

# Atomic Bethe-Goldstone Calculation of the Hyperfine Structure of Li(2<sup>2</sup>P)

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(Received 18 March 1970)

A variational formulation of Brueckner's theory has been applied to the calculation of hyperfine parameters for the 2<sup>2</sup>P excited state of atomic lithium. The hierarchy of *n*th-order (or *n*-particle) Bethe-Goldstone equations defined previously has been modified so that complete electronic configurations occur at each level of the hierarchy. Thus  $\vec{L}^2$ ,  $\vec{S}^2$  eigenfunctions could be used throughout the calculations, although for practical reasons such functions are not explicitly constructed. Each net increment of any mean-value electronic property defined within the hierarchy is shown to be equivalent to a sum, to infinite order, of a certain well-defined set of linked diagrams in the many-particle perturbation theory. Computed results are in excellent agreement (within roughly 1%) with experimental data and with a previously published accurate perturbation calculation.

## I. INTRODUCTION

A nuclear magnetic moment  $\vec{\mu}$  interacts with atomic electrons through three interaction operators of different tensorial character.<sup>1</sup> These are referred to as the Fermi contact, spin-dipolar, and orbital hyperfine operators, respectively;

$$H_c = \frac{8}{3} \pi g_e (e/2mc) \vec{\mu} \cdot \sum_i \vec{s}_i \delta(\vec{r}_i), \quad (1)$$

$$H_{\text{dip}} = g_e \frac{e}{2mc} \vec{\mu} \cdot \sum_i r_i^{-5} [3(\vec{s}_i \cdot \vec{r}_i) \vec{r}_i - r_i^2 \vec{s}_i], \quad (2)$$

$$H_{\text{orb}} = (e/mc) \vec{\mu} \cdot \sum_i r_i^{-3} \vec{l}_i. \quad (3)$$

Here *m* is the electronic mass,  $-e$  the electronic charge, and

$$g_e = 2.00232. \quad (4)$$

The index *i* is summed over the *N* electrons in an atom.

Since each of these operators is the scalar product of  $\vec{\mu}$  and an electronic vector operator, their combined effect in an electronic state of quantized total angular momentum  $\vec{J}$  can be parametrized by an effective Hamiltonian

$$h a_J \vec{I} \cdot \vec{J}, \quad (5)$$

where  $\vec{I}$  is the nuclear spin. Both spin vectors are expressed in atomic units (angular momentum divided by  $\hbar$ ), and *a<sub>J</sub>* is defined in frequency units (energy divided by  $\hbar$ ).

For light atoms, the electronic wave function can be assumed to have definite quantum numbers *L* and *S*. Although the relative contributions of the three magnetic hyperfine operators differ in different *J* states within the *L-S* term, they are completely determined by the mean values of the hyperfine operators in the state with *J=L+S*, *M<sub>L</sub>=L*, *M<sub>S</sub>=S*, and *M<sub>J</sub>=J*. In this particular state, the electronic contribution to the hyperfine interaction is determined

by mean values computed for a given electronic wave function

$$\hbar a_0^{-3} \chi_c = [\vec{s} \delta] = \langle 8\pi \sum_i s_{zi} \delta(\vec{r}_i) \rangle_{LS}, \quad (6)$$

$$\hbar a_0^{-3} \chi_{\text{dip}} = [\vec{s} \vec{C}^{(2)}] = \langle 2 \sum_i s_{zi} r_i^{-3} C_0^{(2)}(\theta_i) \rangle_{LS}, \quad (7)$$

$$\hbar a_0^{-3} \chi_{\text{orb}} = [\vec{l}] = \langle \sum_i r_i^{-3} l_{zi} \rangle_{LS}. \quad (8)$$

Two other mean values evaluated in the present work are

$$[\delta] = \langle 4\pi \sum_i \delta(\vec{r}_i) \rangle_{LS}, \quad (9)$$

$$[\vec{C}^{(2)}] = \langle \sum_i r_i^{-3} C_0^{(2)}(\theta_i) \rangle_{LS}. \quad (10)$$

Here  $C_0^{(2)}$  is the spherical tensor function

$$C_0^{(2)}(\theta) = (4\pi/5)^{1/2} Y_2^0(\theta, \phi) = P_2(\cos \theta), \quad (11)$$

defined in terms of the normalized spherical harmonic  $Y_l^m(\theta, \phi)$ .

The square-bracket notation introduced here will be used throughout the present paper.

In the state with *J=L+S*, the coupling constant *a<sub>J</sub>* is the sum of three terms

$$a_{J,c} = \gamma_{JI} (g_e/6) \chi_c, \quad (12)$$

$$a_{J,\text{dip}} = \gamma_{JI} (g_e/2) \chi_{\text{dip}}, \quad (13)$$

$$a_{J,\text{orb}} = \gamma_{JI} \chi_{\text{orb}}. \quad (14)$$

Here

$$\gamma_{JI} = G_{en} \mu_I / JI, \quad (15)$$

where  $\mu_I$  is the nuclear magnetic moment in nuclear magnetons, and *I* is the nuclear-spin quantum number. The fundamental constant *G<sub>en</sub>* is

$$G_{en} = 2 \beta_e \beta_n / \hbar a_0^3, \quad (16)$$

where  $\beta_e$  is the Bohr magneton,  $\beta_n$  the nuclear magneton, and *a<sub>0</sub>* is the Bohr radius. If the following values are used<sup>2</sup>

$$\begin{aligned}
 \beta_e &= 9.274\,096 \times 10^{-21} \text{ erg/G} , \\
 \beta_n &= 5.050\,951 \times 10^{-24} \text{ erg/G} , \\
 a_0 &= 5.291\,772 \times 10^{-9} \text{ cm} , \\
 \hbar &= 6.626\,196 \times 10^{-27} \text{ erg sec} ,
 \end{aligned}
 \tag{17}$$

then

$$G_{en} = 95.4129 \text{ MHz} . \tag{18}$$

If the parameters  $\chi_c$ ,  $\chi_{dip}$ , and  $\chi_{orb}$  are defined to be nondimensional, as in Eqs. (6)–(8), then Eqs. (12)–(14) define the independent contributions to the hyperfine coupling constant  $a_J$  in frequency units.

A nuclear electric quadrupole moment  $eQ$  interacts with atomic electrons through  $[\vec{C}^{(2)}]$  defined by Eq. (10). The magnitude of the interaction is determined by the quadrupole coupling constant  $eqQ$ , where

$$q = -2e [\vec{C}^{(2)}] , \tag{19}$$

in atomic units, is the electric field gradient at the nucleus due to the atomic electrons.

It is convenient to denote the three independent contributions to  $a_J$  with  $J = L + S$  simply by  $a_c$ ,  $a_{dip}$ , and  $a_{orb}$ . Together with  $eqQ$ , these parameters determine all hyperfine interactions within or among the substates of a given  $LS$  term. Only rarely are enough experimental data available to determine all four parameters. If the experimental data are incomplete, they cannot be analyzed or used for prediction unless augmented by data from theoretical calculations. In the theory of hyperfine interactions, this has often been done at the primitive level of assuming that  $a_{dip}$ ,  $a_{orb}$ , and  $q$  all depend on a single parameter  $\langle r^{-3} \rangle$  through coefficients determined by angular momentum coupling of equivalent  $p$  orbitals in the atomic valence shell. This is valid in the traditional Hartree-Fock approximation to the electronic wave function,<sup>3</sup> but cannot be maintained when internal electronic polarization and correlation are taken into account.

The work of Harvey<sup>4</sup> on atomic oxygen and fluorine demonstrates the need for three independent parameters to describe the observed magnetic hyperfine interactions, in addition to the quadrupole coupling constant. As Harvey points out, the fact that different effective values of  $\langle r^{-3} \rangle$  must be used in  $a_{dip}$  and  $a_{orb}$  implies that a still different value must be used in  $q$ . Hence,  $q$  cannot be obtained directly from measurements of magnetic hyperfine structure. The profound implication of this is that measured values of  $eqQ$  can be used to determine nuclear quadrupole moments  $Q$  only to the extent that accurate values of  $q$  are available from theory. It is clear that the required theory must go beyond the limits of the Hartree-Fock approximation.

