

Projected general spin-orbital wavefunctions for three-electron systems

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Abstract. Spin-projected Hartree-Fock calculations using general spin orbitals are performed on some S, P, D and F states of Li, and on the ground states of its isoelectronic ions with $Z = 4-10$. The energy -7.447596 au is obtained for Li 2^2S , compared to -7.447565 au with the spin-optimized SCF method and -7.432727 au with the ordinary restricted Hartree-Fock method. Full configuration-interaction results for the same basis sets are also reported.

1. Introduction

The projected Hartree-Fock (PHF) method was suggested by Löwdin (1955) as an extension of the ordinary Hartree-Fock method. In this method, the total wavefunction is written as a projected determinant

$$\Psi = \mathcal{O}|\psi_1(x_1) \dots \psi_N(x_N)| \quad (1)$$

where \mathcal{O} is a symmetry projection operator and the spin orbitals $\{\psi_k(x)\}$ in the general case are of the form

$$\psi_k(x) = \psi_k^+(r)\alpha + \psi_k^-(r)\beta. \quad (2)$$

The wavefunction (1) contains for a three-electron system as a special case (Lunell 1968, 1972) the so-called spin-optimized SCF (SOSCF) or best orbital (Kotani 1958) wavefunction, which for a three-electron doublet state has the form

$$\psi = \mathcal{A}\phi_1(r_1)\phi_2(r_2)\phi_3(r_3)[a_1\Theta_1 + a_2\Theta_2]. \quad (3)$$

Here Θ_1 and Θ_2 are two linearly independent doublet spin functions, for example:

$$\Theta_1 = (2)^{-1/2}(\alpha\beta\alpha - \beta\alpha\alpha) \quad (4a)$$

$$\Theta_2 = (6)^{-1/2}(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha). \quad (4b)$$

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The wavefunction (3) is obtained from (1) by choosing the restricted form

$$\psi_k(\mathbf{x}) = \phi_k(\mathbf{r})[A_k\alpha + B_k\beta] \quad (5)$$

for the general spin orbitals (GSO) (2).

Spin-projected Hartree-Fock calculations using GSO of the form (2) have been reported before for some members of the He isoelectronic series (Lunell 1970). In this paper, the method (PGSO) is applied to different states of the Li atom, as well as some of its isoelectronic ions, which have several mathematical and physical features which are not present in the two-electron systems previously investigated. The projection operator θ has the form

$$\begin{aligned} \mathcal{O}_{SM_S} &= \mathcal{O}_S \mathcal{O}_{M_S}, \\ \mathcal{O}_S &= \prod_{k \neq S} \frac{\hat{S}^2 - k(k+1)}{S(S+1) - k(k+1)}, \end{aligned} \quad (6)$$

$$\mathcal{O}_{M_S} = \prod_{k \neq M_S} \frac{\hat{S}_z - k}{M_S - k} \quad (7)$$

with $S = M_S = \frac{1}{2}$ for the doublet states considered.

For comparison purposes, full configuration-interaction (FCI) calculations for some of the systems using the same basis sets are also reported.

2. Method of calculation

The spin orbitals (2) were determined according to a method described elsewhere (Lunell 1970 section IIB, 1973). As input for the iterations, the SOSCF functions were used, written in the form (1). These functions have been published previously for Li 2^2S , Li 2^2P and B^{2+} 2^2S (Ladner and Goddard 1969, Kaldor and Harris 1969) and were calculated for the other states. The same basis sets were used for both the PGSO and SOSCF calculations, in order to eliminate basis-dependent differences from the comparisons. In the cases where only SOSCF energies, and not wavefunctions, have been published, basis sets were found which reproduced the published energies.

