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Lithium atom spin density from the Hiller–Sucher–Feinberg identity

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Summary. The electronic spin density, which determines the observed Fermi contact hyperfine splitting, is usually represented by a delta function operator at the nucleus. Approximate wavefunctions determined by overall energetic considerations may show large errors for such a highly localized property. Hiller, Sucher, and Feinberg (HSF) have shown that the delta function operator can be replaced by a global operator. The possibility that this may lead to an improved method for calculation of the spin density is examined for the ground and first excited states of the lithium atom. Particular attention is given to simple spin polarization wavefunctions that provide the leading contributions to the spin density. It is found that the delta function and HSF formulations give very nearly the same results when the wavefunctions are determined by essentially exact numerical methods. However, the HSF approach shows clear advantages in calculations carried out with finite Slater or contracted Gaussian type basis sets.

Key words: Spin density – Hyperfine coupling constant – Lithium atom – Hiller–Sucher–Feinberg identity – Slater basis sets – Contracted Gaussian basis sets

Introduction

Theoretical calculation of Fermi contact hyperfine splitting is an important yet difficult problem. The observed hyperfine coupling constant for a magnetic nucleus is proportional to $q(0)$, the electronic spin density at the nucleus, i.e., $\rho_\alpha(0) - \rho_\beta(0)$. This can be expressed as an expectation value over the normalized electronic wavefunction Ψ by using the delta function operator as

$$q^\delta(0) = \langle \Psi | \sum_i \delta(r_i) 2 s_{zi} | \Psi \rangle,$$

where summation is carried out over all electrons i, with eigenvalues of the operator s_{zi} being $+1/2$ for α- and $-1/2$ for β-spin electrons (LS coupling is assumed throughout this work). However, in practice this formulation is subject to considerable error since approximate wavefunctions are usually determined by methods designed to accurately represent global properties of the exact wavefunction, i.e., energy or moments, and may still be inaccurate for such a highly localized property as the amplitude at a nucleus.

Hiller, Sucher, and Feinberg (HSF) have recently [1] demonstrated that the localized delta function operator may be replaced by a global operator. Sucher and Drachman [2] and Harriman [3] have pointed out the extension of this idea to determination of spin density. These works show that the spin density can alternatively be obtained from the expression

$$q^{\mathrm{HSF}}(0) = \frac{1}{2\pi}\langle\Psi|\sum_i \left(\frac{\partial V}{\partial r_i} - \frac{L_i^2}{r_i^3}\right) 2s_{zi}|\Psi\rangle,$$

where V is the potential energy operator appearing in the total nonrelativistic Hamiltonian and L_i^2 is the total orbital angular momentum operator for the ith electron. When evaluated with an exact eigenfunction of the total Hamiltonian, $q^{\delta}(0)$ and $q^{\mathrm{HSF}}(0)$ give identical results. For an approximate wavefunction, the use of a global operator in $q^{\mathrm{HSF}}(0)$ may give an improved calculation of hyperfine splitting. Balancing this potential advantage is the drawback that the HSF formulation is more complicated to implement than the delta function, particularly since difficult two-electron terms appear in the potential energy part of the operator.

The HSF formulation has been tested in several previous spin density studies. For the hydrogen atom approximated with various Gaussian basis sets, HSF expectation values showed [3] errors smaller by an order of magnitude or more than those from the traditional delta function calculation of $q(0)$. For the ground state of lithium atom treated by a sequence of configuration interaction wavefunctions based on Slater type orbitals [4], $q^{\mathrm{HSF}}(0)$ had consistently lower errors than $q^{\delta}(0)$, and HSF also showed much improved convergence behavior with respect to enlargement of the configuration list. It has been proven [5] that $q^{\delta}(0)$ and $q^{\mathrm{HSF}}(0)$ give identical results within the unrestricted Hartree–Fock (UHF) method, provided that the exact UHF wavefunction is used. In the same work [5], calculations on excited helium and ground state lithium, nitrogen, sodium, and phosphorous atoms using the UHF method approximated with Slater type orbitals showed generally better results with HSF than with the delta function. Calculations on the ground state first-row atoms boron, carbon, nitrogen, oxygen, and fluorine and on methyl radical using the UHF method with Gaussian type orbitals [6] gave mixed behavior, with $q^{\mathrm{HSF}}(0)$ most often but not always agreeing better than $q^{\delta}(0)$ with the exact numerical UHF results. HSF was also found [7] to be much superior to the delta function in small Gaussian basis set treatments of H_2^+. For BeH radical, singles plus doubles configuration interaction calculations with Gaussian basis sets [7, 8] showed good performance for HSF spin densities, but unfortunately no direct comparisons with delta function results were provided.