In atomic  $S$  states (with  $L = 0$ ), the Fermi contact interaction  $a_c$  is the only hyperfine constant that does not vanish identically. This constant, which measures the electronic spin density at the nucleus, is due entirely to  $s$  orbitals ( $l = 0$ ), because orbitals with  $l > 0$  vanish at the nucleus. In the traditional Hartree-Fock approximation for an atom with closed  $s$  shells, but with an open  $p$  shell, the contact interaction must vanish because of cancellation between doubly occupied  $s$  orbitals with identical spatial functions but opposite spin. The observed hyperfine interaction in such states, for example,  $N(^4S)$  or  $P(^4S)$ , is entirely due to effects neglected in the traditional Hartree-Fock approximation.

It is to be expected that an unbalanced spin distribution in an incomplete atomic valence shell will induce spin polarization in the nominally closed inner shells and result in a nonvanishing Fermi contact hyperfine interaction.<sup>5</sup> In fact, this physical effect is neglected in the traditional Hartree-Fock approximation only as a result of somewhat artificial constraints that are built into the formalism.<sup>6</sup> The Fermi contact interaction has been computed for a number of atoms by Hartree-Fock calculations that retain the use of a single determinantal variational wave function but drop the constraint of doubly occupied spatial orbitals.<sup>7</sup> While a very good result is obtained in the simplest case, the  $2^2S$  state of Li, calculations for other atoms show serious quantitative errors. For quantitatively reliable results, it is necessary to include electronic correlation effects that are neglected in the Hartree-Fock approximation, even when the traditional symmetry constraints are relaxed.

The  $2^2P$  excited state of Li is interesting because it is the simplest case in which none of the hyperfine coupling constants vanish identically. A nominally closed inner shell ( $1s^2$ ) can be polarized by the open valence shell ( $2p$ ) to give an induced Fermi contact interaction. The  $2^2P$  term has two fine-structure levels,  $2^2P_{1/2}$  and  $2^2P_{3/2}$ . Thus, only two magnetic hyperfine coupling constants  $a_{1/2}$  and  $a_{3/2}$  are defined in the absence of external fields. In fact, for experimental reasons, only the constant  $a_{1/2}$  has been measured directly.<sup>8</sup> However, experiments on the crossing of Zeeman levels in an applied magnetic field give enough data to determine all three magnetic hyperfine constants.<sup>9,10</sup> The quadrupole coupling constant has not yet been determined to useful accuracy.

The spin polarization of the  $1s^2$  shell in Li ( $2^2P$ ) due to the open  $2p$  shell was studied by Goodings,<sup>7</sup> who carried out a Hartree-Fock calculation without the traditional constraint of identical  $1s$  spatial orbitals. Although referred to by Goodings as a UHF (unrestricted Hartree-Fock) calculation, this

is a misnomer because the symmetry constraint of neglecting  $d/s$  polarization was imposed, even though this effect in inner shells due to an open  $p$  shell had previously been cited as an example of polarization effects in the Hartree-Fock formalism.<sup>6</sup> In fact, the  $d$  polarization of the  $1s$  orbitals in Li ( $2^2P$ ) makes an important contribution to the contact interaction and to the difference among effective  $\langle r^{-3} \rangle$  values for the other hyperfine interaction terms. The value of  $a_{1/2}$  computed by Goodings was found to differ by approximately 7% from the subsequently measured experimental value.<sup>8</sup>

More recently, several calculations have gone beyond the framework of the Hartree-Fock approximation. In calculations with a wave function that allows for correlation effects and spin polarization of the  $1s^2$  shell, Goddard<sup>11</sup> has obtained a value of  $a_{1/2}$  in good agreement with experiment. The effective  $\langle r^{-3} \rangle$  values were all constrained to be equal, in conflict with values deduced from level-crossing experiments.<sup>9,10</sup> The computed value of  $a_{3/2}$  is in serious disagreement with the value deduced from these experiments.

A multiconfiguration wave function for Li ( $2^2P$ ) obtained by Weiss<sup>12</sup> was used by Ardill and Stewart<sup>13</sup> to compute the hyperfine constants. This was the first work in which correlation effects that affect differently the various  $\langle r^{-3} \rangle$  values were taken into account. No systematic procedure was used to examine or ensure convergence of the computed hyperfine constants with respect to approximations inherent in such a wave function. The computed value of  $a_{1/2}$  was close to the experimental value,<sup>8</sup> but  $a_{3/2}$  is in serious disagreement with the value subsequently deduced from level-crossing experiments.<sup>9,10</sup>

It is clear from this survey of prior work that a theoretical method is needed that provides internal criteria of accuracy and convergence and that is free of the constraints of the Hartree-Fock approximation. Two such methods are available, both based upon formalism originally developed for many-body theory in nuclear physics. The first of these methods is the Brueckner-Goldstone perturbation formalism,<sup>14</sup> developed for practical application to atomic electrons by Kelly.<sup>15</sup> As applied to hyperfine structure, each of the operator mean values defined by Eqs. (6)–(10) is expressed as an infinite sum of perturbation diagrams with a single vertex representing the appropriate hyperfine operator. The magnitude of the contribution due to any given diagram can be estimated, and, in principle, all diagrams can be computed whose effect exceeds a given criterion of accuracy.

A calculation of this kind has been carried out by Lyons, Pu, and Das<sup>16</sup> on the  $2^2P$  state of lithium. The calculated value of  $a_{1/2}$  is within the ex-

perimental limits of error. The effective values of  $\langle r^{-3} \rangle$  were found to be significantly different for the mean values  $[\vec{S}\vec{C}^{(2)}]$ ,  $[\vec{I}]$ , and  $[\vec{C}^{(2)}]$ . Because the level-crossing experiments<sup>9</sup> had originally been analyzed on the assumption that a unique value of  $\langle r^{-3} \rangle$  could be defined, Lyons and Das<sup>16</sup> undertook a reanalysis of this data using three independent parameters for the magnetic hyperfine interaction. The values of  $a_{3/2}$  and of various level-crossing data obtained from this new analysis are in excellent agreement with the perturbation calculations.<sup>10</sup> One of the principal purposes of the present work is to verify these results by an independent method of calculation.

The second general method capable of extension to ultimate convergence, with internal criteria of accuracy, is the use of a hierarchy of  $n$ -electron Bethe-Goldstone equations, where  $n = 1, 2, 3, \dots, N$  for a system of  $N$  electrons. This method is a generalization of the many-particle theory of Brueckner.<sup>17</sup> In Brueckner's theory the two-particle problem is solved exactly for each pair of particles in an  $N$ -particle system, while each two-particle wave function is constrained to be orthogonal to the remaining  $N-2$  orbital functions describing particles in an assumed Fermi sea. The two-particle equation of Brueckner's theory, derived originally as an integral equation,<sup>17</sup> was expressed as a differential equation by Bethe and Goldstone,<sup>18</sup> and the two-particle equation is commonly referred to as a Bethe-Goldstone equation.<sup>19</sup> A third form of this equation, a sum to infinite order of so-called ladder diagrams in perturbation theory, has been derived by Goldstone.<sup>14</sup> The "exact-pair" equation proposed by Sinanoğlu<sup>20</sup> is a variational form of the Bethe-Goldstone equation.<sup>19</sup>

If a Fermi sea is defined by the occupied orbitals  $\phi_i$  of a reference-state Slater determinant  $\Phi_0$ , the Bethe-Goldstone equation for pair  $ij$  is equivalent to a variational calculation with an  $N$ -particle trial function<sup>19</sup>,

$$\Psi_{ij} = \Phi_0 + \sum_a \Phi_i^a c_i^a + \sum_b \Phi_j^b c_j^b + \sum_{ab} \Phi_{ij}^{ab} c_{ij}^{ab} . \quad (20)$$

In the notation used here, a Slater determinant obtained from  $\Phi_0$  by replacing occupied orbitals  $\phi_i, \phi_j, \dots (i < j < \dots < N)$  by unoccupied orbitals  $\phi_a, \phi_b, \dots (N < a < b < \dots)$  taken from a postulated complete orthonormal set of orbital functions is denoted by  $\Phi_{ij\cdots}^{ab\cdots}$ . In Eq. (20), the summations extend over all values of the indices  $a$  and  $b$ , but indices  $i$  and  $j$  are fixed and denote specific occupied orbitals in  $\Phi_0$ . The summation over  $ab$  denotes a double sum with  $a < b$ .

