PHYSICAL REVIEW A VOLUME 44, NUMBER 1 1 JULY 1991

Theory of hyperfine interactions in positive ions isoelectronic with the noble-metal atoms

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(Received 14 January 1991)

The relativistic linked-cluster many-body perturbation theory has been applied to calculate the hyperfine fields in the Zn^+, Cd^+, and Hg^+ ions. We calculate field strengths of 451±9, 795±15, and 2642±63 T, respectively, values in good agreement with experiment for Cd^+, and in excellent agreement for Hg^+. No experimental data are available for the Zn^+ system. We will discuss the contributions to these total fields coming from the valence, one-electron perturbation, and many-body correlation mechanisms, and compare these contributions with those calculated in the alkali-metal atom and alkaline-earth ion systems that also have a single electron outside closed shells. We will also discuss the importance of third- and higher-order correlation contributions, which are rather large in these systems.

I. INTRODUCTION

An understanding of the hyperfine interaction in the Zn^+, Cd^+, and Hg^+ ions is important for several reasons. One of these is the fact that the analogous alkali-metal atoms and alkaline-earth ions have already been studied [1] in detail, and it would be interesting to make comparisons between these systems. The alkaline-earth ions consist of a single electron orbiting outside a compact system of rare-gas ion-type closed shells, while the Zn^+, Cd^+, and Hg^+ systems possess an additional *d* shell lying between the valence electron and the other core electrons. It would be interesting to know what effect these intervening electrons have on the hyperfine interactions of these otherwise similar systems. Intuitively, one might expect that the systems under study in this work might display a smaller core polarization contribution than the corresponding alkali-metal atoms and alkaline-earth ions because the intervening *d* shells would tend to insulate the core electrons from the perturbing valence electron. One might also anticipate a larger contribution from correlation mechanisms due to the presence of these easily deformed *d* shells. Additionally, one might expect a significant contribution to the hyperfine field to come from third- and higher-order correlation mechanisms, since the interaction between the valence electron and the outermost *d*-shell electrons is expected to be strong. It would also be interesting to note the effect of the extra *d*-shell electrons on the trends observed in individual perturbation mechanisms as one proceeds from Zn^+ down to Hg^+. The Hg^+ ion possesses an additional *f* shell which may produce a significant contribution.

Finally, experimental data are available for the hyperfine fields in the Cd^+ and Hg^+ ions [2,3], and the accuracy of our procedure may be checked by comparison with these results. We hope that our calculation will stimulate an experimental study of the Zn^+ ions, and also that calculations of the hyperfine interactions in these ions might be carried out by others using different procedures [4–7], as we believe that comparison between the results of different procedures leads to better understanding of all of them.

II. PROCEDURE

The relativistic linked-cluster many-body perturbation theory (RLCMBPT) procedure we use is one of the oldest and best tested [8,9]. As it has been described extensively in previous works, we will give only a brief summary of those points pertinent to the systems at hand. The atomic basis states are generated by a relativistic Hartree-Fock procedure [9]. For the core states the V^N potential is used. The excited states are generated using the V^{N-1} potential obtained from the (frozen) V^N core states mentioned above, but with the effect of the valence electron excluded [9] from the potential. These V^{N-1} excited states are more physically meaningful than V^N excited states would be since, for a neutral atom, the V^{N-1} potential resembles that of a single positive point charge at large distances, just as the actual potential experienced by an electron on the atom does, while the V^N potential resembles that of an electrically neutral system. For a singly ionized system, as is the case for the systems we are studying here, the V^{N-1} potential leads, at large distances, to the potential due to a double positive charge at the nuclear site, while the V^N potential leads to the potential due to a single positive charge. In both cases we use a restricted Hartree-Fock potential—that is, we assume that all the electrons in a given shell have the same radial wave function. We generate bound states [9] with principal quantum number up to $N=12$, and 15 continuum states with energies corresponding to the mesh points of a 15-point Gauss-Laguerre quadrature formula. The nucleus is taken to be a uniformly charged sphere of radius $(1.2)A^{1/3}$ fermi, as the volume distribution of the nu-