3. Results

The energies obtained for Li and some isoelectronic ions are shown in table 1, together with the ordinary (restricted) Hartree-Fock (RHF) energies and the SOSCF energies. From this table one can see that the PGSO energy for Li 2^2S is -7.447596 au, which is only 3×10^{-5} au lower than the SOSCF energy -7.447565 au (Ladner and Goddard 1969, Kaldor and Harris 1969). This can be compared to the two-electron case (Lunell 1970), where for Li^+ an energy difference of 10^{-3} au is obtained between the wavefunctions

$$\Phi^{Li^+}(\mathbf{x}_1, \mathbf{x}_2) = \mathcal{A} \tilde{\phi}_1(\mathbf{r}_1) \tilde{\phi}_2(\mathbf{r}_2) (\alpha_1 \beta_2 - \beta_1 \alpha_2) 2^{-1/2} \quad (8)$$

and

$$\Psi^{Li^+}(\mathbf{x}_1, \mathbf{x}_2) = \mathcal{O}_{00} |\tilde{\psi}_1(\mathbf{x}_1) \tilde{\psi}_2(\mathbf{x}_2)| \quad (9)$$

Table 1. Energies of different states of Li and Li-like ions. The soscf and pgso results were obtained using the same basis set for a given state.

	RHF ^a	SOSCF	PGSO	Experiment ^b
Li 2 ² S	-7.432727 ^c	-7.447565 ^{d,e}	-7.447596	-7.47807
2 ² P	-7.365068	-7.380087 ^{d,e}	-7.380191	-7.41016
3 ² S	-7.310209	-7.325179 ^d	-7.325183	-7.35410
3 ² P	-7.293185	-7.308198 ^d	-7.308233	-7.33715
Be ⁺ 2 ² S	-14.27739	-14.291637 ^{d,e}	-14.291693	-14.32481
B ²⁺ 2 ² S	-23.37599	-23.389920 ^{d,e}	-23.389978	-23.42478
Ne ⁷⁺ 2 ² S	-102.6311	-102.644482	-102.644578	-102.68271

^a Weiss (1963).^b Scherr *et al* (1962).^c Roothaan *et al* (1960).^d Ladner and Goddard (1969).^e Kaldor and Harris (1969).

(the tilde indicates that the orbitals are optimized for the positive ion). Previous experience has shown that the energy decrease resulting from an improved description of the core is virtually independent of the presence or absence of a valence orbital. One therefore expects the wavefunction

$$\Psi_1 = \mathcal{A}\Psi^{\text{Li}^-}(x_1, x_2)\phi_3(r_3)\alpha \quad (10)$$

to have an energy which is approximately 10^{-3} au lower than the function

$$\Psi_2 = \mathcal{A}\tilde{\phi}_1(r_1)\tilde{\phi}_2(r_2)(\alpha\beta - \beta\alpha)\phi_3(r_3)\alpha. \quad (11)$$

The energy of the latter is very close to the soscf energy of the atom (Lunell 1968). The reason that a corresponding energy lowering is not obtained in the pgso calculation for Li is that (10) cannot be written in the form (1) with \mathcal{O}_S given by (6). There is thus an analogy with the difference between the spin-extended Hartree-Fock (SEHF) or GF function and the soscf function, where the use of the simple projection operator (6) gives a much smaller energy improvement than a more flexible spin-coupling procedure (Lunell 1968, Hameed *et al* 1969, Kaldor and Harris 1969, Ladner and Goddard 1969).

To provide material for a fuller comparison of the different types of wavefunctions, the Fermi contact term (f) and orbital hyperfine-structure parameter (a_l) were also calculated. With the definitions used by Schaefer *et al* (1968) these are

$$f = \left\langle 8\pi \sum_i \delta(r_i) \hat{S}_{zi} \right\rangle, \quad (12)$$

$$a_l = \left\langle \sum_i \frac{\hat{l}_{zi}}{r_i^3} \right\rangle. \quad (13)$$

The results obtained in the present calculations are given in tables 2 and 4 and a comparison with some other methods is given in table 4.

