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# Hyperfine Structure Constants Calculated by Using Finite Basis Sets Constructed with B-splines\*

Wu Li-jin, LI Yong, GAO ke-lin

(Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, China)

**Abstract:** The effective-operator form of many-body theory is applied to the calculation of hyperfine structure. The zeroth order hyperfine constants are evaluated with Hartree-Fock wavefunction. The finite basis sets of Schrödinger's equation are constructed by using B-splines. With the finite basis sets, we have calculated the core polarization, and the correlation diagrams. The hyperfine constants of the  $s_{1/2}$ ,  $p_{1/2}$  and  $p_{3/2}$  states of  ${}^7\text{Li}$ ,  ${}^{23}\text{Na}$ ,  ${}^{39}\text{K}$ ,  ${}^{43}\text{Ca}^+$  as well as the  $d_{3/2}$  and  $d_{5/2}$  of  ${}^{43}\text{Ca}^+$  are evaluated.

**Key word:** hyperfine structure; B-splines; many-body perturbation

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## 1 Introduction

Narrow transition in laser-cooled trapped ions are applied to new optical frequency standards. Odd isotopes are particularly appealing as frequency standards because their half-integral nuclear spin leads to integer values of total angular momentum  $F$ , thereby making possible clock transitions between states with magnetic quantum number  $m=0$ . The transitions have no first-order Dc Zeeman shift and greatly suppressed broadening from residual AC magnetic fields<sup>[1]</sup>. Experimental studies of the new optical frequency standards make investigation of the hyperfine structure to be significant.

The effective operator form of many-body theory is developed and applied to calculate hyperfine interaction by Garpman et al<sup>[2]</sup> and Lindgren and Morrison<sup>[3]</sup>. Lindgren applied the many-body perturbation theory in the coupled-cluster formulation to perform the calculations on the  $2^2S$  and  $2^2P$  states of the lithium atom<sup>[4]</sup>. An important task of the perturbative calculation is to carry out summa-

tions (and/or integration) over all intermediate states. Lindgren used the single-particle function and the pair function by solving inhomogeneous one- and two-particle equation<sup>[3]</sup> instead of the summations (and/or integrations). However, in this work, we have explicitly constructed a complete set of virtual states with B-splines, which we will discuss in following section.

## 2 Calculation of the Hyperfine Constants

For single-electron systems outside the closed shells, the generalized hyperfine constants in non-relativistic case are

$$a = \begin{cases} \alpha^2 \frac{l(l+1)}{j(j+1)} \frac{\mu_I}{I} \langle r^{-3} \rangle_{nl} & l > 0 \\ \frac{2}{3} \alpha^2 \frac{\mu_I}{I} \left[ \frac{1}{r} P_{nl}(r) \right]_{r=0}^2 & l = 0, \end{cases} \quad (1)$$

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**Biography:** Wu lijin (1944-), male(汉族), Hubei Daye, Professor, Works on atomic excited state and quantum information.

$$b = \frac{2j-1}{2j+2} Q \langle r^{-3} \rangle_{nl}. \quad (2)$$

The effective hyperfine operator for the hyperfine interaction is<sup>[3]</sup>

$$\begin{cases} t^1 = \alpha^2 [1 \langle r^{-3} \rangle_l - \sqrt{10} (s C^2)^1 \langle r^{-3} \rangle_{s,d} + \\ \quad s \langle r^{-3} \rangle_c] \\ t^2 = -\frac{1}{2} C^2 \langle r^{-3} \rangle_q, \end{cases} \quad (3)$$

where  $\langle r^{-3} \rangle_l$ ,  $\langle r^{-3} \rangle_{s,d}$ ,  $\langle r^{-3} \rangle_c$  and  $\langle r^{-3} \rangle_q$  represent the radial integral of orbital, spin-dipole, contact and quadrupole terms, respectively. The matrix elements of the effective hyperfine operator can be evaluated by following expression:

$$\langle i | t_Q^{(\omega)K} | j \rangle = \langle i | t^{(\omega)K} || j \rangle F, \quad (4)$$

where

$$F = [(2j+1)(2j'+1)(2K+1)]^{1/2} \cdot \begin{Bmatrix} j & K & j' \\ -m & Q & m' \end{Bmatrix} \begin{Bmatrix} s & s' & k \\ l & l' & \lambda \\ j & j' & K \end{Bmatrix}, \quad (5)$$

$$\begin{aligned} \langle i || t^{(\omega)K} || j \rangle &= \langle s || s^k || s' \rangle \cdot \\ \langle l || v^k || l' \rangle \langle i | f_{(\omega)K} | j \rangle, \end{aligned} \quad (6)$$

the radial integral is

$$\langle i | f_{(\omega)K} | j \rangle = \int P_i(r) f_{(\omega)K}(r) P_j(r) dr.$$

## 2.1 Finite basis set

In order to evaluate second-order perturbational diagrams and third-order perturbational diagrams, we need a complete set of single-particle states. We can construct a complete finite basis set of Schrödinger's equation with B-splines. Spline algorithms for Hartree-Fock equation is discussed by Fischer *et al.*<sup>[5]</sup>.