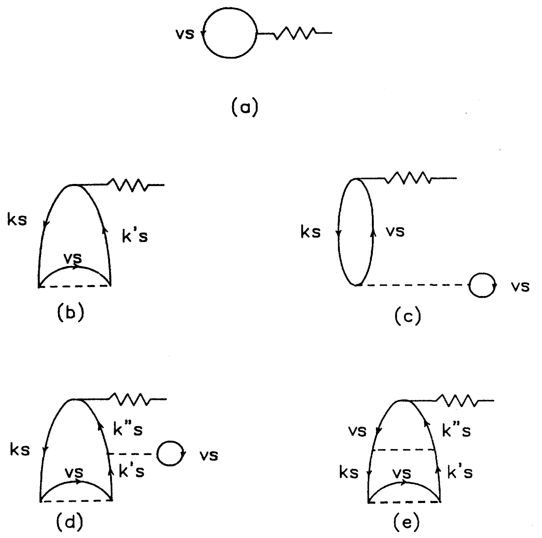

FIG. 1. Zero-order and important first- and higher-order one-electron diagrams. In all the diagrams (a)–(e) the *vs* refer to the occupied valence *s* state, except in (e) where the particle state *vs* refers to the unoccupied down-spin valence orbital. The *ks* refer to core states and the *k's* and *k"s* to excited or particle states.

clear charge has been shown in previous works [10] to have a significant effect on the contributions to the hyperfine field, especially for the heavier atoms and ions. The effect of the spatial distribution of the nuclear magnetic moment may also be significant for the heavier atoms [11]. We estimate the magnitude of this distributed-nuclear-moment (DNM) effect using the method due to Kopfermann [12]. Finally, the Hamiltonian we use ignores the effect of the Breit interaction and other radiative effects [13] since we have seen in previous works that these interactions are insignificant in effect on the hyperfine interaction in the type of systems under study here, where we have a single valence electron orbiting outside a system of closed shells.

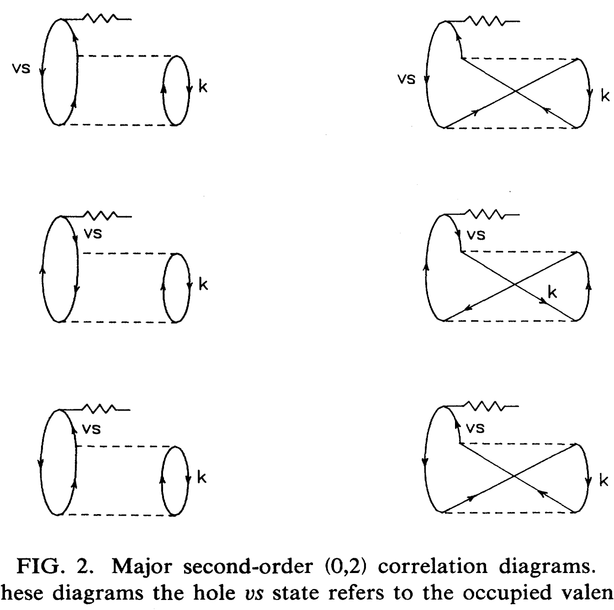

FIG. 2. Major second-order (0,2) correlation diagrams. In these diagrams the hole *vs* state refers to the occupied valence state while the particle *vs* state refers to the unoccupied down-spin valence orbital. The hole states *k* refer to the outermost *s*, *p*, *d*, and *f* core states.

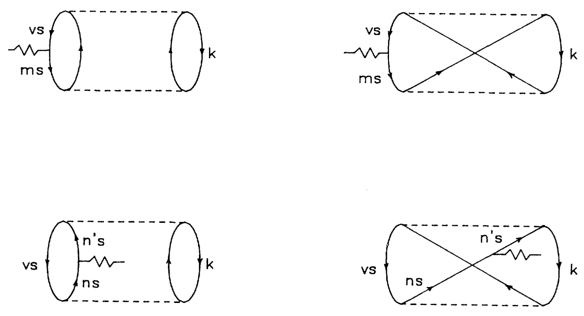

FIG. 3. Second-order (1,1) correlation diagrams. Here the hole states *k* refer to the outermost *s*, *p*, *d*, and *f* core states. The hole state *ms* refers to the outermost core *s* state, while *ns* and *n's* are excited *s* states.

