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Angular and self-consistency contributions to the Sternheimer hexadecapole antishielding factor η_∞

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Linked-cluster many-body perturbation theory has been used to calculate the Sternheimer hexadecapole antishielding factor η_∞ in Pr^{3+}. This parameter is a measure of enhancement of a possible nuclear electric hexadecapole (16-pole) moment due to polarization of the core electrons in an atom or ion. Large and predominant contributions due to the angular mode of excitations neglected in earlier works have been found. Self-consistency contributions to η_∞ are found to be small (about 3%), similar to those in the quadrupole antishielding factor γ_∞. These contributions in the case of quadrupole polarizability α_q and the crystal-field shielding parameter σ_2 in Pr^{3+} were found to be larger (about 17% but of opposite sign in both cases).

I. INTRODUCTION

Nuclei with spin $I \geq 2$ can possess a nonvanishing nuclear electric hexadecapole moment which is several orders of magnitude smaller than the quadrupole moment. Experimentally it is very difficult to detect hexadecapole interactions, because their small size makes it very difficult to distinguish them from the much stronger effects of quadrupole interactions. Typical quadrupole energies lie in the range $1-100$ MHz, whereas hexadecapole energies are in the region of $1-100$ Hz. Such small interactions can only be detected in very favorable circumstances.[1] This explains why the literature of hexadecapole interaction is so scanty. Nevertheless, their existence is now confirmed and in a few cases they have been experimentally detected. One of the earliest claims to detect this interaction is due to Wang[2] followed by several other workers.[3] More recently, Dankwort *et al.*[4] have detected a nuclear hexadecapole interaction in the ground state of ^{165}Ho ($I = \frac{7}{2}$) using the atomic-beam magnetic-resonance method.

Even if the nuclear hexadecapole moments are small, their effects can be amplified considerably via an antishielding effect similar to that for the nuclear quadrupole moment. It was with this notion that Sternheimer[5,6] introduced the nuclear antishielding factor η_∞, the counterpart of the commonly known Sternheimer quadrupole antishielding factor γ_∞ in the case of hexadecapole interactions.

As the experimental efforts to detect hexadecapole interactions are still continuing, accurate calculations on η_∞ could prove to be a step forward in this direction. The purpose of the present calculation has been basically twofold. Firstly, to carry out a complete calculation for η_∞ including all possible mechanisms that might be anticipated to contribute. In previous calculations, angular contributions have altogether been omitted. Secondly, to study the role of self-consistency effects to this parameter. Self-consistency effects to various spectroscopic parameters have been calculated in the past and have been found varying in magnitudes and signs.[7] Therefore, it was also of considerable interest to calculate such contributions in the case of η_∞. We have chosen Pr^{3+} for the present calculations owing to the fact that self-consistency contributions to γ_∞, α_q (quadrupole polarizability), and σ_2 (crystal-field parameter) have already been calculated[8] by the same procedure employing the same basis set as in the present case. This choice will make the comparison more realistic.

In Sec. II we give a brief outline of the procedure. Results of the present calculation are given in Sec. III. Section IV gives the discussions and main conclusions of the present work.

II. PROCEDURE

A. Method of calculation

Linked-cluster many-body perturbation theory has been adopted for the present calculation. This

theory was developed by Goldstone[9] and is now commonly known as the Brueckner-Goldstone (BG) linked-cluster many-body perturbation theory (LCMBPT). It was first introduced to atomic physics problems by Kelly.[10]

A discrete basis set of occupied as well as excited wave functions was generated by confining the Pr^{3+} ion in an infinite potential well of suitable radius. The potential inside the spherical well is the Pr^{3+} Hartree-Fock-Slater potential, and at the boundary it is infinite. Because of the nature of the potential well continuum states are transferred to the excited bound-state spectrum. This model of generating one-electron wave functions has been successfully used in our previous many-body calculations[8] and its detailed characteristics are given by Ahmad and Newman.[11]