The general definition of a Bethe-Goldstone equation of order  $N$ , as used here,<sup>21,22</sup> is the equivalent of a variational calculation with a trial function that is a linear combination of  $\Phi_0$  and of all Slater de-

terminants  $\Phi_{ijk\dots}^{abc\dots}$  whose indices  $ijk\dots$  are any subset of a specified list of  $n$  occupied orbital indices. The variational wave function of order  $n$ ,  $\Psi_{ijk\dots}$  for the specified indices  $ijk\dots$ , is determined by the coefficients  $c_{ijk\dots}^{abc\dots}$ , obtained as components of an eigenvector of the  $N$ -particle Hamiltonian matrix over the Hilbert space of Slater determinants included in the trial function. The gross increment  $\Delta F_{ijk\dots}$  of the mean value of any operator  $F$  is defined as the mean value evaluated for  $\Psi_{ijk\dots}$ , less the reference-state mean value  $F_{00}$ . Then the net increment  $f_{ijk\dots}$  of any such mean-value property is defined as the difference between the corresponding gross increment and the sum of all net increments of lower order whose indices form a subset of the given set  $ijk\dots$ .

For example, the net energy increment for pair 2, 5 is defined by

$$e_{25} = \Delta E_{25} - e_2 - e_5, \quad (21)$$

where  $\Delta E_{25}$  is the directly computed lowest eigenvalue of the configuration interaction matrix (matrix of the  $N$ -particle Hamiltonian) for  $\Psi_{25}$ , and  $e_2$  and  $e_5$  are net increments obtained from first-order Bethe-Goldstone calculations for  $\Psi_2$  and  $\Psi_5$ , respectively. Thus,  $e_{25}$  is that part of  $\Delta E_{25}$  not contained in  $e_2$  and  $e_5$  separately. If carried to  $N$ th order, this method of bookkeeping gives the exact mean value of any operator  $F$  in the form

$$\langle F \rangle = f_0 + \sum_i f_i + \sum_{ij} f_{ij} + \dots + f_{1\dots N}, \quad (22)$$

where  $f_0 = F_{00}$  is the mean value in the reference state.

This formalism has been used to compute the contact hyperfine interaction in the ground states of Li ( $^2S$ ) and N( $^4S$ ), taking into account one-, two-, and three-electron net increments of  $[\mathfrak{S}\delta]$ , defined by Eq. (6).<sup>23</sup> This mean value is usually denoted by  $f$  and referred to as the Fermi contact parameter. In these calculations, there was significant cancellation among the one-electron (first-order) net increments of  $f$ , and the three-particle net increments were not at all negligible, especially for N( $^4S$ ). Because of the practical difficulty of computing three-particle terms, it could not be certain that the finite orbital basis sets used in these calculations gave results near the practical limit of completeness even though the computed hyperfine constants were close to their experimental values.

The present paper will describe a modified Bethe-Goldstone formalism based on excitations of electronic configurations rather than of individual orbitals. This has the considerable advantage, especially for the study of hyperfine structure, that each of the variational wave functions  $\Psi_{ijk\dots}$  is a strict eigenfunction of  $\bar{L}^2$  and  $\bar{S}^2$ . This is not true

except in special cases for the wave functions defined by a hierarchy of Bethe-Goldstone equations based upon individual orbital excitations. Calculations of electronic correlation energies by a Bethe-Goldstone formalism defined in terms of configurational excitations have been carried out on several atoms by Schaefer and Harris<sup>24</sup> and on diatomic molecules by Bender and Davidson.<sup>25</sup>

The hierarchy of Bethe-Goldstone equations for configurational excitations is defined in Sec. II. The computational method is described in Sec. III. A systematic procedure used in the present calculations to extrapolate orbital basis sets to completeness is described in Sec. IV. Results of the specific computations on Li ( $2^2P$ ) are given in Sec. V. In Sec. VI it is shown that net contributions to mean values defined in terms of configurational excitations can be equated to certain sums of perturbation theory diagrams. A general discussion of the present method and of the particular results for Li ( $2^2P$ ) is given in Sec. VII.

## II. HIERARCHY OF CONFIGURATIONS

The definition of a Bethe-Goldstone equation of order  $n$ , for orbital excitations, is based upon a systematic subdivision of the Hilbert space of  $N$ -particle Slater determinants. A countable complete orthonormal set of orbital functions is assumed, of which the first  $N$ , denoted by  $\phi_i$ ,  $i = 1, \dots, N$ , are occupied in a reference-state Slater determinant  $\Phi_0$ . A complete set of normalized Slater determinants  $\Phi_{ijk\dots}^{ab\dots}$  is defined in terms of virtual excitations of  $\Phi_0$ , in which orbitals  $\phi_a$ ,  $N < a$ , replace the occupied orbitals of  $\Phi_0$ . In practice, finite sets of orbitals are used, and computed results are extrapolated to the limit of completeness of the orbital set.

The set of Slater determinants formed by all possible virtual excitations from a given set of occupied orbitals, with indices  $ijk\dots$ , constitutes a Hilbert space that can be denoted by the symbol  $(ijk\dots)$ . For example,  $(ij)$  is the linear function space spanned by  $\{\Phi_{ij}^{ab}\}$ ,  $N < a < b$ , for fixed  $i, j$ , but all values of  $a, b$ . If  $[\Phi]$  is the complete Hilbert space of  $N$ -particle Slater determinants, then this space can be decomposed into a direct sum of disjoint subspaces,

$$[\Phi] = (0) + \sum_i (i) + \sum_{ij} (ij) + \sum_{ijk} (ijk) + \dots \quad (23)$$

Here (0) denotes the reference state.

A Bethe-Goldstone equation with indices  $ijk\dots$  is defined as the equivalent of a variational calculation within a Hilbert space that can be denoted by  $[ijk\dots]$ , defined as the direct sum of (0) and of all subspaces  $(ij\dots)$  whose indices form a subset of  $ijk\dots$ . For example,

$$[ij] = (0) + (i) + (j) + (ij) . \quad (24)$$

These *variational subspaces* of  $[\Phi]$  form a *lattice* in the technical sense that

$$[0] \subset [ijk \dots] \subset [\Phi] \quad (25)$$

for any  $[ijk \dots]$ , and simple ordering holds for variational spaces with nested indices,

$$[0] \subset [i] \subset [ij] \subset [ijk \dots] , \quad (26)$$

but no ordering relation is defined otherwise.

This lattice structure of Hilbert spaces is used to define net increments of numerical properties of the variational wave functions. Thus if  $\Delta F_{ij}$  is the gross increment of  $\langle F \rangle$  computed for  $\Psi_{ij}$  defined within  $[ij]$ , then, by definition of net increments  $f_{ij \dots}$

$$\Delta F_{ij} = f_0 + f_i + f_j + f_{ij} , \quad (27)$$

exactly parallel to Eq. (24). This defines

$$f_{ij} = \Delta F_{ij} - f_0 - f_i - f_j , \quad (28)$$

just as

$$(ij) = [ij] - (0) - (i) - (j) . \quad (29)$$

The computational procedure based on Bethe-Goldstone equations defined by orbital excitations can be generalized to make use of any decomposition of the  $N$ -particle Hilbert space into a direct sum of disjoint subspaces. Within any lattice structure built up from these subspaces, in analogy to Eqs. (24), (25), and (26), variational computations can be defined that lead to systematic definitions of gross and net increments of properties of an  $N$ -particle wave function.