Cioslowski and Challacombe [9] have recently shown that use of the HSF identity to determine the charge density at all points in space may lead to a total density that asymptotically falls off too slowly to be integrable. A similar statement will apply to the spin density. This is not a concern for contact spin density calculations in atoms, as in this work, since we are considering only the amplitude at the nucleus. Whether or not this will have an adverse effect in calculations on large polyatomic radicals remains to be seen.

It may be noted that most of the previous studies reviewed above have utilized UHF wavefunctions. However, UHF spin densities do not agree well with experiment for many atomic [10] and molecular [11] systems, even with spin projection modifications [11]. Closely related spin polarization (SP) wavefunctions can be evaluated by augmenting spin-restricted open-shell Hartree–Fock (ROHF) configurations with single-excitation configuration interaction (SCI). By not attempting to consider the more complicated effects of dynamical electron correlation, this approach retains the virtues of simplicity of interpretation and ease of evaluation. Such SP wavefunctions have shown considerable promise for delta function evaluation of the spin density in various atomic [12–14] and molecular [11, 14, 15] applications. It is therefore of interest to examine the accuracy of HSF spin densities in connection with SP wavefunctions. This work is the first step in a planned comprehensive study of that topic.

We treat here the ground ^{2}S and first excited ^{2}P states of the lithium atom. To determine the inherent accuracy obtainable within the simple SP wavefunction model, without ambiguities arising from questions of basis set incompleteness, we first evaluate the wavefunctions with essentially exact numerical grid methods. Then basis set considerations are examined, both with Slater and contracted Gaussian type orbital (STO and CGTO) expansions.

It is not necessary to review here the huge number of previous delta function spin density calculations on lithium. A comprehensive bibliography of ground state determinations carried out previous to about 1973 is available [16]. Leading references to more recent studies on both the ground and first excited states may be found in the report by Sundholm and Olsen [17], which describes the most ambitious multiconfigurational calculations undertaken to date.

Wavefunctions

The ROHF wavefunction for the lithium atom ground state is a single determinant of the form

$$\Psi^{\mathrm{ROHF}} = |1s\,1s\,2s\,\alpha\beta\alpha|,$$

where $|\ldots|$ implies antisymmetrization. The core pair of electrons are constrained to occupy identical $1s$ spatial orbitals. The $1s$ and $2s$ orbitals are freely taken as mutually orthonormal and are determined by a self-consistent-field (SCF) optimization to minimize the total electronic energy [18]. The “direct” contribution to the total spin density is defined here to be simply the result determined from the ROHF wavefunction alone. For the delta function this reduces to simply $\{2s(0)\}^2$, which is clearly the direct contribution solely due to the unpaired electron.

Indirect contributions from the core electrons arise from spin polarization, which is introduced in this context by adding another configuration to the wavefunction [19]

$$\Psi^{\mathrm{SP-SCI}} = C_0\,\Psi^{\mathrm{ROHF}} + C_1\,\Psi^{S}.$$

Here Ψ^S corresponds to a $1s \rightarrow s^*$ single excitation

$$\Psi^S = |1s\,s^*\,2s\{2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha\}/\sqrt{6}|$$

and C_0, C_1 are linear variational coefficients. In practice, the normalized s^* spin polarization orbital may be originally produced as a linear combination of all the

Table 1. Spin densities determined numerically for ^{2}S ground and ^{2}P excited states of lithium atom