The Hartree-Fock calculation alone does not give good agreement with experiment. We therefore use the RLCMBPT technique [9] to improve upon the Hartree-Fock results. One of the major advantages of this method is the fact that the individual terms in the perturbation series may be easily expressed [14] as diagrams and associated with specific physical processes. The major diagrams we have evaluated are given in Figs. 1 through 4. Figure 1(a) is the diagrammatic representation of the zero-order Hartree-Fock result. Only the unpaired valence electron contributes. The exchange core polarization (ECP) effect is represented by Fig. 1(b), while Fig. 1(c), a phase-space diagram associated with Fig. 1(b), arises because the valence *s* shell is only half-filled, which means that it is possible for a core electron to be excited into the available empty state in the valence *s* shell. Such an excitation will not be canceled out because a similar

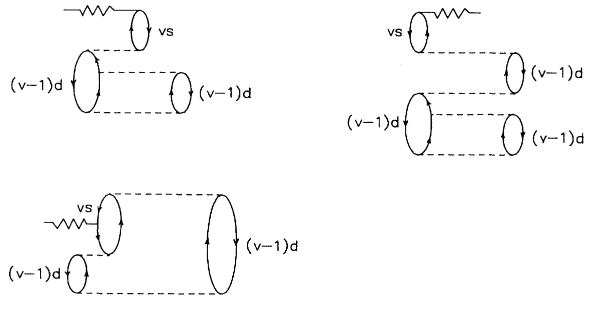

FIG. 4. Selected third- and fourth-order correlation diagrams.

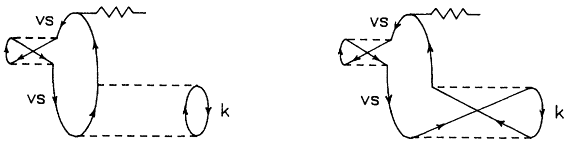

FIG. 5. Diagrams involving renormalization corrections to (0,2) diagrams.

TABLE I. Breakdown of the contributions to the hyperfine fields (in tesla) in Zn^+, Cd^+, and Hg^+ from various one-electron and many-body mechanisms.

	Zn^+	Cd^+	Hg^+
Valence	353.5	647.5	2291.5
ECP+ Phase Space	39.5	69.3	214.8
EVP+ Consistency	4.3	3.1	19.5
Second-order correlation	54.1	88.2	176.8
Higher-order correlation	-3.8	-12.6	-60.4
Total	447.6	795.5	2642.2
	±10.6	±19.4	±68.7
Experiment		826.1[a]	2626.1[b]
		±0.8	

[a] Reference [2].

[b] Reference [3]. This value has been rounded off to the same number of digits that we give for our final result.

excitation into the already occupied state cannot occur. Figures 1(d) and 1(e) are typical exclusion principle violating (EPV) and consistency diagrams, respectively. Figure 2 shows the (0,2) correlation diagrams, while Fig. 3 shows the (1,1) correlation diagrams. The diagrams in Figs. 2 and 3 involve the simultaneous excitations of two electrons due to the Coulomb interaction between them, and thus represent true many-body effects, while the diagrams in Fig. 1 are essentially one-electron diagrams which correct for the use of a restricted Hartree-Fock potential.

Figure 4 shows some of the higher-order diagrams we have evaluated. A complete investigation of orders higher than 2 is not possible because of the large number of diagrams involved, so we have limited our calculation to all diagrams which represent the effects one expects to be large—specifically, the effect on the valence electron of the change in the potential caused by correlation between the outermost *d*-shell electrons. This *d* shell is rather deformable, so that one might suspect that strong intrashell correlation will significantly distort the structure of this shell. This would, in turn, alter the potential seen by the valence electron, thereby changing the valence wave function enough to produce a significant alteration of the hyperfine field. Fig. 4 diagrams illustrate this effect. Finally, the renormalization diagrams of Fig. 5 have been evaluated by altering the energy denominators of the diagrams of Fig. 2. These diagrams correct for the difference between the Hartree-Fock eigenvalues used in calculating the diagrams and the true energies in the correlated system.

The rules for deriving the mathematical expressions represented by these diagrams have been given elsewhere [9]. We have evaluated these expressions for multipole components of the $1/r_{12}$ operator associated with the electron-electron interaction up to and including $l=4$, which is found to give good convergence.