The non-relativistic Hamiltonian is

$$H = -\frac{1}{2} \sum_{i=1}^N \left( \nabla_i^2 + \frac{2Z}{r_i} \right) + \sum_{i>j} \frac{1}{r_{ij}}. \quad (7)$$

The action is

$$S = \sum_a q_a I_a + \frac{1}{2} \sum_{abk} q_a q_b [c(abk) F^k(ab) + d(abk) G^k(ab)] - \sum_a q_a \lambda_{aa} N_{aa}, \quad (8)$$

where

$$I_a = \int_0^\infty P_a(r) \left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l_a(l_a+1)}{2r^2} - \frac{Z}{r} \right] P_a(r) dr,$$

$$F^k(ab) = \int_0^\infty P_a^2(r) \frac{1}{r} Y_k(bb, r) dr,$$

$$G^k(ab) = \int_0^\infty P_a(r) P_b(r) \frac{1}{r} Y_k(ab, r) dr,$$

$$Y_k(ab, r) = r \int_0^\infty \sum_{r' \leq r}^{r' \leq r} \frac{r'^k}{r^{k+1}} P_a(r') P_b(r') dr',$$

$$\begin{cases} c(abk) = \delta(k, 0) \\ d(abk) = -\frac{1}{2} \begin{Bmatrix} l_a & k & l_b \\ 0 & 0 & 0 \end{Bmatrix}^2, \end{cases}$$

$$N_{(a)} = \int_0^\infty P_a(r) P_b(r) dr.$$

We expand the radial function  $P_a(r)$  in terms of B-splines of order  $k$  as  $P_a(r) = \sum_{i=1}^N \omega_i^a B_{i,k}(r)$ . The boundary conditions  $P_a(0) = P_a(R) = 0$  can be imposed on the solution, we obtain  $\omega_1^a = \omega_N^a = 0$ . In terms of the variational principle, we can obtain the equation systems  $dS/d\omega_i = 0$ . These equations can be expressed in the form of a  $(N-2) \times (N-2)$  symmetric generalized eigenvalue equation

$$A\omega = \varepsilon B\omega. \quad (9)$$

## 2.2 Evaluation of the Polarization Diagrams and the Lowest-order Correlation

Following Lindgren<sup>[3]</sup>, the contribution of the core polarization to hyperfine interaction can be calculated to all orders:

$$\begin{aligned} \Delta_u^{(\omega)K} &= 2F \sum_{ar k} (2l+1) [(2l_r+1)(2l_a+1)]^{1/2} \cdot \\ &\quad \left[ (-1)^{l+l_a} 2\delta(\kappa, 0) \frac{\delta(\kappa, \lambda)}{2\lambda+1} \begin{Bmatrix} l & k & l \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} l_r & k & l_a \\ 0 & 0 & 0 \end{Bmatrix} R^k(mr, na) - \right. \end{aligned}$$

$$(-1)^{\lambda} \begin{Bmatrix} l & k & l_a \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} l_r & k & l \\ 0 & 0 & 0 \end{Bmatrix} \left\{ \begin{matrix} l & \lambda & l \\ l_r & k & l_a \end{matrix} \right\} R^k(mr, an) \Big] \overline{h}_a^r, \quad (10)$$

$$(\epsilon_a - \epsilon_r) \overline{h}_a^{r(N)} = \langle r \| t^{(\kappa)K} \| a \rangle + \sum_{b_s} [G_1 X^k(rb, as) - G_2 X^k(br, as)] \overline{h}_b^{(N-1)}, \quad (11)$$

where

$$\overline{h}_a^{r(0)} = \frac{\langle r \| t^{(\kappa)K} \| a \rangle}{\epsilon_a - \epsilon_r}, \quad (12)$$

$$G_1 = \frac{2\delta(\kappa, 0)\delta(\kappa, \lambda)}{2\lambda + 1}, \quad G_2 = (-1)^{\lambda} \left\{ \begin{matrix} l_a & \lambda & l_r \\ l_s & k & l_b \end{matrix} \right\}. \quad (13)$$