Disjoint subspaces defined in terms of orbital excitations, such as  $(1s\beta)$ ,  $(2p_{-1}\beta)$ , or  $(1s\alpha 2p_0\alpha)$ , are not invariant under space or spin rotations. Hence, for atoms, symmetry-adapted eigenfunctions of  $\bar{L}^2$  and  $\bar{S}^2$  cannot, in general, be constructed within the variational subspaces defined by orbital excitations. Especially in the case of hyperfine interactions, which are intimately related to orbital and spin angular momenta, it is desirable to have a Bethe-Goldstone formalism which works with symmetry-adapted functions at each stage of computation. This can be achieved by defining disjoint subspaces of  $[\Phi]$  that are closed under space or spin rotations. In an unperturbed atom, neglecting relativistic effects, quantum numbers  $M_L$  and  $M_S$  are well defined, even for orbital excitations. To obtain subspaces closed under rotations, it is necessary to include all Slater determinants, with given  $M_L$  and  $M_S$ , in the same *configuration* as any determinant in the subspace. Here a configuration is defined in the usual way: For atoms in  $L$ - $S$  coupling, quantum numbers  $nl$  are defined

for each occupied orbital in a typical Slater determinant of the configuration, which consists of all determinants with the specified  $nl$  values, but with all possible values of the quantum numbers  $m_l$ ,  $m_s$  for each orbital.

Disjoint subspaces of  $[\Phi]$  are defined in terms of configurational excitations of a reference configuration (0) by specifying the subset of orbitals whose quantum numbers  $nl$  are changed by virtual excitations. For example, the subspace (1s) consists of all configurations obtained from (0) by decreasing the number of occupied 1s orbitals by one, while increasing the number of orbitals with some other value of  $nl$ . A variational subspace is defined as the direct sum of those disjoint subspaces whose indices (sets of  $nl$  values) form subsets of the indices of the variational subspace. For example, variational subspaces are defined by

$$\begin{aligned} [1s 2s] &= (0) + (1s) + (2s) + (1s 2s) , \\ [1s^2] &= (0) + (1s) + (1s^2) , \\ [1s^2 2p] &= (0) + (1s) + (2p) + (1s^2) + (1s 2p) + (1s^2 2p) . \end{aligned} \quad (30)$$

Configurational Bethe-Goldstone equations can be defined as the equivalent of variational calculations with trial functions confined to the lattice of variational subspaces defined as in Eqs. (30). Physical mean-value properties of an electronic system can be computed from this hierarchy of Bethe-Goldstone equations by defining net and gross mean-value increments as in Eqs. (27) and (28), but indexed according to the lattice structure of configurational variational subspaces. For example, corresponding to the variational spaces indicated in Eqs. (30), gross increments of a mean value  $\langle F \rangle$ , evaluated for the implied variational wave functions, can be expressed as

$$\begin{aligned} \Delta F_{1s2s} &= f_0 + f_{1s} + f_{2s} + f_{1s2s} , \\ \Delta F_{1s1s} &= f_0 + f_{1s} + f_{1s1s} , \\ \Delta F_{1s1s2p} &= f_0 + f_{1s} + f_{2p} + f_{1s1s} + f_{1s2p} + f_{1s1s2p} . \end{aligned} \quad (31)$$

This has the effect of defining net increments

$$\begin{aligned} f_{1s2s} &= \Delta F_{1s2s} - f_0 - f_{1s} - f_{2s} , \\ f_{1s1s} &= \Delta F_{1s1s} - f_0 - f_{1s} , \\ f_{1s1s2p} &= \Delta F_{1s1s2p} - f_0 - f_{1s} - f_{2p} - f_{1s1s} - f_{1s2p} . \end{aligned} \quad (32)$$

The general definition of a net increment of  $\langle F \rangle$  with indices  $n_1 l_1, n_2 l_2, \dots$  is the difference between the corresponding gross increment, directly computed from a variational wave function, and the sum of all distinct net increments of lower order whose indices are a subset of those given.

Because the subspace (0) or  $[0]$  must be taken to consist of the configuration containing the refer-

ence-state Slater determinant  $\Phi_0$ , it is convenient to retain a zeroth-order net increment  $f_0$  in the definitions used here. If gross increments  $\Delta F$  are defined relative to  $F_{00}$ , the mean value evaluated for  $\Phi_0$ , then  $f_0$  denotes the change of  $\langle F \rangle$  due to interaction of determinants within the configuration (0). Such a definition is required when several independent symmetry-adapted functions with identical quantum numbers  $L$  and  $S$  occur in the same configuration, or when  $\Phi_0$  is not symmetry adapted.

These definitions of a hierarchy of configurational Bethe-Goldstone equations are applied in the present work to computations of the mean values of the hyperfine interaction operators given by Eqs. (6)–(10) for the  $2^2P$  excited state of Li.

### III. COMPUTATIONAL METHOD

The  $n$ th-order variational wave function  $\Psi_{ij\dots}$  is expressed as a linear combination of the basis Slater determinants  $\Phi_\mu$  of the variational Hilbert space  $[ij\dots]$ ,

$$\Psi_{ij\dots} = \sum_\mu \Phi_\mu c_\mu, \quad (33)$$

where the coefficients  $c_\mu$  are computed as elements of an eigenvector of the Hamiltonian matrix  $H_{\mu\nu}$ . The gross increment of some mean value  $\langle F \rangle$  is given by

$$\Delta F_{ij\dots} = \sum_\mu \sum_{\nu'} (F_{\mu\nu} - F_{00} \delta_{\mu\nu}) c_\mu^* c_{\nu'} / \sum_\mu c_\mu^* c_\mu. \quad (34)$$

All of the matrix elements  $F_{\mu\nu}$  required for the various hyperfine interaction operators can be expressed in terms of raw orbital matrix elements

$$F_{pq} = N_p N_q, \quad l_p = l_q = 0, \quad n_p = n_q = 1 \quad (35)$$

$$F_{pq} = N_p N_q (p|r^{-3}|q), \quad l_p = l_q \neq 0 \text{ or } l_p = l_q + 2.$$

Here  $N_p$ ,  $N_q$  are the radial normalization factors of basis orbital functions of the form

$$\eta(r, \theta, \phi) = N r^{n-1} \exp(-\zeta r) Y_l^m(\theta, \phi), \quad (36)$$

where  $Y_l^m$  is a normalized spherical harmonic. The matrix element in Eq. (36) is

$$\begin{aligned} (p|r^{-3}|q) &= \int_0^\infty r^{n_p + n_q - 3} \exp(-\zeta_p r - \zeta_q r) dr \\ &= (n_p + n_q - 3)! / (\zeta_p + \zeta_q)^{n_p + n_q - 2}. \end{aligned} \quad (37)$$

The occupied orbitals  $\phi_i$  of the reference state  $\Phi_0$  and the orthogonal set of unoccupied orbitals  $\phi_a$  are constructed as orthonormal linear combinations of basis orbitals of the form indicated in Eq. (36). The coefficients of these linear combinations are used to transform  $F_{pq}$  to the basis of orthonormal radial orbitals. The usual symmetry and equivalence restrictions of Hartree-Fock theory<sup>6</sup>

are used, so the radial factor of each matrix element is independent of  $m$ .

Each of the orthonormal orbital functions is characterized by quantum numbers  $(nlmm_s)$ , where  $n$  is a counting index within the set of orbitals of given  $l$ . Matrix elements of the hyperfine operators between any two orbitals  $\phi_a$ ,  $\phi_b$  (occupied or unoccupied) vanish unless  $m_a = m_b = m$  and  $m_{sa} = m_{sb} = m_s$ . The specific dependence on the angular quantum numbers is

$$\begin{aligned} (a|\delta|b) &= F_{ab}, \quad l_a = l_b = 0 \\ (a|\tilde{S}^2|b) &= 2m_s F_{ab}, \quad l_a = l_b = 0 \\ (a|\tilde{C}^{(2)}|b) &= c^2(l_a m; l_b m) F_{ab}, \quad l_a = l_b (\neq 0), \quad l_b + 2 \quad (38) \\ (a|\tilde{S}\tilde{C}^{(2)}|b) &= 2m_s c^2(l_a m; l_b m) F_{ab}, \quad l_a = l_b (\neq 0), \quad l_b + 2 \\ (a|\tilde{I}|b) &= m F_{ab}, \quad l_a = l_b (\neq 0) \end{aligned}$$

where  $F_{ab}$  is the radial matrix element defined by Eqs. (35), transformed to the orthonormal basis, and  $c^2(lm; l'm')$  is a matrix element of  $P_2(\cos \theta)$ . These are the Gaunt coefficients tabulated by Condon and Shortley.<sup>25</sup> The different tensorial character of each of the hyperfine operators is obvious from these formulas for the dependence on  $m$  and  $m_s$  of the one-electron matrix elements.