State	$q^{\delta}(0)$			$q^{\mathrm{HSF}}(0)$			$q(0)$
	Direct	Spin pol	Total	Direct	Spin pol	Total	Expt
^{2}S	0.1666	0.0516	0.2182	0.1741	0.0449	0.2191	0.2313[a]
^{2}P	0.0000	−0.0161	−0.0161	−0.0013	−0.0151	−0.0163	−0.0170[b]

[a] Ref. [23]
[b] Ref. [25]

virtual orbitals available within the given basis set, after which it may easily be collapsed to the simpler single configuration form indicated above. The other possible independent doublet spin coupling for the *1s* → *s** single excitation is expected to make only a small contribution due to Brillouin's theorem [20] and so is neglected here. We define here the spin polarization contribution to the spin density to be simply the difference between the full value obtained from the SP–SCI wavefunction and the direct contribution from the ROHF wavefunction.

Here, and throughout the remainder of this paper, ^2P excited state wavefunctions can be obtained from the ^2S ground state case by simply substituting *2p* for the *2s* orbital. Since *2p* has a node at the nucleus, the delta function approach gives a direct contribution of exactly zero for the excited state and the full SP–SCI value of the spin density is then due only to spin polarization effects.

A further refinement can be made to the excited state (but not the ground state due to spatial symmetry considerations) by adding another configuration to describe orbital polarization

$$\Psi^{\mathrm{SOP-SCI}} = C_0 \Psi^{\mathrm{ROHF}} + C_1 \Psi^S + C_2 \Psi^d,$$

where Ψ^d corresponds to a *1s* → d^* single excitation

$$\Psi^d = |P\{1s\, d^*\, 2p\}\, \{2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha/\sqrt{6}\}|.$$

Here the operator P projects the spatial orbital product into an L^2 eigenfunction with $L = 1$. In principle, still another orbital polarization configuration can contribute, corresponding to the other possible spin coupling of the three "unpaired" electrons in Ψ^d. However, explicit testing has shown its coefficient to be nearly two orders of magnitude smaller than C_2, so the other possible orbital polarization configuration is neglected in this work.

Essentially exact numerical wavefunctions were determined with Fisher's program [21] and additional programs were written to numerically evaluate the relevant HSF operator integrals. For the case of finite STO and CGTO basis sets, wavefunctions were obtained with the MOLE program [22]. Additional programs were written to analytically evaluate atomic integrals for the HSF operator over STO and CGTO functions. The two electron part of the HSF operator was evaluated through expansion of $1/r_{12}$ in spherical harmonics. Full details of each basis set are given below in connection with discussion of the corresponding results.

All spin densities in this paper are given in atomic units.

Results and discussion

Numerical calculations

As a test of the wavefunction model, exact numerically determined spin densities are compared to experiment in Table 1. For the ^{2}S ground state, the direct ROHF contribution provides a substantial fraction of the total. The spin polarization corrections included in SP–SCI give significant additional contributions that then lead to agreement within 5–6% of experiment, with HSF performing slightly better than the delta function. For the ^{2}P excited state, ROHF gives a result of exactly zero with the delta function and a nonzero but still very small result with HSF. With spin polarization included, the excited state results agree within 4–5% of experiment with HSF again slightly better than the delta function.

These results are very close to multiconfigurational SCF numerical results both for the ground and excited state. In these SP–MCSCF calculations the *1s* and *2s* orbitals were variationally optimized along with the s^* orbital, rather than carried over from ROHF. For the ground state the delta function result changes 1% from 0.2182 for SP–SCI to 0.2210 for SP–MCSCF, and HSF changes 1% from 0.2191 to 0.2216. Very small changes are found for the excited state, the delta function result remaining at −0.0161 and HSF changing from −0.0163 to − 0.0164.

It is also of some interest to examine the individual terms that contribute to yield the net HSF spin density with the SP–SCI wavefunction. For the ^{2}S state, 0.2519 comes from the one-electron part of V, a smaller −0.0329 from the two-electron part of V, and exactly zero from the $\boldsymbol{L}^2$ term. The net result for the ground state is then dominated by the contribution from the one-electron part of V. for the ^{2}P state, 0.0316 comes from the one-electron part of V, −0.0293 from the two-electron part of V, and −0.0186 from the $\boldsymbol{L}^2$ term. Here the contributions from the one- and two-electron parts of V nearly cancel one another and the net result for the excited state is close to that from just the $\boldsymbol{L}^2$ term.