Two types of FCI calculations were performed. The first, which is here denoted as CI1, uses only s and p_{+1} functions for the ²P^o states and correspondingly for the other symmetries (cf table 2). In this way only configurations of the type $ss'p_{+1}$ occur after symmetry-projection of each determinant. The pgso and soscf wavefunctions contain only configurations of this type. The second, CI2, adds the p_0 and p_{-1} components to the

Table 2. FCI results for several systems. The lowest roots of the secular problem are reported, as well as the total charge density at the nucleus and some HFS parameters. The number of configurations, basis sets, and projections applied are also listed. The basis sets are in each case originally optimized for the state which is underlined in the table.

System	Type of basis set and projections	Total energy	$\rho(0)$	f	a_i
Li 2S	s only	<u>-7.448571</u>	174.257	2.8009	0.0
112 CI ^a					
Li $^2P^o$	s, p_+	<u>-7.381428</u>	171.626	-0.2306	0.06070
80 CI ^b	L^2, L_z projection	<u>-7.305232</u>	171.776	-0.1108	0.02612
Li $^2P^o$	s, p_0, p_+, p_-	<u>-7.394667</u>	170.977	-0.2260	0.06038
330 CI ^b	L_z projection	<u>-7.318509</u>	171.120	-0.1090	0.02600
Li $^2P^o$	s, p_0, p_+, p_-	<u>-7.394921</u>	171.799	-0.1880	0.06075
250 CI ^c	L_z, L^2 projections	<u>-7.318697</u>	171.911	-0.0954	0.02594
Li $^2P^o$	s, p_+	<u>-7.381693</u>	172.433	-0.1924	0.06131
175 CI ^d	L_z, L^2 projections	<u>-7.309338</u>	172.593	-0.0617	0.01807
		<u>-7.284090</u>	172.636	-0.0246	0.007081
Li 2D	s, d_{+2}	<u>-7.307910</u>	172.671	-0.00033	0.004999
125 CI ^e	L^2, L_z projections				
Li 2F	s, f_{+3}	<u>-7.283229</u>	171.912	-0.00027	0.001205
80 CI ^f	L^2, L_z projections				

^a 1s(3.0), 3s(5.4, 2.9972, 1.3465, 0.8451), 4s(5.33, 0.7257).

^b 1s(2.944), 3s(9.546, 4.3055, 2.9228), 2p(1.5053), 4p(2.1161, 1.2041, 0.7316, 0.5316).

^c 1s(5.3, 2.443), 2s(5.3, 2.443), 3s(2.443), 2p(1.5053), 4p(2.1161, 1.2041, 0.7316, 0.5316).

^d 1s(5.3, 2.443), 2s(5.3, 2.443), 3s(2.443), 2p(1.5), 4p(2.12, 1.275, 0.785, 0.63, 0.37, 0.21).

^e 1s(5.3, 2.443), 2s(5.3, 2.443), 3s(2.443), 3d(1.0), 5d(1.762, 0.98, 0.60, 0.404).

^f 1s(2.944), 3s(9.546, 4.3055, 2.9228), 4f(0.7859), 6f(1.473, 0.8382, 0.5093, 0.37).

basis set, allowing also configurations such as $p_0 p'_0 p_{+1}$, and then only an L_z projection is applied. Since this is an FCI, the solution of the secular equation should find the remaining L^2 symmetry. A third type of CI, CI3, was also performed, where in addition an L^2 projection was applied to CI2. This reduces the number of configurations since some are annihilated and others become identical. As an example, the number of configurations for basis b in table 2 was reduced from 330 to 205. The CI2 and CI3 calculations produced identical energies and HFS expectation values within the numerical accuracy of the calculations.

4. Discussion

In table 3, we present the natural spin-orbital occupation numbers obtained from the first-order reduced density matrix for the SOSCF, PGSO and FCI wavefunctions computed in the same basis set. The PGSO and SOSCF values are quite similar, but the former are nearer the FCI values. The differences follow the general trend that a decrease in large occupation numbers and an increase in small ones is the normal behaviour as the correlation in a wavefunction is increased. It can be noted that, neglecting the valence orbital, the occupation numbers for the PGSO function for Li^+ are much closer to the accurate (FCI) occupation numbers for Li than either the SOSCF or the PGSO ones for the neutral

Table 3. Occupation numbers from NSO analysis of different wavefunctions for Li 2²S and 2²P and Li⁺ 1S.