A modified version of the Herman and Skillman[12] Hartree-Fock-Slater program was used to generate the occupied orbitals and the self-consistent HFS potential for Pr^{3+}. In line with the suggestion made by Lenander[13] and Newman and Taylor,[14] the Slater exchange term of the potential was multiplied by a correction factor of 0.8. Lenander has shown that this correction factor produces solutions for Pr^{3+} whose matrix elements agree well with those of Freeman and Watson's[15] Hartree-Fock solutions. Excited states were generated under the boundary conditions which are equivalent to placing the ion at the center of an infinite spherical potential barrier of radius R. It has been demonstrated[11] that the calculated physical quantities are always independent of the choice of the size of the potential well. However, from the computational point of view, it is found that the larger the well radius the greater is the effort required in determining the states because the spacing between excited-state energies decreases with increasing radius and the orbitals become more sensitive to the precise energy values. It is also because of this that, for a larger well, convergence of perturbation series in terms of the sum over the excited states is slower compared with that of a smaller well. For the present calculation the adopted value was $R = 11.621$ au. (This value for the potential-well radius may seem rather odd but is taken because it occurs at a grid point in the integration mesh.)

B. Diagrams and expressions

The lowest-order and the major self-consistency diagrams contributing to η_∞ are given by Figs. 1 and 2, respectively. The physical mechanisms represented by these diagrams and other details have been extensively discussed earlier.[7] Algebraic derivations corresponding to similar diagrams are also available in the literature.[8] For the present purposes, therefore, we consider it sufficient to give the final algebraic expressions corresponding to these diagrams. Thus for Fig. 1 one can write

$$\eta_\infty(1) \equiv -\frac{4}{[k]} \sum_{nl,n'l'} [l,l'] \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \frac{\langle nl \,|\, r^{-k-1} \,|\, n'l' \rangle \langle n'l' \,|\, r^k \,|\, nl \rangle}{E(nl \rightarrow n'l')} \,. \tag{1}$$

Where the notation $[a]$ stands for $2a+1$ and the $3-j$ symbol is presented in its standard form. The minus sign appearing in this expression ensures that the sign of the calculated factor is consistent with the definition—that a negative value corresponds to antishielding while a positive value corresponds to shielding. The multiplicative factor 4 takes into account the summation over spin and the diagram multiplicity.[7]

Similarly, the diagrams of Fig. 2 correspond to the following expressions:

$$\eta_\infty(2a) \equiv -\frac{16}{[k]^2} \sum_{l_1 l_1' l_2 l_2'} [l_1,l_1',l_2,l_2'] \begin{pmatrix} l_2 & k & l_2' \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} l_1' & k & l_1 \\ 0 & 0 & 0 \end{pmatrix}^2$$

$$\times \sum_{n_1 n_1' n_2 n_2'} \frac{\langle n_2 l_2 \,|\, r^{-k-1} \,|\, n_2' l_2' \rangle R^{(k)}(n_1 l_1 n_2' l_2' n_1' l_1' n_2 l_2) \langle n_1' l_1' \,|\, r^k \,|\, n_1 l_1 \rangle}{E(n_1 l_1 \rightarrow n_1' l_1') E(n_2 l_2 \rightarrow n_2' l_2')} \,, \tag{2}$$

$$\eta_\infty(2b)\equiv\frac{4}{[k]}\sum_{Ll_1l_1'l_2l_2'}[l_1,l_1',l_2,l_2']\begin{pmatrix}l_2 & k & l_2'\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_2' & L & l_1'\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_1 & L & l_2\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_1' & k & l_1\\ 0 & 0 & 0\end{pmatrix}$$
$$\times\begin{Bmatrix}l_1 & k & l_1'\\ l_2' & L & l_2\end{Bmatrix}\sum_{n_1n_1'n_2n_2'}\frac{\langle n_2l_2\,|\,r^{-k-1}\,|\,n_2'l_2'\rangle R^{(L)}(n_2'l_2'n_1l_1n_1'l_1'n_2l_2)\langle n_1'l_1'\,|\,r^k\,|\,n_1l_1\rangle}{E(n_1l_1\rightarrow n_1'l_1')E(n_2l_2\rightarrow n_2'l_2')}, \tag{3}$$