III. RESULTS AND DISCUSSION

The primary results of our calculations of the hyperfine fields, in tesla, are shown in Table I, along with the available experimental results. All the values given in this and later tables have been reduced by the amount given by Kopfermann's formula [12] to estimate the magnitude of the DNM effect [11]. The first line gives the zero-order valence contribution for each ion. The second gives the sum of the first-order ECP and phase-space diagrams [9,14] of Figs. 1(b) and 1(c), while the third gives the sum of the EPV and consistency second-order one-electron diagrams [9, 14] of the type shown in Figs. 1(d) and 1(e). The second and third lines are grouped together because they both represent one-electron contributions to the hyperfine field. The fourth line gives the sum of the (0,2) and (1,1) correlation diagrams of Figs. 2 and 3, and the fifth gives the total of all the higher-order correlation diagrams of the types shown in Figs. 4 and 5. As these two lines both represent many-body effects, they are grouped together. The next line gives the sum of all mechanisms we have calculated, and the last line gives the experimentally observed value for those systems where they are available [2, 3]. Perhaps the most striking feature of Table I is found in the results for the higher-order correlation entries. They are significantly more important than in the case of other systems with single valence electrons like the alkali-metal atoms [15], ranging in values from 2–3 % of the final result in going from Hg^+ to Zn^+. This fact, along with the fact that a complete calculation of higher-order effects involves too many diagrams to make it manageable at present, makes an estimation of our confidence limits more difficult than in other systems. There is a substantial number of higher-order diagrams and significant cancellation among the high-order diagrams, so the estimation of the high-order correlation contribution can have a substantial margin of error. We believe that the true value of the higher-order correlation effects may differ from the quoted value of 2–3 % by more than one-half of this value. Other sources of error, such as the omission of the correlation diagrams with multipole component greater than $l=4$, and normal computational error, are not expected to lead to an error of more than 1% of the valence contribution. We therefore quote a confidence limit for our calculation of 3% of the valence contribution. The calculated net hyperfine constant for the Hg^+ ion is in excellent agreement with experiment [3], probably because the total correlation contribution, the major source of error in the calculation, is smaller in comparison to the valence contribution in the other two cases, the second-order correlation contribution being only about 8% of the valence contribution for Hg^+, in comparison to the 15% and 14% for Zn^+ and Cd^+, respectively. Figure 6 displays this trend graphically, along with the trend of the ratio of the net ECP (total one-electron contribution of order greater than zero) contributions to the valence contributions. A similar rapid decrease in the ratio of the correlation contribution to the valence contribution was observed at the heavier end in both the alkali-metal atoms and the alkaline-earth ions, and is believed to result from the competition between the increasing deformability of the valence state and its increasing distance from the core electrons as one goes down the series [15]. Our result for the Cd^+ ion is in slightly lesser agreement with the experimental results as compared to Hg^+, being about 4% lower than the experimental result [2], which, as a result of this, lies a little outside the confidence limit of 3% we have estimated for our calculation. There is no experimental result available for the Zn^+ ion. It would be interesting to have such a result to compare with our calculation, and we hope that one will become available soon.

We next analyze the one-electron perturbation and correlation contributions in somewhat more detail. Table II gives the contribution of each core s shell to the ECP plus phase-space sum. As expected [15], it is the outermost s shell which gives the greatest contribution because it is in closer proximity to the polarizing valence electron as compared to other s shells and hence experiences a greater exchange interaction with the valence electron. The deeper s shells do not give an insignificant contribution, but the sum of the contributions of all of them is significantly smaller than that of the outermost s shell in all three cases. The ratios of the net ECP contributions to the valence contributions are about 12%, 11%, and 10% for Zn^+, Cd^+, and Hg^+, respectively. This is shown graphically in Fig. 6. These ratios are considerably smaller than the corresponding ratios in both [1, 16] the alkali-metal atoms and the alkaline-earth ions (the ratio is in the region of about 20% for the alkali-metals), although the trend of a slow decrease in the ratio as one goes down the series is qualitatively identical to the trends observed in the other series. This slow decrease results from the contraction of the core orbitals as the nuclear charge increases, which results in both a less deformable core and a smaller exchange interaction with the valence electron, which has expanded outward because of the greater shielding of the nucleus. The smaller magnitudes of the ratios in the current systems are almost certainly a result of the shielding effect of the intervening d shells. These shells separate the valence electrons and the core s shells so that the core electrons do not experience as great an exchange interaction with the valence electron as was the case for the alkali-metal atoms and the alkaline-earth ions. A similar marked decrease in the ratio of the ECP and valence contribution was found [17] in going from the lithium atom, which did not have a p shell separating the valence electron and the outermost core s shell (there is only a single core s shell, 1s, in lithium), to other alkalis metals which did have a p shell.

TABLE II. Breakdown of the contributions of individual core shells to the ECP and phase-space part of the hyperfine fields in Zn^+, Cd^+, and Hg^+. All values are in units of tesla.