Following Lindgren, the diagrams involved at least one double excitation are called the lowest-order correlation, which are third-order hyperfine diagrams. There are 65 diagrams of this kind. The algebraic expression for one of these diagrams is

$$\begin{aligned} & a_m^+ a_n \sum_{nta} \frac{\langle m | t_Q^{(\kappa)K} | t \rangle \langle ta | r_{12}^{-1} | rs \rangle \langle rs | r_{12}^{-1} | na \rangle}{(\epsilon_m - \epsilon_t)(\epsilon_n + \epsilon_a - \epsilon_r - \epsilon_s)} \\ &= a_m^+ a_n 2F \sum_{ntak} \delta(l_t, l) \frac{(2l_r + 1)(2l_a + 1)(2l_s + 1)}{2k + 1} \begin{Bmatrix} l & k & l_r \\ 0 & 0 & 0 \end{Bmatrix}^2 \\ & \quad \begin{Bmatrix} l_a & k & l_s \\ 0 & 0 & 0 \end{Bmatrix}^2 \frac{\langle m | t^{(\kappa)K} | t \rangle R^k(ta, rs) R^k(rs, na)}{(\epsilon_m - \epsilon_t)(\epsilon_n + \epsilon_a - \epsilon_r - \epsilon_s)}, \end{aligned} \quad (14)$$

where  $F$  is a spin-angular factor,  $t_Q^{(\kappa)K}$  is hyperfine operator. From this expression, we can see that the sums run over the all virtual states of  $r$ ,  $s$  and  $t$  as well as core states of  $a$ . Two  $3j$  symbols  $\begin{Bmatrix} l & k & l_r \\ 0 & 0 & 0 \end{Bmatrix}$  and  $\begin{Bmatrix} l_a & k & l_s \\ 0 & 0 & 0 \end{Bmatrix}$  show out  $|l - l_r| \leq k \leq l + l_r$  and  $|l_a - l_s| \leq k \leq l_a + l_s$ , and  $0 \leq l_r, l_s < \infty, l_t = l$ . In above expression,  $l_m = l_n = l$  are the angular momentum for valence state. It is impossible to take  $l_r, l_s$  up to infinite. We can choose a finite value  $l_{max}$ , as maximum and let  $l_r, l_s \leq l_{max}$ . How can we choose  $l_{max}$ ? First we take a small positive floating number  $eps$  and search a  $l_{try}$  to make the absolute value of the difference of the calculated results of correlation diagram for two neighbor  $l_{try}$  less than  $eps$ . If we find such a  $l_{try}$ , we take this  $l_{try}$  as  $l_{max}$ .

### 3 Results and Discussion

We have evaluated the values of the hyperfine constants for  ${}^7\text{Li}$ ,  ${}^{23}\text{Na}$ ,  ${}^{39}\text{K}$ ,  ${}^{43}\text{Ca}^+$ . Our calculated results are listed in Table 1. The second column

shows the valence orbitals outside core. The fourth column tabulates the zeroth-order hyperfine constants obtained by using HF potential. The fifth column is the contribution from core polarization, which include all-order contributions. The contribution of the lowest-order correlation, which are the remaining third-order hyperfine correction are listed in the sixth and seventh column. The data at the sixth column are calculated with  $l_{max} = 4$ , the data at the seventh column are calculated with  $l_{max} = 8$ . In the eighth and ninth column we tabulate total hyperfine constants for  $l_{max} = 4$  and  $l_{max} = 8$ , respectively. For the states with the different  $j$  and the same  $l$ , the radial hyperfine parameters are the same.

The tenth column presents the experimental results. From these tables, we can see that our results are in good agreement with that for  ${}^7\text{Li}$ ,  ${}^{23}\text{Na}$ ,  ${}^{39}\text{K}$ , and  ${}^{43}\text{Ca}^+$  except  $2p_{3/2}$  state of  ${}^7\text{Li}$ , for which a special calculation is needed. For  $a$  constants of  $2p_{1/2}$  and  $2p_{3/2}$  states of isotope  ${}^7\text{Li}$ , Lindgren<sup>[4]</sup> obtained an accurate results 46.20 and

-3.32 MHz with coupled-cluster approach, which solve coupled inhomogeneous one- and two-particle equations in an iterative way. Johnson<sup>[6]</sup> also calculated the  $a$  constants for  ${}^7\text{Li}$  by using many-body perturbation with B-splines basis sets, their results are 45.9 and -3.71 MHz for  $2p_{1/2}$  and  $2p_{3/2}$  states, respectively.