$$\eta_\infty(2c)\equiv\frac{4}{[k]}\sum_{Ll_1l_1'l_2l_2'}[l_1,l_1',l_2,l_2']\begin{pmatrix}l_1 & k & l_1'\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_2 & k & l_2'\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_1 & L & l_2'\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_1' & L & l_2\\ 0 & 0 & 0\end{pmatrix}$$
$$\times\begin{Bmatrix}l_1' & k & l_1\\ l_2' & L & l_2\end{Bmatrix}\sum_{n_1n_1'n_2n_2'}\frac{R^{(L)}(n_1l_1n_2l_2n_2'l_2'n_1'l_1')\langle n_2'l_2'\,|\,r^{-k-1}\,|\,n_2l_2\rangle\langle n_1'l'\,|\,r^k\,|\,n_1l_1\rangle}{E(n_1l_1\rightarrow n_1'l_1')E(n_2l_2\rightarrow n_2'l_2')}, \tag{4}$$

where the standard notation for the $6j$ symbols has been used and L gives the multipolarity of the electron-electron interaction. $R^{(k)}$ is the conventional Slater radial integral.

III. RESULTS

A. Present calculations

The results of the present calculations for η_∞ in Pr^{3+} are presented in Tables I and II. Table I corresponds to the lowest-order (zero-order) contributions to η_∞ which are obtained by numerically evaluating expression (1). All possible combinations of n, l, and l' are included and the summation over the excited states is carried out up to $n'=30$. This choice is crucial in all the calculations employing a similar basis set. The upper limit of the basis set would be decided by the convergence required. Fairly good convergence is not necessarily always obtained, and therefore, there remains an uncertainty in estimating the contributions from the remaining higher excited states.

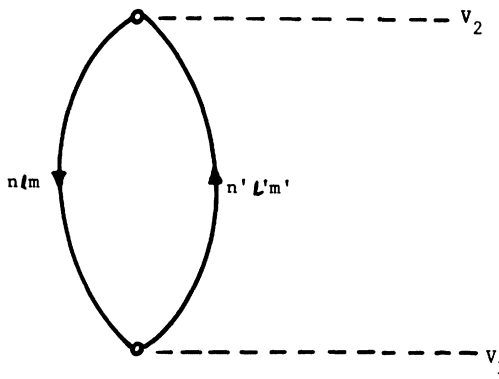

FIG. 1. Lowest-order contribution to η_∞. nlm and $n'l'm'$ represent the ground and excited states, respectively. V_1 and V_2 are perturbations representing the crystalline and nuclear multipole fields.

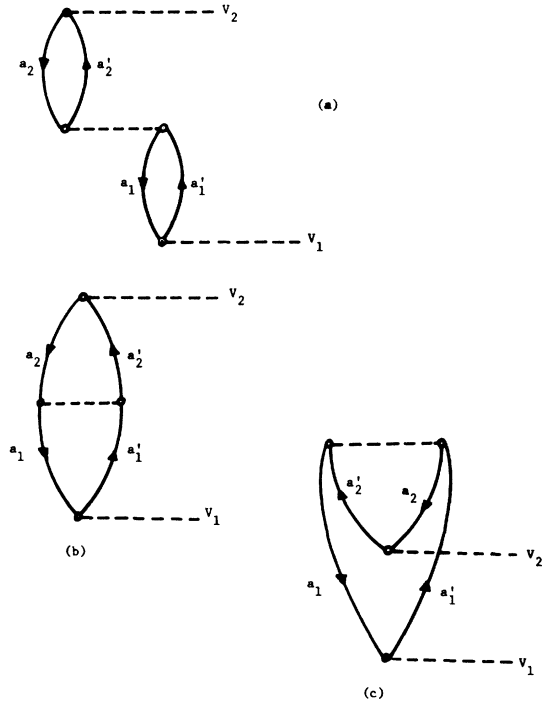

FIG. 2. Dominantly contributing self-consistency diagrams. Diagrams (b) and (c) are exchange diagrams of type (a). $a_i\equiv n_il_im_i$ and $a_i'\equiv n_i'l_i'm_i'$.

