MC SCF WAVEFUNCTIONS FOR THE FERMI-CONTACT HYPERFINE STRUCTURE OF LITHIUM ATOM

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MC SCF wavefunctions which describe accurately the Fermi-contact hyperfine structure of the lithium atom in lowest P and S doublet states are obtained. The physical picture of the Fermi-contact hyperfine structure of the states is discussed on the basis of the wavefunctions.

In the multi-configuration (MC) SCF method, the wavefunction of a system

$$\Psi = \sum_K a_K \Phi_K \qquad (1)$$

is optimized with respect to both the configurational coefficients a_K and the component orbitals in the configurations Φ_K. Consequently, this method improves the "slow convergence" of the conventional CI method so that one may achieve a good approximation for a state even with a few configurations [1]. In the present communication, we investigate the Li atom by the MC SCF method in order to search for a physical mechanism which contributes mainly to the spin density at the nucleus (hereafter referred to as $[s_z\delta]$) on the basis of the physical significance of the configurations.

In order to study the nature of the hyperfine structure of atoms, the simplest problem to treat may be the P doublet state of the Li atom. We discuss this state firstly and the S doublet state of the Li atom subsequently. The following three configurations are considered in the present calculations for the P doublet state:

$$\Phi_1 = |1s\bar{1}s2p_+|\,, \quad \Phi_2 = |2s\bar{2}s2p_+|\,,$$

and

$$\Phi_3 = 6^{-1/2}\,[2|2s1s\overline{2p}_+| - |2s\bar{1}s2p_+| - |\bar{2}s1s2p_+|]\,,$$

where Φ_1 is the Hartree–Fock configuration which gives the reference state for taking into account electron correlation effects. Φ_2 is the P doublet configuration arising from two-electron excitation from the 1s to the 2s orbital, and Φ_3 is the singly excited configuration (this could contribute to $[s_z\delta]$ as a spin-polarization mechanism [2]).

In table 1, we summarize the results obtained from these two- and three-configuration MC SCF calculations. The nature of $[s_z\delta]$ is clarified by considering the meaning of these configurations within the MC SCF framework. Let u_+ and u_- be the orbitals defined by the linear transformation of the MC SCF orbitals, 1s and 2s;

$$\begin{pmatrix} u_+ \\ u_- \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ \cos\theta & -\sin\theta \end{pmatrix} \begin{pmatrix} 1s \\ 2s \end{pmatrix}\,, \qquad (2)$$

where $0 < |\theta| \ll \pi/2$. Then, an MC SCF wavefunction $\Psi[2C]$ consisting of the two configurations Φ_1 and Φ_2 is transformed to

$$\Psi[2C] = a_1\Phi_1 + a_2\Phi_2 = (N/2)|u_+u_-2p_+(\alpha\beta-\beta\alpha)\alpha|, \qquad (3)$$

where $a_1 = N\cos^2\theta$, $a_2 = -N\sin^2\theta$ and N is the normalization constant. Eq. (3) means that configuration Φ_2 causes the radial splitting of the 1s orbital in Φ_1 and that the split orbitals u_+ and u_- are occupied by an electron of α and/or β spin with the same probability of 0.5. In terms of u_+ and u_-, the configuration

Table 1
The calculated spin density and energy of the P doublet state of the Li atom by the MC SCF method

Configuration	$[s_z\delta]$ (au)	Energy (au)	Virial theorem	Ref.
2 conf. (Φ_1 and Φ_2)	0	−7.380082	2.000174	a)
2 conf. (Φ_1 and Φ_3)	−0.01402	−7.365088	2.000033	b)
3 conf. (Φ_1, Φ_2 and Φ_3)	−0.01693	−7.380087	2.000173	a)
nearly full CI within S		−7.379062		[7]
experimental	−0.01693 ± 0.00020	−7.41013		[8]

a) This work; the basis set used in the present calculations is the same as that in ref. [6].
b) This work; the basis set is the same as in ref. [9].

Table 2
The calculated spin density and energy of the S doublet state of the Li atom by the MC SCF method

Configuration	$[s_z\delta]$ (au)	Energy (au)	Virial theorem	Ref.
3 conf.	0.2139	−7.4465527	1.999988	a)
5 conf.	0.2265	−7.4475648	1.999990	a)
7 conf.	0.2265	−7.4475654	1.999990	a)
nearly full CI within S		−7.44754		[7]
experimental	0.2313	−7.47805		[5]

a) This work; the basis set used in the present calculations is the same as that in ref. [6].

