Application of Relativistic Coupled-cluster Theory to Heavy Atomic Systems with Strongly Interacting Configurations: *Hyperfine Interactions in $^{207}Pb^+$*

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This work presents a first time accurate calculation of the magnetic dipole hyperfine structure constants for the ground state and some low-lying excited states of Pb+. By comparing different levels of approximation with experimental results, we demonstrate the importance of correlation effects which reach beyond lower order relativistic many body perturbation theory. Employing relativistic coupled-cluster theory we obtain a quantitative understanding of the core-polarization and correlation effects inherent in this system and observe completely different trends compared to Ba^+.

Coupled-cluster theory has been used to study a wide range of many-body systems[1]. Although the non-relativistic version of this theory has been very successfully applied to a variety of light atoms and molecules[2], its extension to the relativistic regime is rather recent[3, 4]. 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[5, 6]. The magnetic dipole hyperfine constants have been measured for the $6p^2P_{1/2}$ and $6p^2P_{3/2}$ states of this ion[7] 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 non-linear RCC in the singles and doubles approximation with partial triples added in some cases has yielded results to an accuracy of about one percent for atoms and ions with a single s valence electron [8, 9, 10]. 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

$$A = \mu_N[\frac{\mu_I}{I}]\frac{\langle J||T^{(1)}||J\rangle}{\sqrt{J(J+1)(2J+1)}} \qquad (0.1)$$

with μ_N being the nuclear magnetic moment and $[\frac{\mu_I}{I}]$ the Lande's nuclear g-factor (g_I). $T^{(1)}$ can be written as [11]

$$T^{(1)} = \sum_q t_q^{(1)} = \sum_{qj} -ie\sqrt{8\pi/3}r_j^{-2}\alpha_j \cdot \mathbf{Y}_{10}^{(q)} \quad (0.2)$$

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 in to obtain the atomic wavefunctions. As pointed out in our earlier work [12] coupled-cluster theory is equivalent to all order many-body perturbation theory (MBPT). In the open-shell coupled-cluster theory [13, 14] the many-body wavefunction for a system with single valence electron can be written as

$$|\Psi_v\rangle = e^T\{1 + S_v\}a_v^\dagger|\Phi_0\rangle , \qquad (0.3)$$

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 excitation operators respectively. In this work both T- and S_v- operators are truncated beyond double excitations and triple excitations are added on the leading order MBPT level.

Explicitly, the T- operator is defined as

$$T = T_1 + T_2$$
$$= \sum_{a,p} a_p^\dagger a_a t_a^p + \frac{1}{2}\sum_{ab,pq} a_p^\dagger a_q^\dagger a_b a_a t_{ab}^{pq} \qquad (0.4)$$

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	$\mathbf{s}_{1/2}$	$\mathbf{p}_{1/2}$	$\mathbf{p}_{3/2}$	$\mathbf{d}_{3/2}$	$\mathbf{d}_{5/2}$	$\mathbf{f}_{5/2}$	$\mathbf{f}_{7/2}$	$\mathbf{g}_{7/2}$	$\mathbf{g}_{9/2}$
	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 I: Description of total number of basis functions, active holes and active particles involved in this calculation

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

$$S_v = S_{1v} + S_{2v}$$
$$= \sum_{p \neq v} a_p^\dagger a_v s_v^p + \frac{1}{2} \sum_{a,pq} a_p^\dagger a_q^\dagger a_a a_v s_{va}^{pq} \qquad (0.5)$$

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

In coupled-cluster theory the expectation value of any operator can be expressed as [9]

$$< O > = \frac{< \Psi_v|O|\Psi_v >}{< \Psi_v|\Psi_v >}$$
$$= \frac{< \Phi_v|\{1+S_v^\dagger\}e^{T^\dagger}Oe^T\{1+S_v\}|\Phi_v >}{< \Phi_v|\{1+S_v^\dagger\}e^{T^\dagger}e^T\{1+S_v\}|\Phi_v >} (0.6)$$

The above expression was applied to compute the hyperfine structure constant 'A' as given in eqn. (0.1).

The orbitals used in the present work were constructed as linear combinations of Gaussian type orbitals(GTOs) of the form [16]

$$F_{i,k}(r) = r^k.e^{-\alpha_i r^2} \qquad (0.7)$$

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

$$\alpha_i = \alpha_0 \beta^{i-1} \qquad (0.8)$$

was used. The occupied orbitals are the DF single particle states for closed-shell Pb^{++}. The virtual V^{N-1} orbitals [17, 18] 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

$$\rho = \frac{\rho_0}{1 + e^{(r-c)/a}} \qquad (0.9)$$

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 which the nuclear charge
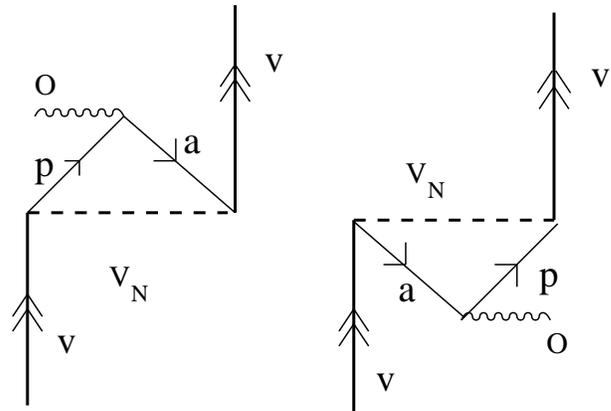

FIG. 1: Goldstone diagrams representing core-polarization in MBPT

States	DF approximation	Experiment [6]
$6p_{1/2}$	11513.5	13000
$6p_{3/2}$	918.3	583(21)
$7s_{1/2}$	7822.9	-
$7p_{1/2}$	1983.1	-

TABLE II: Dirac-Fock and Experimental results for magnetic dipole hyperfine structure constants of Pb^+ in MHz

density falls from near one to near zero The number of basis functions used for generating the occupied and virtual orbitals are given in table I. The active virtual ('particle') and core ('hole') electrons considered for the coupled-cluster calculations are also displayed. The upper energy limits above which the virtual orbitals were truncated during the RCC computation are given in atomic units. We have chosen α_0 as 0.00825 and β as 2.73 for all the symmetries for the generation of the GTO's.