The matrix elements  $F_{\mu\nu}$  between Slater determinants, required in Eq. (34), are expressed in terms of one-electron matrix elements by formulas given by Condon and Shortley.<sup>25</sup> There are only two kinds of nonvanishing matrix elements – diagonal elements and those between Slater determinants that differ by a single occupied orbital. In the latter case, the general formula can be deduced from the special case

$$(\Phi_i^a, F\Phi_0) = (a|F|i). \quad (39)$$

If  $\mu$  denotes a determinant  $\Phi_{ij\dots}^{ab\dots}$ , the required diagonal matrix element is

$$F_{\mu\mu} - F_{00} = \sum_a (a|F|a) - \sum_i (i|F|i), \quad (40)$$

where the summations run over just those indices indicated in the notation for  $\Phi_\mu$ , defined by relative virtual excitation of  $\Phi_0$ .

A counting algorithm has been devised and programmed that lists all Slater determinants in a variational subspace  $[nl, n'l', \dots]$ , given the dimensions of the occupied and unoccupied orbital basis sets. Only determinants with the same values of  $M_L$ ,  $M_S$ , and parity as the reference determinant  $\Phi_0$  are included in the tabulation. For configurational excitations, all determinants of the same configuration occur as a contiguous subset of the determinant list. This will facilitate the eventual construction of symmetry-adapted eigenfunctions of  $\tilde{L}^2$  and  $\tilde{S}^2$ , but such functions are not constructed in the present work prior to diagonali-

zation of  $H_{\mu\nu}$ . The inclusion of complete configurations in the determinant list ensures that the eigenvectors of  $H_{\mu\nu}$  represent symmetry-adapted functions.

The mean values indicated by Eq. (34) are computed by a double count through the determinant list, constructing each element  $F_{\mu\nu}$  as it arises in the order of the lower triangle of a symmetric matrix by combining angular and phase factors with tabulated values of the radial matrix elements.

#### IV. ORBITAL BASIS SETS

The hyperfine interactions are found to be much more sensitive to fine details of the electronic wave function than is the total energy. In earlier calculations of correlation energies, adequate convergence of the orbital basis set was found with "double-zeta" basis sets, augmented by sequences of orbitals as indicated in Eq. (36), with a common value of  $\zeta$  for each atomic shell.<sup>22</sup> Preliminary calculations of hyperfine interactions in several atoms showed that this did not give sufficiently stable convergence.

The orbital basis set shown in Table I was used as a base for extrapolation. It contains 1s and 2p basis orbitals obtained in a matrix Hartree-Fock calculation that gave -7.365 054 Hartree units for the  $2^2P$  state of Li.<sup>26</sup> Because of the near degeneracy between the 2p and 2s valence orbitals, 2s basis orbitals were included with the same exponents as those used for 2p. Virtual excitations from 1s to virtual d orbitals have an important influence on the hyperfine interactions. The two 3d exponents included in Table I were obtained by a two-parameter minimization of the energy of the [1s] variational wave function. This was required to stabilize the dominant contribution to the Fermi contact parameter [ $\bar{s}\delta$ ]. A single 4f exponent is included in Table I. It was obtained by minimizing the energy of the [1s2p] variational wave function.

Extrapolations were carried out by augmenting the basis set of Table I with additional orbitals with a common exponent  $\zeta = 5.543$  appropriate to the K shell of Li<sup>23</sup> and an increasing sequence of

TABLE I. Exponents  $\zeta$  for basis orbitals  $r^{n-1}e^{-\zeta r} Y_l^m(\theta, \phi)$ .

$nl$	$\zeta$ list
1s	1.9635, 2.6270, 5.1370
2s	2.3348, 0.6024, 0.4859
2p	2.3348, 0.6024, 0.4859
3d	1.25, 2.23
4f	2.451

powers of  $r$ . It is well known that such sequences form countable complete sets of radial functions for each  $l$  value. The technique of extrapolation was to add, successively, one through five basis orbitals to the base set for each  $l$  value. Five terms allowed two successive applications to the computed hyperfine parameters of an extrapolation formula,<sup>27</sup> equivalent to assuming geometric convergence. In cases of obviously irregular convergence, mean values computed for the final calculation in the sequence were used instead of extrapolated values. A typical example of the extrapolation procedure is shown in Table II. It can be seen that the energy increments  $e$  form a monotonic decreasing sequence, as they must from the variational nature of the computations within a specified variational Hilbert space.

The significant result of each extrapolation is the set of quantities indicated by  $\Delta$  in Table II, the extrapolated increments to the hyperfine parameters obtained with the base orbital basis set (denoted by 6321 and defined in Table I). It is assumed as a working hypothesis that the extrapolated increments  $\Delta$  obtained separately for different  $l$  values can simply be added. All of these results are listed in Table III and are summed to give extrapolated estimates of the various net increments of the hyperfine parameters.

#### V. RESULTS

Final computed values of the hyperfine parameters are listed in Table IV. The Hartree-Fock results, denoted by net increment (0), are obtained

TABLE II. Example of extrapolation. Convergence of 1s2p net increments for d-orbital completeness. Energy increment  $e$  and hyperfine parameters in atomic units. Basis sets are 6, 3, 2 +  $n_d$ , 1.  $\Delta$  denotes extrapolated correction. "n m" means  $n \times 10^m$ .

$n_d$	$e$	$[\delta]$	$[\bar{s}\delta]$	$[\bar{C}^{(2)}]$	$[\bar{s}\bar{C}^{(2)}]$	$[\bar{I}]$
base 0	-0.153 960 - 2	-0.109 150	0.405 990 - 3	-0.114 643 - 2	-0.879 037 - 3	0.452 026 - 2
1	-0.154 486 - 2	-0.109 162	0.211 480 - 3	-0.106 916 - 2	-0.956 174 - 3	0.455 699 - 2
2	-0.154 937 - 2	-0.109 189	0.138 180 - 3	-0.113 617 - 2	-0.901 238 - 3	0.457 834 - 2
3	-0.155 093 - 2	-0.109 105	0.117 550 - 3	-0.109 888 - 2	-0.941 009 - 3	0.458 484 - 2
4	-0.155 143 - 2	-0.109 065	0.115 150 - 3	-0.112 409 - 2	-0.918 599 - 3	0.458 526 - 2
5	-0.155 171 - 2	-0.109 064	0.124 520 - 3	-0.110 304 - 2	-0.933 904 - 3	0.458 499 - 2
$\Delta$		0.000 093	-0.287 350 - 3	0.003 325 - 2	-0.049 422 - 3	0.006 482 - 2

TABLE III. Summary of extrapolated corrections for angular completeness. Net increments of hyperfine parameters in atomic units. Data are in floating decimal notation: fraction followed by power of ten.