	Zn^+	Cd^+	Hg^+
1s	5.89	5.08	6.17
2s	8.71	8.11	14.66
3s	24.90	14.20	21.76
4s		41.88	41.17
5s			131.07
Total	39.50	69.27	214.83

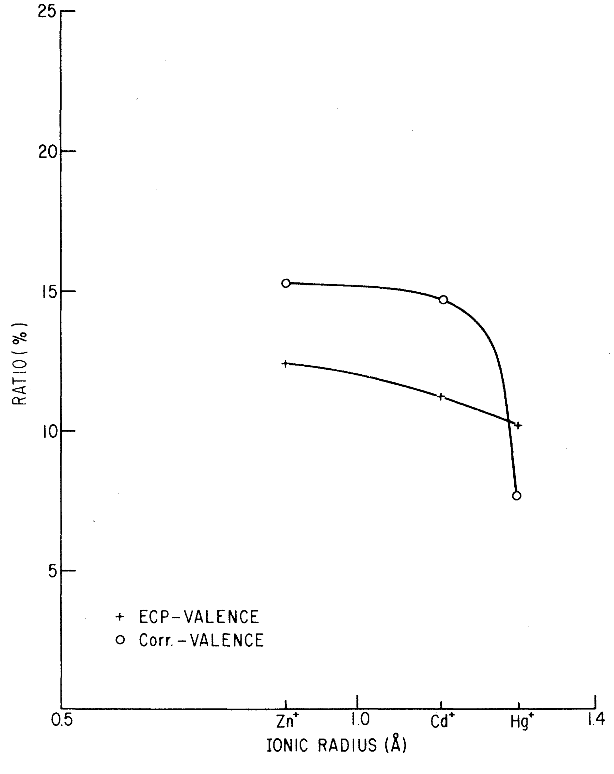

FIG. 6. Trends in the ratios of the ECP and correlation contributions over the series Zn^+, Cd^+, and Hg^+.

Table III gives the contribution to the total (0,2) correlation contribution from each of the core shells (the state k in Fig. 2) for which we have evaluated the corresponding diagrams. As expected [15], it is the outermost d shells, which are highly deformable themselves and in close proximity to the valence electron, which give the greatest contribution in each case, followed by the outermost p shell and the outermost s shell in Zn^+ and Cd^+. The Hg^+ system also has an f shell which gives a contribution larger than the s shell's but smaller than that of

TABLE III. Contributions of various core shells (in tesla) to the total (0,2) correlation contribution to the hyperfine fields in Zn^+, Cd^+, and Hg^+.

	Zn^+	Cd^+	Hg^+
$(v-1)s$	0.95	2.42	4.00
$(v-1)p$	5.35	9.74	53.63
$(v-1)d$	48.43	103.68	205.47
$(v-2)f$			32.53

the p shell. The trend of the ratio of the total second-order correlation contribution to the valence contribution has already been discussed. The magnitudes of the ratios, however, are smaller than those observed in the alkali-metal atoms and alkaline-earth ions, indicating that the contraction of the orbitals as the nuclear charge increases overwhelms the increased shielding of the nucleus by the core electrons as one goes across the periodic table, resulting in a more tightly bound system that displays less correlation.

In summary, we have calculated the hyperfine fields in the Zn^+, Cd^+, and Hg^+ systems and have obtained excellent agreement with the experimental results in the Hg^+ system, and good results for the Cd^+ system. There are no experimental data for the Zn^+ system, and hence no comparison is possible. We have seen that, although the total correlation contribution to the hyperfine field in these systems is smaller than that of the corresponding alkali-metal atoms and alkaline-earth ions, it is necessary to go to high orders in perturbation theory to obtain accurate results, since the high-order correlation contribution is rather important, on the order of a few percent of the total field. Finally, we hope that this paper will encourage other investigators to make similar calculations using different methods for these systems, so that comparisons may be made between the different techniques [4-7], and we hope that an experimental determination of the hyperfine field in the Zn^+ ion will be available in the near future, so that it could be compared to our theoretical result.

ACKNOWLEDGMENTS

The authors are grateful to Processor R. Neugart of the University of Mainz in Germany for valuable discussions about this work. This research was conducted using the Cornell National Supercomputing Facility, a resource of the Center for Theory and Simulation in Science and Engineering at Cornell University, which is funded in part by the National Science Foundation, New York State, and the IBM Corporation.

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