2 ² S	PGSO; Li ⁺ ^a	SOSCF	PGSO	FCI (112 CI)
s α	—	0.999999	0.999994	0.999993379
s α	0.998512	0.998654	0.998649	0.998537199
s β	0.998512	0.998654	0.998644	0.998533796
s α	0.001459	0.001346	0.001355	0.001433150
s β	0.001459	0.001345	0.001352	0.001428369
s α	0.000024	0.000001	0.000004	0.000032339
s β	0.000024	—	0.000002	0.000033029
s α	—	—	4×10^{-7}	0.000003364
s β	—	—	2×10^{-8}	0.000003965
s α	—	—	10^{-10}	0.000005666
s β	—	—	10^{-11}	0.000008366
s β	—	—	10^{-12}	0.000000006
2 ² P	PGSO; Li ⁺ ^a	SOSCF ^b	PGSO	FCI (80 CI)
p $+\alpha$	—	0.999999	0.999977	0.999866520
s α	0.998512	0.998599	0.998590	0.998400108
s β	0.998512	0.998598	0.998572	0.998429793
s α	0.001459	0.001402	0.001423	0.001571642
s β	0.001459	0.001401	0.001410	0.001489442
s α	0.000024	—	0.000005	0.000069007
s β	0.000024	—	10^{-9}	0.000036108
s α	—	—	10^{-9}	0.000002179
s β	—	—	10^{-12}	0.000001721
p $+\beta$	—	0.000001	0.000014	0.000042836
p $+\alpha$	—	—	0.000005	0.000089600
p $+\beta$	—	—	0.000003	0.000000099

^a Lunell (1970).^b Lunell (1973).**Table 4.** Hyperfine-structure parameters for Li (au). The SOSCF, PGSO and FCI results were obtained using the same basis set for a given state.

System	Method	f	a_i	Reference
Li 2 ² S	RHF	2.095	0.0	Sachs (1960)
	SOSCF	2.849	0.0	Kaldor and Harris (1969), Ladner and Goddard (1969)
	PGSO	2.802	0.0	This paper
	FCI (112 CI)	2.801	0.0	This paper
	Experiment	2.906		Kusch and Taub (1949)
Li 2 ² P	RHF	0.0	0.05856	Goodings (1961)
	SOSCF	-0.2132	0.05876	Lunell (1973)
	PGSO	-0.2243	0.05926	This paper
	Radial FCI (80 CI)	-0.2306	0.06070	This paper
	Experiment	-0.2128	0.06258	Lyons and Das (1970)

atom. This illustrates the fact that the PGSO wavefunction for the ion gives a better description of the radial correlation in the core than the PGSO function for the atom, as discussed in § 3.

Comparing the energies in tables 1 and 2, we find that for Li 2^2S , SOSCF obtains 93.6% of the correlation energy, and PGSO 93.8%, where the correlation energy is here understood as the difference between the FCI (CI1) and RHF energies within this basis set. These are radial correlation energies, since the basis set contains only s functions. For Li 2^2P , the figures are 91.8% and 92.4%, respectively, and these are also radial correlation energies. The total correlation energy for this basis set obtained from an FCI calculation with angular correlation included (CI2) consists of 64.8% radial correlation and 35.2% angular correlation.

Turning to the Fermi contact term, which is given in tables 2 and 4, one can note that for both the 2^2S and 2^2P states the SOSCF values agree somewhat better with experiment than either the PGSO or the FCI results, which on the other hand are relatively close to each other. One can thus see that a full CI calculation within a certain basis, even though it necessarily must yield a better energy than other methods that are defined within the same basis set such as RHF, SOSCF or PGSO, not necessarily gives better results for expectation values, such as the Fermi contact term. Whether the good agreement between the SOSCF results and experiment should be considered as caused by a fortuitous cancellation of errors or as a more deep-rooted optimal property of the method can only be decided after a closer analysis.