Increment		$[\delta]$	$[\tilde{s}\delta]$	$[\tilde{C}^{(2)}]$	$[\tilde{s}\tilde{C}^{(2)}]$	$[I]$
1s	base	-0.856 136 - 2	-0.205 005	0.161 244 - 2	-0.977 886 - 3	0.598 643 - 5
	s	0.050 136 - 2	0.006 798	0.000 045 - 2	0.000 145 - 3	-0.000 117 - 5
	p	-0.004 277 - 2	-0.000 388	0.000 032 - 2	-0.001 683 - 3	0.002 823 - 5
	d	0.002 215 - 2	0.000 025	-0.022 271 - 2	0.134 374 - 3	-0.038 488 - 5
	f	0.0	0.0	0.0	0.0	0.0
	total	-0.808 062 - 2	-0.198 570	0.139 050 - 2	-0.845 050 - 3	0.562 861 - 5
2p	base	0.0	0.0	-0.312 296 - 7	-0.312 296 - 7	0.156 148 - 6
	s	0.0	0.0	0.266 151 - 7	0.266 151 - 7	-0.133 075 - 6
	p	0.0	0.0	0.301 665 - 7	0.301 665 - 7	-0.150 832 - 6
	d	0.0	0.0	0.0	0.0	0.0
	f	0.0	0.0	0.0	0.0	0.0
	total	0.0	0.0	0.255 520 - 7	0.255 520 - 7	-0.127 759 - 6
1s <sup>2</sup>	base	0.424 231	-0.214 648 - 1	0.755 078 - 4	-0.048 681 - 4	0.014 252 - 4
	s	-0.472 857	0.012 747 - 1	-0.003 847 - 4	0.001 752 - 4	0.000 180 - 4
	p	0.267 549	0.031 212 - 1	-0.009 053 - 4	0.065 662 - 4	0.118 949 - 4
	d	-0.003 927	0.005 927 - 1	-0.171 498 - 4	-0.128 526 - 4	0.000 152 - 4
	f	-0.006 777	0.001 611 - 1	0.008 312 - 4	0.002 652 - 4	0.000 068 - 4
	total	0.208 219	-0.163 151 - 1	0.578 992 - 4	-0.107 141 - 4	0.133 601 - 4
1s2p	base	-0.109 150	0.040 599 - 2	-0.114 643 - 2	-0.879 037 - 3	0.452 026 - 2
	s	-0.000 150	0.122 403 - 2	-0.000 119 - 2	-0.000 894 - 3	0.000 533 - 2
	p	-0.010 578	-0.090 584 - 2	-0.002 432 - 2	-0.024 121 - 3	0.003 746 - 2
	d	0.000 093	-0.028 735 - 2	0.003 325 - 2	-0.049 422 - 3	0.006 482 - 2
	f	-0.000 856	-0.017 099 - 2	-0.001 171 - 2	-0.004 160 - 3	0.001 783 - 2
	total	-0.120 641	0.026 584 - 2	-0.115 040 - 2	-0.957 634 - 3	0.464 570 - 2

with the s and p orbital basis of Table I extended to eight and five radial basis functions, respectively. The energy computed with this approximate Hartree-Fock function is -7.365 0670 hartree units. Net increments of the hyperfine parameters for all one- and two-particle configurational excitations possible in the 2<sup>2</sup>P state are included in Table IV.

For comparison with experiment, the computed hyperfine parameters must be multiplied by the conversion factors indicated in Eqs. (12)–(14). If 2.792 782  $\mu_N$  is used for the magnetic moment of the proton,<sup>2</sup> the recalibrated value of the magnetic moment of the Li<sup>7</sup> nucleus ( $I = \frac{3}{2}$ ) is<sup>28</sup>

$$\mu_I = 3.256\,355\,\mu_N. \quad (41)$$

Then from Eq. (15), with  $J = \frac{3}{2}$  and the constant  $G_{en}$

given by Eq. (18),

$$\gamma_{JI} = 138.088 \quad (42)$$

in MHz/a. u.

Although not required by the expected accuracy of the present results, additional correction factors arise from the finite mass of the Li<sup>7</sup> nucleus. These factors convert from atomic units in which the electronic mass is the reduced mass in the Li atom to the units given by Eq. (17), appropriate to infinite nuclear mass. The Li-based atomic units are inherent in the atomic calculations. If  $M$  is the nuclear mass<sup>29</sup> (7.016 01 C<sup>12</sup> mass units for Li<sup>7</sup>), and  $m$  is the electronic mass<sup>2</sup> ( $5.485\,93 \times 10^{-4}$  C<sup>12</sup> mass units), then  $[\tilde{s}\delta]$  and  $[\tilde{s}\tilde{C}^{(2)}]$  must be multiplied by the factor

TABLE IV. Net increments of hyperfine parameters in atomic units.

Increment	$[\delta]$	$[\tilde{s}\delta]$	$[\tilde{C}^{(2)}]$	$[\tilde{s}\tilde{C}^{(2)}]$	$[I]$
0	0.0 <sup>a</sup>	0.0	-0.011 711	-0.011 711	0.058 553
1s	-0.008 081	-0.198 570	0.001 391	-0.000 845	0.000 006
2p	0.0	0.0	0.0	0.0	0.0
1s <sup>2</sup>	0.208 219	-0.016 315	0.000 058	-0.000 011	0.000 013
1s2p	-0.120 641	0.000 266	-0.001 150	-0.000 958	0.004 646
total	0.079 497 <sup>a</sup>	-0.214 619	-0.011 412	-0.013 525	0.063 218

<sup>a</sup>The Hartree-Fock value of  $[\delta]$ , 173.845 568 a.u., is not included in the tabular entries.



$$\gamma_{sp} = (1 + m/M)^{-3} = 0.999\ 7654 \quad (43)$$

to give  $\chi_c$  and  $\chi_{dip}$  in the usual atomic units. This is the mass correction for  $a_0^{-3}$ . In the case of the orbital hyperfine interaction, the Bohr magneton is also inherently defined in terms of the electronic reduced mass. This correction compensates for one of the factors in  $\gamma_{sp}$ , and  $[\vec{l}]$  must be multiplied by the factor

$$\gamma_{orb} = (1 + m/M)^{-2} = 0.999\ 8436 \quad (44)$$

to give  $\chi_{orb}$  in standard atomic units. To facilitate comparison with future calculations of higher accuracy than those reported here, these mass correction factors have been included in the present final results, converted to hyperfine coupling constants in MHz.

These results are listed in Table V. The hyperfine interactions are computed directly in the state  $J = \frac{3}{2}$ . In a  $^2P$  state, the  $J = \frac{1}{2}$  coupling constants can be obtained from the formulas derived from the Wigner-Eckart theorem<sup>16</sup>

$$\begin{aligned} a_{1/2,c} &= -a_{3/2,c} , \\ a_{1/2,dip} &= -10a_{3/2,dip} , \\ a_{1/2,orb} &= 2a_{3/2,orb} . \end{aligned} \quad (45)$$

These coupling constants are included in Table V.

Except for the value of  $a_{1/2}$ , a directly measured result,<sup>8</sup> the experimental data included in Table V have been deduced by Lyons and Das<sup>10</sup> by a recent reanalysis of experimental data on Zeeman level crossing in Li.<sup>9</sup> This new analysis assumes three independent magnetic hyperfine parameters, as implied by perturbation theory calculations<sup>16</sup> and by the present work.

A comparison of the computed and experimental data in Table V indicates substantial quantitative agreement. The present results fall generally within 1% of the experimental data or in most cases within the indicated error limits.

Existing experimental data do not provide a value of the quadrupole coupling constant  $eqQ$  of use-

ful accuracy. However, judging from the results obtained here for the magnetic hyperfine parameters, the electric field gradient  $q$  obtained by Eq. (19) from the computed value of  $[\vec{C}^{(2)}]$  listed in Table IV should be accurate to 1% of its value. Hence, if  $eqQ$  can eventually be measured to this accuracy, a comparably accurate value of the nuclear moment  $Q$  can be deduced.

The electric field gradient  $q$  is often expressed in terms of an approximate value  $q_0$ , obtained by a one-electron model calculation by the formula

$$q = q_0(1 - R) , \quad (46)$$

where  $R$  is the Sternheimer quadrupole shielding factor.<sup>30</sup> Calculations of intershell polarization in the  $2^2P$  state of Li give a value of 0.1156 for this factor.<sup>31</sup> The Brueckner-Goldstone calculations of Lyons *et al.* lead to  $R = 0.1700$ .<sup>16</sup> The present calculation of  $[\vec{C}^{(2)}]$ , indicated in Table IV, is equivalent to  $R = 0.0255$ , in very marked disagreement with earlier results. It should be noted that the present (1s) net increment by itself would give  $R = 0.1188$ , in reasonable agreement with the result of Sternheimer. However, this is nearly canceled by the (1s2p) pair correlation effect. There is no evidence of such cancellation in the perturbation diagrams considered by Lyons *et al.*. In the present calculations, this cancellation between (1s) and (1s2p) appears quite clearly for the orbital basis set indicated in Table I and persists in the extrapolated net increments. This provides some internal evidence that the cancellation effect is real.

## VI. COMPARISON WITH PERTURBATION THEORY

The perturbation-theory equivalent of a mean-value net increment defined by the hierarchy of  $n$ th-order Bethe-Goldstone equations for *orbital* excitations has been described previously.<sup>22</sup> The net increment with indices (*ij*. . .) is equal to the sum, to infinite order, of all connected linked Goldstone diagrams<sup>14,15</sup> whose backward directed lines are labeled by just this set of indices with every index

TABLE V. Hyperfine coupling constants for  $Li^7$  in state  $2^2P_J$ , in MHz.