Φ_3 can be rewritten as

$$\Phi_3 = N'|u_+u_-2p_+(2\alpha\alpha\beta-\alpha\beta\alpha-\beta\alpha\alpha)|\,, \quad (4)$$

where N' is the normalization constant. Then, the MC SCF wavefunction consisting of three configurations, Φ_1, Φ_2 and Φ_3 can be expressed as

$$\begin{aligned}\Psi[3C] &= a_1\Phi_1 + a_2\Phi_2 + a_3\Phi_3 \\ &= |u_+u_-2p_+[(Nc_1/2)(\alpha\beta-\beta\alpha)\alpha \\ &\quad + N'c_2(2\alpha\alpha\beta-\alpha\beta\alpha-\beta\alpha\alpha)]|\,,\end{aligned} \quad (5)$$

where $a_1 = Nc_1\cos^2\theta$, $a_2 = -Nc_1\sin^2\theta$ and $a_3 = c_2$. As seen in the last term of eq. (5), there arises some probability that each of the split orbitals is occupied by an α-spin electron. That is, the additional configuration Φ_3 causes a slight imbalance in the occupational probabilities of α and β electrons in the split 1s orbitals by the effect of the unpaired electron in the $2p_+$ orbital. Since table 1 indicates that $\Psi[3C]$ is superior in energy to the nearly full CI within S, the S-character* of the exact wavefunction of the state may be sufficiently reproduced by $\Psi[3C]$. As only an S-character could contribute to the $[s_z\delta]$, $\Psi[3C]$ should give a good $[s_z\delta]$. Indeed, the very good value of −0.01693 which just agrees with the experimental value of −0.01693 ± 0.00020 can be obtained by $\Psi[3C]$. On the other hand, as the calculated $[s_z\delta]$ is −0.01402 for $a_1\Phi_1 + a_3\Phi_3$, the proper description of a radial correlation should be a prerequisite for a good $[s_z\delta]$†.

Next, we discuss the ground state of the Li atom (S doublet). The following seven configurations are considered in the present calculations for the state;

$$\Phi_1 = |1s\overline{1s}\,2s|\,, \quad \Phi_2 = |3s\overline{3s}\,2s|\,,$$

$$\Phi_3 = 6^{-1/2}\,[2|3s1s\overline{2s}| - |3s\overline{1s}\,2s| - |\overline{3s}\,1s2s|]\,,$$

$$\Phi_4 = |1s\overline{1s}\,3s|\,, \quad \Phi_5 = |1s\overline{3s}\,3s|\,,$$

$$\Phi_6 = |1s\overline{2s}\,2s|\,, \quad \Phi_7 = |3s\overline{2s}\,2s|\,.$$

The results are summarized in table 2. First, we take up the first three configurations on the simple analogy

* By the "S-character", we denote a nodeless character at an origin (nucleus).

† This agrees with the conclusion in ref. [3].

of the previous discussion of the P doublet state. However, this wavefunction gives a poor $[s_z\delta]$ as table 2 shows. This is obvious since this wavefunction does not take the radial correlation sufficiently into account (compare the energies of this wavefunction and of the nearly full CI within S) and is insufficient for a 2s-orbital correction. To remedy these defects, we substitute the 2s orbital by the sum

$$\sum_{j=1}^{3} |js\rangle f_j , \tag{6}$$

with certain coefficients f_j so that we have two configurations, Φ_4 and Φ_5, in addition to the original three ones. The configuration Φ_4 corrects the 2s orbital in Φ_1 as follows:

$$a_1\Phi_1 + a_4\Phi_4 = |1s1s2s'| , \tag{7}$$

where the corrected orbital is

$$|2s'\rangle = |2s\rangle a_1 + |3s\rangle a_4 . \tag{8}$$

The configuration Φ_5 can be interpreted as the intershell correlation between 1s (K shell) and 2s (L shell) electrons. Since the unpaired electron is in an s-shell, it seems that the contribution from Φ_4 and Φ_5 becomes important (spin-delocalization contribution [2]). Indeed, table 2 shows that the wavefunction of the five configurations gives the good $[s_z\delta]$ value of 0.2265 (only 2% error) and that its energy may approach the S-limit. For the first-row atoms, B to F, in which unpaired electrons are all in 2p orbitals, contributions similar to those of Φ_4 and Φ_5 may be ignored just as in the case of the P doublet state of the Li atom. We further investigate two other configurations, Φ_6 and Φ_7. Table 2 indicates that these two additional configurations play no important role for the $[s_z\delta]$. This suggests that one can disregard the internal correlation of Φ_6 and the semi-internal one of Φ_7 in comparison with the important semi-internal correlation included in Φ_3.

In both doublet states of P and S of the Li atom, the $[s_z\delta]$ can be described excellently by the MC SCF method. Therefore, it appears that a physical mechanism for providing contributions mainly to the $[s_z\delta]$ is obtained as follows:

(i) each doubly-occupied s-orbital is split radially by the pair correlation of each electron pair;

(ii) the occupational probability of an α electron in each split orbital is different, to a certain extent, from that of β due to the unpaired electron (or generally unpaired electrons).

If the unpaired electron is in an s-shell (e.g., the ground state of alkali atoms), the orbital correction contribution, like Φ_4, and the intershell correlation contribution, like Φ_5, should be taken into account.

Computational details and a comparison with other work (Lunell [4], Ladner and Goddard [5], Kaldor and Harris [6], and others) will be published in the near future.

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