TABLE I. Lowest-order contributions to hexadecapole antishielding factor η_∞ in Pr^{3+}. Contributions smaller than 0.001 are omitted as they are negligible compared to the large magnitude of η_∞. Contributions for Cs^+ ion, which is isoelectronic with Pr^{3+} apart from the $4f$ shell, are given for comparison.

Perturbations	Contribution to η_∞	Cs^+ Sen and Narasimhan (Ref. 18)	Pr^{3+} Sen and Narasimhan (Ref. 18)
$3s \rightarrow g$	0.008		
$4s \rightarrow g$	0.028		
$5s \rightarrow g$	0.082		
$2p \rightarrow f$	0.021(0.003)[a]		
$3p \rightarrow f$	−0.854(−0.483)		
$4p \rightarrow f$	10.075(37.817)		
$5p \rightarrow f$	−1805.997(−2818.569)		
$3p \rightarrow h$	0.002		
$4p \rightarrow h$	0.043		
$5p \rightarrow h$	0.124		
$3d \rightarrow d$	−1.136	−11.018	
$4d \rightarrow d$	−624.842	−866.58	
$3d \rightarrow g$	0.045		
$4d \rightarrow g$	−0.124		
$3d \rightarrow i$	0.001		
$4d \rightarrow i$	0.054		
Total	−2422.470(−2781.232)	−877.59	−557.54

[a]Bracketed quantities are the $4f$ contributions.

For the present calculations, however, convergence has posed no problem. In fact, for the accuracy with which the results are presented here an upper limit of $n'=22$ could have been enough.

Self-consistency contributions to η_∞ were obtained by evaluating expressions (2)–(4) for $k=4$. Dominant contributions to this effect are presented in Table II. As before, summations over excited n' values up to 30 were taken.

B. Previous calculations of η_∞

Calculations of η_∞ were first carried out by Sternheimer[6,16] for Cu^+, Ag^+, and Hg^{2+}, all of which have configurations of completed shells; with nd ($n=3$, 4, and 5, respectively) being the outermost shell for all of them. Very large values of $\eta_\infty=-1200$, -8050, and $-63\,000$ were found in these ions. These values correspond to antishielding and arise from the radial mode of excitations $nd \rightarrow d$. In the case of Ag^+ and Hg^{2+}, where there are two d shells, major contribution ($>99\%$) came due to the outermost shell. Compared to γ_∞ values, the magnitudes of η_∞ are large suggesting that the detection of nuclear hexadecapole moments may be possible in favorable circumstances.

Further calculations by Sternheimer[17] suggested

TABLE II. Dominant self-consistency contributions to η_∞ in Pr^{3+} corresponding to the three appropriate diagrams of the type represented by Figs. 2(a), 2(b), and 2(c). Symbols $l_1,l_1';l_2,l_2'$ imply the summation over all the occupied values of n_1,n_2 and the excited n_1',n_2' values up to 30.

$l_1,l_1';l_2,l_2'$	Diagram type	L values	Contributions to η_∞
$p,f;p,f$	a	4	388.8
	b	2	−93.2
	c	2	−217.3
	c	4	−3.5
$d,d;d,d$	a	4	8.6
	b	0	−117.2
	b	2	−3.3
	b	4	−0.1
	c	0	−15.9
	c	2	−1.3
	c	4	−0.1
		Total	−54.5
	Others[a]		−19.5
		Net Total	−74.0

[a]Sum of other diagrams not shown in the figure.

similar values of η_∞ for other ions, except that the value of −670 obtained for Cs^+ is much smaller than the values for other ions. It should be remembered that this value like others arises from $nd \rightarrow d$ excitations, but the nd shell in Cs^+ is internal to the $5s$ and $5p$ shells. We will comment on this aspect later.