	$J = 1/2$			$J = 3/2$		
	Present <sup>a</sup>	LPD <sup>b</sup>	Expt <sup>c</sup>	Present <sup>a</sup>	LPD <sup>b</sup>	Expt <sup>c</sup>
$a_{J,c}$	9.8880	9.5788	$9.806 \pm 0.116$	-9.8880	-9.5788	$-9.806 \pm 0.116$
$a_{J,dip}$	18.6937	18.9638	$19.080 \pm 0.340$	-1.8694	-1.8964	$-1.908 \pm 0.034$
$a_{J,orb}$	17.4566	17.3453	$17.282 \pm 0.074$	8.7283	8.6727	$8.641 \pm 0.037$
$a_J$	46.0383	45.8879	$46.17 \pm 0.35$	-3.0291	-2.8025	$-3.073 \pm 0.126$

<sup>a</sup>Hyperfine parameters shown in Table IV multiplied by conversion factors defined in the text.

<sup>b</sup>J. D. Lyons, R. T. Pu, and T. P. Das, Phys. Rev. **178**, 103 (1969). Original results, in atomic units, have been multiplied by conversion factors used in present paper.

<sup>c</sup>Values of coupling constants implied by experimental data discussed in text. The value of  $a_{1/2}$  is a direct experimental result [G. J. Ritter, Can. J. Phys. **43**, 770 (1965)].

value appearing at least once. For the mean value of an operator  $F$ , each diagram contains one  $F$  vertex and has no external lines.

This theorem can be extended to the present case of configurational excitations, if care is taken in dealing with the so-called EPV (exclusion principle violating) diagrams. Of various classes of EPV diagrams considered by Kelly,<sup>32</sup> the only class that requires special analysis arises originally from factorization of unlinked diagrams prior to cancellation of the denominator that represents the renormalization of the unperturbed wave function. In EPV diagrams of this class, repeated values of particle ( $a$ ) or hole ( $i$ ) indices may occur at a cross section across the diagram between successive vertices. The exclusion principle is violated in that the implied intermediate wave function cannot be defined, since a Slater determinant does not allow repeated particle or hole indices. Except for certain diagrams that cancel exactly in pairs, Kelly has shown that EPV diagrams of this class can be decomposed into unlinked segments such that the exclusion principle is valid within each segment. Then a Slater determinant wave function, or set of such wave functions, can be identified with each cross section of each diagram.

If EPV diagrams are taken into account as described above, the configurations that enter into any linked diagram can be determined by examining the Slater determinants associated with each cross section of the diagram. In terms of relative virtual excitations from a reference configuration, the change of occupancy of an originally closed or completely empty subshell of orbitals ( $nl$ ) is obvious. The change of occupancy of a partially occupied shell is given by the excess of holes over particles with the same ( $nl$ ) value. Each cross section of a linked Goldstone graph determines a set of indices  $\gamma(nl)$ , the excess of holes over particles for each ( $nl$ ) value needed to describe the Slater determinant wave functions at that cross section within each linked part of a factored EPV diagram. The set of maximum values of these indices taken over all cross sections of the diagram describes the maximum complexity of virtual excitation required in a wave function that would lead to the diagram in question. This set of indices uniquely determines a variational Hilbert space for configurational excitations, denoted in Sec. II by a notation equivalent to

$$[\dots(nl)^\gamma\dots] \quad (47)$$

It follows from the bookkeeping procedure used to define net increments that the diagram in question is part of the net increment denoted by

$$(\dots(nl)^\gamma\dots) \quad (48)$$

Conversely, this net increment is the sum of all such diagrams characterized by a set of maximum relative excitation indices  $\gamma(nl)$  for each ( $nl$ ) value of the reference configuration.

This simple rule shows how any fully labeled mean-value Goldstone diagram can be assigned to a definite configurational net increment.

## VII. DISCUSSION AND CONCLUSIONS

The present results indicate that the method used here, a hierarchy of variational Bethe-Goldstone equations, is capable of obtaining hyperfine parameters within an error of 1% of their experimental values. Although the method is, in principle, applicable to much heavier atoms than lithium, it remains to be shown that results of high accuracy can be obtained as the number of electrons increases. It is encouraging to note that calculations on the  $^2P$  ground state of boron, to be reported separately, appear to maintain the level of accuracy indicated here for  $^2P$  lithium.

The crucial practical question is whether net three-particle terms can be neglected, and if not, whether they can be estimated without carrying out computations as elaborate as those reported here for one- and two-particle terms. In  $^2P$  lithium, calculations using a somewhat truncated orbital basis set were carried out and indicated that the only possible three-particle term here ( $1s^2 2p$ ) gives net increments of the same magnitude as the residual error (roughly 1%) in the present results. Thus, it is justified to omit the ( $1s^2 2p$ ) net increments, as has been done here. However, this does not justify neglecting *intrashell* three-particle terms, such as ( $2s^2 2p$ ) in boron, which might be considerably larger than the intershell term  $1s^2 2p$ . This point will be examined in calculations on heavier atoms.

The present method classifies corrections to the Hartree-Fock approximation in a hierarchy that is based on the underlying physics of electronic correlation. Because of the apparently rapid convergence and high accuracy of the present results, it is justified to associate a physical meaning with each of the net increments listed in Table IV. The ( $1s$ ) net increments correspond to virtual one-particle excitations from the  $1s^2$  shell, corrected for rotational invariance by the method of configurational excitations. Thus, it is reasonable to attribute ( $1s$ ) net increments to a physical polarization distortion of the inner shell orbitals because of the asymmetry of the open  $2p$  outer shell. The corresponding polarization of the  $2p$  orbital vanishes to six decimal places.

The two-particle net increments ( $1s^2$ ) and ( $1s 2p$ ) must be considered to be true correlation effects requiring the virtual polarization of two electrons at a time. These correlation effects, as indicated

in Table IV, are smaller than the dominant Hartree-Fock terms for the spin-dipolar and orbital interactions and smaller than the (1s) contact interaction (a polarization effect), but their magnitude is roughly one-tenth of the total in each case. Thus, correlation effects must be computed accurately if computations are to be compared with experimental data in the range of 1% errors.

A detailed comparison with perturbation-theory results<sup>16</sup> will not be attempted here. The very detailed agreement shown in Table V with the LPD magnetic hyperfine constants is encouraging because perturbation theory and the present method are complementary in their essential approximations. The linked cluster perturbation method, as implemented by Kelly,<sup>15</sup> takes into account with relative ease a complete basis of radial functions for each  $l$  value, but must truncate the sum of all Goldstone diagrams at a rather low order. In contrast, the present method inherently sums an infinite set of Goldstone diagrams at each level of the hierarchy of computations, but must truncate the set of radial orbital functions severely for each  $l$  value, depending on extrapolation to approach completeness.

Because of these complementary limitations of

the two methods, it is encouraging when they come into agreement with calculations that are practicable within either method, and this agreement gives some credibility to the results.

A serious disagreement exists between the correlation contribution to the electric field gradient  $q$  as computed by the present method and by perturbation theory.<sup>16</sup> All of the present calculations, including basis set extrapolations, were carried out in a uniform manner in the present work with no arbitrary choices such as are possible in selecting Goldstone diagrams in perturbation theory. Because of this, it is unlikely that the present value of  $q$  is grossly less accurate than are the magnetic hyperfine parameters. It can be concluded that resolution of the disagreement is most likely to be found by including more Goldstone diagrams of the (1s2p) class in the perturbation calculations.

The calculations reported here were carried out on an IBM 360/91 computer.

#### ACKNOWLEDGMENT

The author is indebted to J. D. Lyons for many helpful discussions and for permission to quote his results prior to publication.

<sup>1</sup>R. E. Trees, Phys. Rev. 92, 308 (1953); C. Schwartz, *ibid.* 97, 380 (1955).

<sup>2</sup>B. N. Taylor, W. H. Parker, and D. N. Langenberg, Rev. Mod. Phys. 41, 375 (1969).