In table II we present the results for the hyperfine constants using the DF approximation 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

Lowest order MBPT terms	$6p_{1/2}$ state	$7p_{1/2}$ state	$6p_{3/2}$ state	$7s_{1/2}$ state
O(DF)	11513.5	1983.1	918.3	7822.9
RMBPT(2)	15722.8	2578.4	302.9	12663.9
core-pol.	1506.2	82.1	-814.6	1624.21
pair-corr.	2297.4	359.6	203.6	3012.7

TABLE III: Second order MBPT results for Pb$^+$ hyperfine structure constants in MHz (second row) and the dominating contributions (third and fourth row) as shown in fig.1 .

Virtual orbital	Core orbital	RMBPT(2)	RCCT
$7s_{1/2}$	$6s_{1/2}$	-190.88	-128.28
$8s_{1/2}$	$6s_{1/2}$	-51.16	-35.99
$9s_{1/2}$	$6s_{1/2}$	-169.96	-123.44
$10s_{1/2}$	$6s_{1/2}$	-468.88	-369.62
$11s_{1/2}$	$6s_{1/2}$	-90.62	-73.46

TABLE IV: Contributions of the $6s_{1/2}$ core electron (in MHz) to the core-polarization effect using the RMBPT(2) approximation (third column) and RCC theory (forth column)

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 based on second order relativistic many-body perturbation theory (RMBPT(2)) which are given in table III. Here the

Terms	$6p_{1/2}$ state	$6p_{3/2}$ state	$7s_{1/2}$ state	$7p_{1/2}$ state
O	11513.5	918.3	7822.9	1983.1
$O - \bar{O}$	665.3	-43.7	983.3	85.4
$\bar{O}S_{1v} + cc$	952.2	78.4	2122.6	326.6
$\bar{O}S_{2v} + cc$	1188.2	-591.0	1916.8	35.6
$S_{1v}^{\dagger}\bar{O}S_{1v}$	21.0	1.6	164.6	14.1
$S_{1v}^{\dagger}\bar{O}S_{2v} + cc$	22.2	0.6	180.2	19.2
$S_{2v}^{\dagger}\bar{O}S_{2v} + cc$	149.6	194.61	298.8	18.7

Important effective two-body terms of $\bar{O}$

$S_{2v}^{\dagger}OT_1 + cc$	-20.2	2.0	14.6	-0.76
$S_{2v}^{\dagger}OT_2 + cc$	-160.2	-12.6	-135.4	-21.64
Norm.	-88.5	-6.7	-181.8	-22.98
Total	12903.7	623.2	11158.6	2263.5
Experiment	13000	583(21)		

TABLE V: Contribtions of different coupled-cluster terms to the Pb$^+$ hyperfine stucture constant. cc stands for the complex conjugate part of the corresponding terms
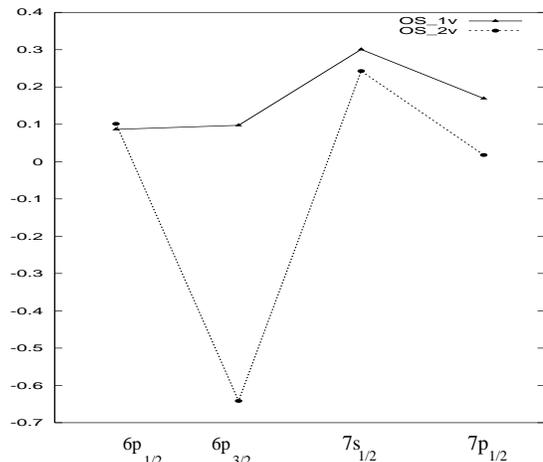

FIG. 2: The ratios of pair-correlation and core-polarization effects w.r.t. the DF values

dominant contributions to RMBPT(2) as shown in Fig. 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. In table IV we give the significant contributions to the core polarization which arises from the interaction of the outermost core 6s and the valence $6p_{3/2}$ electrons (third column). 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 tremendous 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 V. Again, the 'bare' operator O represents the DF approximation, i.e. excluding any correlation effects. Several important correlation contributions for our RCC calculations are also presented in table V. $\bar{O} = e^{T^\dagger}Oe^T$ denotes the 'dressed' operator containing the contributions of the closed-shell cluster amplitudes in Eq. (0.6). 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 V leads to significant improvements in our calculated values of the hyperfine constants of the $6p_{1/2}$ and $6p_{3/2}$ states. The sub one percent (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 level of RMBPT(2) is 48%. It is interesting to note from table IV (fourth column) that the core-polarization contributions in RCC

theory follow the same trend as in RMBPT(2).

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^+ [9], 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 strength of RCC theory has been exploited to obtain for the first time a quantitative understanding of the interplay of relativistic and correlation effects in the magnetic dipole hyperfine constants for Pb^+. It has been demonstrated that the results of the DF and RMBPT(2) approximations differ substantially from the measured values of the hyperfine constants. However, the inclusion of single, double and a subset of triple 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 RCC theory can yield accurate results for properties that are sensitive to the nuclear region. Indeed, this has important implications for Tl, which like Pb^+ is a heavy atomic system with strongly interacing configurations and is one of the leading candidates for the study of parity nonconservation due to neutral weak currents [4, 19, 20].

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