)] and H^v results for Pb^+ hyperfine structure constants in MHz (second row) and the dominating contributions as shown in Fig. 1.

Lowest-order MBPT terms	$6p_{1/2}$ state	$7p_{1/2}$ state	$6p_{3/2}$ state	$7s_{1/2}$
O(DF)	11 513.5	1983.1	918.3	7822.9
RMBPT(2)	15 722.8	2578.4	302.9	12 663.9
Core pol. [RMBPT(2)]	1506.2	82.1	−814.6	1624.21
Pair corr. [RMBPT(2)]	2297.4	359.6	203.6	3012.7
H^v	12 972	—	484	—
Core pol. (H^v)	1522.6	—	−791.9	—
Experiment	13 000		583(21)	

approximation; i.e., excluding any correlation effects. Several important correlation contributions for our RCC calculations are also presented in Table III. $\bar{O}=e^{T^\dagger}Oe^T$ denotes the "dressed" operator containing the contributions of the closed-shell cluster amplitudes in Eq. (6). Although core polarization (OS_{2v}) and pair correlation (OS_{1v}) are the dominant correlation effects, core correlation effects ($\bar{O}$-O) are by no means negligible; they amount to about 9% for the $7s$ state. Summing up all the contributions given in Table III leads to significant improvements in our calculated values of the hyperfine constants of the $6p_{1/2}$ and $6p_{3/2}$ states. The sub-1% (0.7%) agreement between the former and experiment is indeed spectacular. A similar agreement cannot be expected for the latter state which is characterised by extremely peculiar correlation effects. Even so, the hyperfine constant for this state differs from experiment (3.6% error bar) by a little less than 7%. This is certainly remarkable considering that the corresponding discrepancy at the levels

TABLE III. Contributions of different coupled-cluster terms to the Pb^+ hyperfine structure constant. c.c. stands for the complex conjugate part of the corresponding terms.

Terms	$6p_{1/2}$ state	$6p_{3/2}$ state	$7s_{1/2}$ state	$7p_{1/2}$ state
$O-\bar{O}$	665.3	−43.7	983.3	85.4
$\bar{O}S_{1v}$+c.c.	952.2	78.4	2122.6	326.6
$\bar{O}S_{2v}$+c.c.	1188.2	−591.0	1916.8	35.6
$S^\dagger_{1v}\bar{O}S_{1v}$	21.0	1.6	164.6	14.1
$S^\dagger_{1v}\bar{O}S_{2v}$+c.c.	22.2	0.6	180.2	19.2
$S^\dagger_{2v}\bar{O}S_{2v}$+c.c.	149.6	194.61	298.8	18.7
Important effective two-body terms of $\bar{O}$				
$S^\dagger_{2v}OT_1$+c.c.	−20.2	2.0	14.6	−0.76
$S^\dagger_{2v}OT_2$+c.c.	−160.2	−12.6	−135.4	−21.64
Norm.	−88.5	−6.7	−181.8	−22.98
Total	12 903.7	623.2	11 158.6	2263.5

TABLE IV. Contributions of the $6s_{1/2}$ core electron (in MHz) to the core-polarization effect for $6p_{3/2}$ state using the RMBPT(2) approximation and RCC theory (RCCT).

Virtual orbital	RMBPT(2)	RCCT
$7s_{1/2}$	−190.88	−128.28
$8s_{1/2}$	−51.16	−35.99
$9s_{1/2}$	−169.96	−123.44
$10s_{1/2}$	−468.88	−369.62
$11s_{1/2}$	−90.62	−73.46

of RMBPT(2) and the H^v method are 48% and 16%, respectively. It is interesting to note from Table IV (third column) that the core-polarization contributions in RCC theory follow the same trend as in RMBPT(2) and H^v. However, the contribution from this effect in RCC (−591 MHz) is significantly different than the corresponding contributions in the other two methods (−814.4 MHz and −791.9 MHz).

The plot in Fig. 2 highlights the relative importance of the core polarization and pair correlation for the different states. It is instructive to point out that, unlike the hyperfine constant in the ground state of Ba^+ [14], core-polarization effects are larger than pair correlation for the ground and first excited state; i.e., $6p_{1/2}$ and $6p_{3/2}$ states of Pb^+. This is the result of the much stronger valence-core interactions in Pb^+ compared to Ba^+.

In summary, the power of RCC theory has been exploited to obtain a quantitative understanding of correlation effects in hyperfine interactions in a heavy atomic system with strongly interacting configurations. It has been demonstrated that the results of the DF, RMBPT(2), and H^v approximations in the case of Pb+ differ substantially from the measured values of the hyperfine constants. However, the inclusion of single, double, and a subset of triple particle-hole excitations to all orders in the framework of RCC theory leads to a dramatic improvement in the results. The relevance of the present work extends beyond hyperfine interactions in Pb^+. Our results highlight the fact that a judicious use of

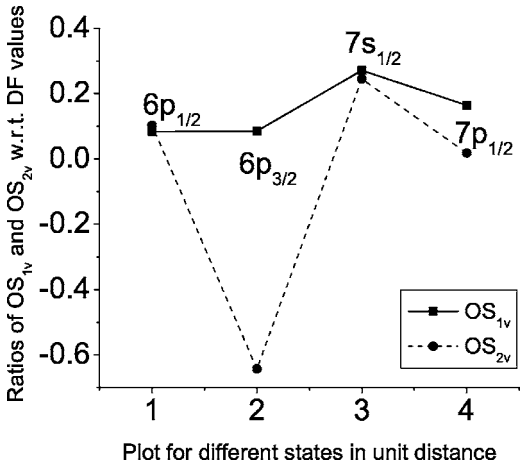

FIG. 2. The ratios of pair-correlation and core-polarization effects with respect to the DF values.

RCC theory can yield accurate results for properties that are sensitive to the nuclear region. Indeed, this has important implications for Tl [7], which like Pb^+ is a heavy atomic system with strongly interacting configurations and is one of the leading candidates for the study of parity nonconservation due to neutral weak currents [22,23]. It also has an important bearing on the electric dipole moment of Tl, which currently provides the best limit for the electron electric dipole moment [24] and would therefore be of interest to particle physicists. This work and our previous work [16] suggest that an accurate calculation of the electric dipole parity non-conserving amplitude for the $6p_{1/2} \rightarrow 6p_{3/2}$ transition in Pb^+ is possible. If an accurate parity nonconservation experiment corresponding to this transition (wavelength=7100 Å [10]) can be performed, then this ion could be a good candidate for testing the Standard Model of particle physics.

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