<sup>3</sup>D. R. Hartree, *The Calculation of Atomic Structures* (Wiley, New York, 1957).

<sup>4</sup>J. S. M. Harvey, Proc. Roy. Soc. (London) A285, 581 (1965).

<sup>5</sup>A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) A205, 135 (1951).

<sup>6</sup>R. K. Nesbet, Proc. Roy. Soc. (London) A230, 312 (1955).

<sup>7</sup>L. M. Sachs, Phys. Rev. 117, 1504 (1960); D. A. Goodings, *ibid.* 123, 1706 (1961); R. K. Nesbet, in *Quantum Theory of Atoms, Molecules, and the Solid State*, edited by P.-O. Löwdin (Academic, New York, 1966), pp. 157-165; P. S. Bagus, B. Liu, and H. F. Schaefer, III, Phys. Rev. (to be published).

<sup>8</sup>G. J. Ritter, Can. J. Phys. 43, 770 (1965).

<sup>9</sup>K. C. Brog, T. G. Eck, and H. Wieder, Phys. Rev. 153, 91 (1967).

<sup>10</sup>J. D. Lyons and R. K. Nesbet, Phys. Rev. Letters 24, 433 (1970); J. D. Lyons and T. P. Das (unpublished).

<sup>11</sup>W. A. Goddard, III, Phys. Rev. 176, 106 (1968).

<sup>12</sup>A. W. Weiss, Astrophys. J. 138, 1262 (1963).

<sup>13</sup>R. W. B. Ardill and A. L. Stewart, Proc. Phys. Soc. (London) 92, 296 (1967); J. Chem. Phys. 47, 4853 (1967).

<sup>14</sup>J. Goldstone, Proc. Roy. Soc. (London) A239, 267 (1957).

<sup>15</sup>H. P. Kelly, Phys. Rev. 131, 684 (1963); 136, B896 (1964); 144, 39 (1966); 173, 142 (1968); in *Perturbation*

*Theory and its Application in Quantum Mechanics*, edited by C. H. Wilson (Wiley, New York, 1966), p. 215.

<sup>16</sup>J. D. Lyons, R. T. Pu, and T. P. Das, Phys. Rev. 178, 103 (1969); 186, 266 (1969).

<sup>17</sup>K. A. Brueckner, Phys. Rev. 96, 508 (1954); 97, 1353 (1955); 100, 36 (1955); in *The Many-Body Problem*, edited by B. Dewitt (Wiley, New York, 1959), pp. 47-241.

<sup>18</sup>H. A. Bethe and J. Goldstone, Proc. Roy. Soc. (London) A238, 551 (1957).

<sup>19</sup>O. Sinanoğlu, J. Chem. Phys. 36, 706 (1962); 36, 3198 (1962); Advan. Chem. Phys. 6, 315 (1964).

<sup>20</sup>R. K. Nesbet, Advan. Chem. Phys. 9, 321 (1965).

<sup>21</sup>R. K. Nesbet, Phys. Rev. 155, 51, (1967); 155, 56 Chem. Phys. 14, 1 (1969).

<sup>22</sup>R. K. Nesbet, Phys. Rev. 175, 2 (1968).

<sup>23</sup>R. K. Nesbet, in *Quantum Theory of Atoms, Molecules, and the Solid State*, edited by P.-O. Löwdin (Academic, New York, 1966), pp. 157-165; Colloq. Intern. Centre Natl. Rech. Sci. (Paris) 164, 87 (1967).

<sup>24</sup>H. F. Schaefer, III, and F. E. Harris, Phys. Rev. 167, 67 (1968); C. F. Bender and E. R. Davidson, J. Chem. Phys. 47, 360 (1967); Phys. Rev. 183, 23 (1969).

<sup>25</sup>E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge U. P., New York, 1951).

<sup>26</sup>J. D. Lyons (private communication).

<sup>27</sup>D. R. Hartree, *Numerical Analysis* (Oxford U. P., New York, 1952), pp. 196-197.

<sup>28</sup>N. F. Ramsey, *Molecular Beams* (Oxford U. P., New York, 1956), p. 172.

<sup>29</sup>*Handbook of Chemistry and Physics* (Chemical Rubber

Cleveland, 1969), 49th ed.

<sup>30</sup>R. Sternheimer, Phys. Rev. 80, 102 (1950); 84, 244 (1951).

<sup>31</sup>R. Sternheimer, Phys. Rev. 164, 10 (1967).

<sup>32</sup>H. P. Kelly, Phys. Rev. 131, 684 (1963).

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VOLUME 2, NUMBER 3

SEPTEMBER 1970

## Rotational Raman Effect: Molecular Impurities in Alkali Halides\*

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(Received 9 March 1970)

Raman scattering of light from representative alkali-halide crystals containing  $\text{CN}^-$ ,  $\text{NO}_2^-$ ,  $\text{OH}^-$ , and  $\text{OD}^-$  impurities is reported and analyzed. The observed spectra have a low-frequency range in which the scattered light is usually shifted from the incident light by less than  $300\text{--}400\text{ cm}^{-1}$ , and a high-frequency range in which the shifts are typically  $1000\text{--}2000\text{ cm}^{-1}$ . Although the low-frequency region does not readily lend itself to quantitative analysis, it is clear that its main features can be interpreted in terms of a mixture of second-order scattering from the pure host, impurity-induced first-order scattering that results from perturbing the pure host, and scattering from the rotational degrees of freedom of the molecular impurity. The high-frequency region, on the other hand, consists of spectra whose frequencies are characteristic of the internal normal coordinates of the molecule. A very narrow totally polarized line with depolarized sideband structure is generally observed. The sharp central component is at the frequency of an internal molecular normal coordinate and, typically, has a linewidth of  $1\text{ cm}^{-1}$ . It is not significantly affected by the type of host or changes in temperature. It is found that the sideband structure gives a measure of the molecular rotational dynamics. Depending on host and impurity, the observed characteristic behavior varies from nearly free rotation to heavily trapped librational motion. The techniques employed here, both theoretical and experimental, demonstrate and define the usefulness of the Raman effect in studying systems of an analogous nature.

### I. INTRODUCTION

In this paper, we discuss the application of spontaneous Raman-scattering techniques to the study of rotational motions of selected molecular impurities in various alkali-halide single crystals. The results suggest that observations and analysis similar to what we report here will enable one to also study rotational motions of other molecular systems, including liquids.<sup>1</sup> The particular impurities and host crystals chosen for detailed examination were  $\text{CN}^-$  in  $\text{KCl}$ ,  $\text{KBr}$ , and  $\text{NaCl}$ , as well as  $\text{OH}^-$  and  $\text{OD}^-$  in  $\text{KCl}$ . In addition, less extensive observations were made on these same molecules in other hosts and also on  $\text{NO}_2^-$  in representative crystals. The choice of these systems for the present work was partially made on the basis that they had previously been studied by a variety of other methods, and although a good deal was already known of their rotational kinetics, there was need for further experimental confirmation of conclusions that were previously somewhat specu-

lative.<sup>2-13</sup> The consistency between conclusions drawn from the present measurements and published results of others supports these previous conclusions. The results reported here can also be taken as some measure of the general suitability of Raman scattering for quantitative measurements of molecular rotations.

Extensive studies, including near-infrared absorption, stress, and specific-heat measurements, have been performed by Seward and Narayanamurti on  $\text{CN}^-$ -doped samples.<sup>2</sup> The detailed structure of the absorption bands in the vicinity of the internal stretching mode of the  $\text{CN}^-$  molecule (near  $2000\text{ cm}^{-1}$ ) was used to determine some features of the molecular rotational motion. The conclusion was that the  $\text{CN}^-$  molecule in  $\text{KCl}$ ,  $\text{KBr}$ , and  $\text{RbCl}$  is a relatively free rotator which could be successfully treated by the Devonshire model.<sup>14</sup> In the case of  $\text{CN}^-$  in  $\text{NaCl}$  and  $\text{NaBr}$ , the results were inconclusive, but it was supposed that the molecule is relatively heavily trapped in a given orientation. Vacancy and entropy studies showed that the  $\text{CN}^-$  mol-