The most recent calculations for η_∞ in the literature are those by Sen and Narasimhan[18] who have employed Sternheimer's method and extended their calculations to a number of ions. Hartree-Fock-Slater ground-state wave functions have been used in these calculations. Sternheimer's values of −1200, −8050, −670, and −63 000 for Cu^+, Ag^+, Cs^+, and Hg^{2+} can be compared with these authors's respective values of −1471, −9580, −877, and −37 390. For the first three ions Sternheimer used Hartree-Fock wave functions while for Hg^{2+} he employed Hartree wave functions (without exchange). The reason for the rather very large difference in the two sets of η_∞ (Hg^{2+}) values can be attributed to this different choice of the ground-state wave functions. This clearly suggests that η_∞ values are highly sensitive to the quality of the wave function.

IV. DISCUSSIONS AND CONCLUSION

From the previous section it can be noted that for all the calculations of η_∞ available in the literature, no attempt has been made to calculate the η_∞ contribution due to the angular mode of excitations. Angular mode of excitation is characterized by one in which change of angular momentum is involved, i.e., an excitation of the type $l \rightarrow l \pm k$ where k represents the multipolarity of the interaction. In earlier calculations it has been assumed that η_∞ (angular) is very small ($\lesssim 1$). This assumption is derived from an argument due to Sternheimer[5] based on the Thomas-Fermi model, and previous results for γ_∞. Since the magnitude of η_∞ (radial) is very large, η_∞ (angular) has been neglected in these calculations and it has been assumed throughout that η_∞ (total) $=\eta_\infty$ (radial). Thus only d and f occupied orbitals are assumed to contribute because selection rules forbid radial contributions to η_∞ from the s and p shells.

In our calculation for Pr^{3+}, we have included both the radial and angular contributions and, as is evident from Table I, we arrive at a very different conclusion concerning their relative magnitudes.

η_∞ (angular) due mainly to $5p \rightarrow f$ excitation, is not only large but also predominates the η_∞ (total), as this contribution is approximately a factor of 3 larger than the radial contribution. In physical terms this result is not unexpected. The $5p$ shell, being the outermost shell in Pr^{3+}, is particularly susceptible to perturbation and therefore should contribute considerably to the relevant physical quantities. In fact, for almost all physical quantities like γ_∞, electric multipole polarizabilities, crystal-field parameters, etc., it has been found consistently that the $5p$ shell makes the largest contribution.[8] Therefore the present result is not unexpected. An unusual aspect of this angular contribution is, however, that it has the same sign as the radial contribution. This is because of the large contribution coming from the $4f$ shell (listed separately in Table I), which appears with the same sign as the radial contribution. Other nf $(n > 5)$ contributions have opposite signs as expected. The large $5p \rightarrow 4f$ contribution can be attributed to the near-degeneracy of the $5p$ and $4f$ levels in the Pr^{3+} ion.[19] This indicates that a similar order of magnitude for $5p \rightarrow f$ contributions can be expected for all the lanthanides, and perhaps also a substantial $6p \rightarrow f$ contribution in the case of actinides. In fact, in the light of the above observation we believe that except in the case where the outermost shell is a d or an f shell, η_∞ (angular) contributions may be large and therefore it is important to calculate them explicitly if any reliable estimate of η_∞ (total) is to be obtained.

This calculation shows that the self-consistency contribution to η_∞ is small (about 3% of the zero-order contribution and of the same sign), a situation very similar to that found in the case of γ_∞ in Pr^{3+}. This seems to be consistent with our expectations because the quantities γ_∞ and η_∞ are of the same physical nature except for the order of the multipolarities they represent. However, this is very different from the situation encountered in the case of α_q and σ_2 in Pr^{3+} where self-consistency contributions were found to be larger (about 17% of the lowest-order contributions, but of opposite signs in both cases). Thus one can conclude that the self-consistency effect cannot alter the zero-order values of η_∞ to any appreciable extent.

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