For the orbital term, which is not so sensitive to the details of the wavefunction, one obtains an improvement for the 2^2P state between the different methods which essentially follows the improvement in energy. One should note that the improvement in a_l which is obtained with general spin orbitals is quite noticeable, which is also the case for the energy of the 2^2P state, where the improvement is more than three times larger than in the 2^2S state. This is reflected also in the eigenvalue spectrum for the natural spin orbitals, which is much more altered for the 2^2P state than the 2^2S state (cf table 3).

5. Conclusions

In the applications considered in this paper the spin-optimized SCF method and the PHF method with general spin orbitals give rather similar results for both energy and HFS constants, in both cases considerably better than the ordinary restricted Hartree-Fock method, or a straight PHF calculation with pure spin orbitals. Judging from the rather limited numerical experience available, the computational complexity of the two methods also seems rather similar. There is, however, one feature which is likely to cause serious trouble if the methods are to be used for larger systems. This is the occurrence of non-orthogonal orbitals or orbital components, which makes the construction of determinantal matrix elements much more time-consuming than with orthogonal orbitals. These difficulties increase severely as the number of electrons, N , increases, because matrix element evaluation requires the determination of overlap matrix co-factors, which at best can be done with the N^3 Cholesky decomposition (Wilkinson 1965). Since this non-orthogonality is fundamental to the methods, it seems rather difficult to circumvent whatever type of computational method is used for the determination of the wavefunctions. The biggest system which so far has been treated with the SOSCF system is the nitrogen atom, with seven electrons (Kaldor 1970).

It should also be mentioned that the convergence of the iterative method described in § 2 was very slow in the PGSO case, typically of the order 10^{-6} au per iteration, except in the first few iterations, and was not improved by any of the extrapolation methods

that were tried. The present calculations may not, however, be representative in this respect, since the same iterative method has been used successfully in other connections (see eg Mayer 1974).

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References

- Goodings D A 1961 *Phys. Rev.* **123** 1706–14
Hameed S, Hui S S, Musher J I and Schulman J M 1969 *J. Chem. Phys.* **51** 502–8
Kaldor U 1970 *Phys. Rev. A* **1** 1586–92
Kaldor U and Harris F E 1969 *Phys. Rev.* **183** 1–7
Kotani M 1958 *Colloq. Int. Centre Natl. Rech. Sci., Paris* **82** 39–47
Kusch P and Taub H 1949 *Phys. Rev.* **75** 1477–80
Ladner R C and Goddard W A III 1969 *J. Chem. Phys.* **51** 1073
Löwdin P O 1955 *Phys. Rev.* **97** 1474, 1490, 1509–20
Lunell S 1968 *Phys. Rev.* **173** 85–93
—— 1970 *Phys. Rev. A* **1** 360–9
—— 1972 *Chem. Phys. Lett.* **13** 93–6
—— 1973 *Phys. Rev. A* **7** 1229–43
Lyons J D and Das T P 1970 *Phys. Rev. A* **2** 2250–9
Mayer I 1974 *Int. J. Quant. Chem.* **8** 363–72
Roothaan C C J, Sachs L M and Weiss A W 1960 *Rev. Mod. Phys.* **32** 186–94
Sachs L M 1960 *Phys. Rev.* **117** 1504–6
Schaefer H F III, Klemm R A and Harris F E 1968 *Phys. Rev.* **176** 49–58
Scherr C W, Silverman J N and Matsen F A 1962 *Phys. Rev.* **127** 830–7
Weiss A W 1963 *Astrophys. J.* **138** 1262–76
Wilkinson J H 1965 *The Algebraic Eigenvalue Problem* (Oxford: Clarendon Press)