Which occupied orbitals and excited angular momentum are included in the perturbative diagrams? This is easy to do for the polarization dia-

grams. From equation (10), we can see that for  $l=1$ ,  $k \leq 2$ . If  $l_u \leq 2$ , then  $l_r \leq 4$ . For  $l=2$ ,  $k \leq 4$  and  $l_r \leq 6$ . But for the correlation diagrams, this is complex because we must choose  $l_{\max}$  to make calculated results to be in given accuracy. In Table 1, we tabulate the results for  $l_{\max}=4, 8$ , respectively. Comparison of the results for  $l_{\max}=4$  and  $l_{\max}=8$  shows difference between the two results for  $l_{\max}=4, 8$  is small.

**Table 1 The Hyperfine constants  $a$  and  $b$  (MHz) calculated by using the Hartree-Fock potential**

isotopes	shells	terms	Hartree-Fock complete polar.		first-order-correla.		total		expt.
${}^7\text{Li}$	$2s$	$a(2s_{1/2})$	284.75	95.40	21.13	21.77	401.23	401.87	401.75
	$2p$	$a(2p_{1/2})$	32.29	10.43	2.06	2.08	44.77	44.79	46.17(0.35)
		$a(2p_{3/2})$	4.46	-9.37	0.51	0.72	-2.41	-2.20	-3.07(13)
		$b(2p_{3/2})$	-0.22	0.03	-0.02	-0.016	-0.21	-0.21	-0.18
${}^{23}\text{Na}$	$3s$	$a(3s_{1/2})$	616.30	135.82	131.97	136.05	884.10	888.18	885.82
	$3p$	$a(3p_{1/2})$	62.94	17.57	17.00	17.32	97.51	97.83	94.3(2)
		$a(3p_{3/2})$	12.59	4.65	3.24	3.31	20.48	20.55	18.65(10)
		$b(3p_{3/2})$	1.53	0.80	0.31	0.32	2.64	2.65	2.723(55)
${}^{39}\text{K}$	$4s$	$a(4s_{1/2})$	141.21	32.24	68.50	70.90	241.95	244.35	230.86
	$4p$	$a(4p_{1/2})$	16.13	4.48	8.23	8.48	28.84	29.09	28.85(30)
		$a(4p_{3/2})$	3.23	1.84	1.54	1.59	6.61	6.66	6.09(4)
		$b(4p_{3/2})$	1.23	0.81	0.50	0.52	2.55	2.57	
${}^{43}\text{Ca}^+$	$4s$	$a(4s_{1/2})$	-564.07	-122.86	-163.71	-165.78	-840.64	-842.71	
	$4p$	$a(4p_{1/2})$	-97.99	-21.98	-31.85	-31.41	-151.82	-151.38	
		$a(4p_{3/2})$	-19.60	-6.83	-4.84	-6.55	-31.27	-32.98	-31.9(0.2)
		$b(4p_{3/2})$	-3.92	-1.58	-0.94	-0.99	-6.45	-6.50	-6.9(1.7)
	$3d$	$a(3d_{3/2})$	-33.83	-0.71	-15.56	-16.00	-50.11	-50.55	-48.3(1.6)
		$b(3d_{3/2})$	-2.26	0.23	-1.01	-1.05	-3.04	-3.08	-3.7(1.9)
		$a(3d_{5/2})$	-14.50	17.80	-7.29	-7.72	-3.99	-4.42	-3.8
		$b(3d_{5/2})$	-3.23	0.34	-1.45	-1.50	-4.33	-4.38	-3.9(6.0)

\* The values in the sixth and eighth columns are calculated for  $l_{\max}=4$ , the values in seventh and ninth columns are calculated for  $l_{\max}=8$ .

For heavy atoms or ions, we must perform a relativistic calculation. For  $D$  states of  ${}^{87}\text{Rb}$  and  ${}^{87}\text{Sr}^+$  we need to calculate high-order correlation, which will take a lot of work and cpu time.

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## 由基样条构造有限基集计算的超精细结构常数\*

吴礼金, 李 勇, 高克林

(中国科学院武汉物理与数学研究所, 波谱与原子分子物理国家重点实验室, 湖北 武汉 430071)

**摘 要:** 多体微扰论有效算符方法应用于超精细结构的计算. 由 HF 波函数计算零阶超精细常数. 使用基样条构造了薛定谔方程的有限基集. 使用这些有限基集计算了原子实极化和关联, 以及  $^7\text{Li}$ ,  $^{23}\text{Na}$ ,  $^{39}\text{K}$  和  $^{43}\text{Ca}$  离子的  $s_{1/2}$ ,  $p_{1/2}$  和  $p_{3/2}$  态的超精细结构常数和  $^{43}\text{Ca}$  离子的  $d_{3/2}$  和  $d_{5/2}$  态的超精细常数.

**关键词:** 超精细结构; 基样条; 多体微扰论

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