Orbital polarization corrections were also evaluated for the ^{2}P state using the SOP–SCI wavefunction, leading to final results of −0.0158 for the delta function and −0.0161 for HSF. Compared to SP–SCI, this represents slightly worse agreement with experiment for both delta function and HSF approaches, and HSF remains a little closer to experiment than the delta function. However, in both cases the spin density correction due to orbital polarization is very small, about 2%, and consequently will not be considered any further in the remainder of this paper.

Slater basis sets

To evaluate the efficacy of various finite basis sets, it is most meaningful to compare with the corresponding numerical results rather than with experiment. This removes attention from the inherent accuracy of the wavefunction model, which has already been assessed above, and allows more immediate comparison to the limiting values that would be obtained if a complete (infinite) one-particle basis set could be used.

First we consider the results in Table 2 for the ^{2}S ground state obtained with STO basis sets. The smallest set, abbreviated [4*s*], is the double zeta ($1s, 1s', 2s, 2s'$) set with exponents optimized for the ROHF ground state energy by Clementi [26]. With this, the delta function approach has an error of less than 1% in the direct contribution but has a larger 13% error in the spin polarization contribution that leads to a net 3% error in the total result. The HSF approach is nearly exact

Table 2. Spin densities with STO basis sets for ^{2}S ground state of lithium atom

Basis set	$q^{\delta}(0)$			$q^{\mathrm{HSF}}(0)$		
	Direct	Spin pol	Total	Direct	Spin pol	Total
[4*s*]	0.1675	0.0582	0.2258	0.1742	0.0459	0.2201
[6*s*]	0.1674	0.0571	0.2246	0.1743	0.0457	0.2200
[10*s*]	0.1666	0.0523	0.2189	0.1741	0.0450	0.2191
[8*s*]	0.1667	0.0516	0.2183	0.1741	0.0449	0.2190
Numerical	0.1666	0.0516	0.2182	0.1741	0.0449	0.2191

Table 3. SP–SCI spin densities with STO basis sets for ^{2}P excited state of lithium atom

Basis set	$q^{\delta}(0)$	$q^{\mathrm{HSF}}(0)$
[2*s*2*p*]	−0.0286	−0.0212
[3*s*2*p*]	−0.0160	−0.0144
[2*s*4*p*]	−0.0149	−0.0106
[4*s*6*p*]	−0.0196	−0.0174
[6*s*6*p*]	−0.0165	−0.0164
[4*s*5*p*]	−0.0152	−0.0154
Numerical	−0.0161	−0.0163

for the direct contribution and has only a small 2% error in the spin polarization contribution that leads to a net error of well under 1% in the total result. Compared to the [4*s*] set, the larger ($1s, 1s', 2s, 2s', 2s'', 2s'''$) set [27], abbreviated [6*s*], treats the core region in nearly the same way while providing an improved description of the valence region. The spin density results, however, are changed very little.

This suggests that further improvements should be sought in the core region, or perhaps the very diffuse part of the valence space. Accordingly, a large [10*s*] basis was constructed by augmenting the [6*s*] basis with both tight and diffuse *1s* and *2s* functions, the exponents being determined by geometric continuation of the nearest exponents found in the [6*s*] set. This is seen to bring the delta function results into very close agreement with the numerical ones, and to make the HSF results essentially exact. Finally, a somewhat different ($1s, 3s, 3s', 3s'', 3s''', 3s'''', 3s''''', 4s$) set [28], abbreviated [8*s*], that was constrained to satisfy the nuclear cusp condition and optimized specifically for delta function spin density calculation of the ground state, was tested. This leads to essentially exact results for both formulations.

Overall, the STO spin densities for the ground state are in very good to excellent agreement with the numerical ones, and HSF generally performs better than the delta function.

Spin densities for the ^{2}P excited state obtained with STO basis sets are given in Table 3. No ROHF results are listed since, as discussed above, they are exactly zero for the delta function and are always very small (less than $|-0.003|$) for HSF. Analogs of the above described [4*s*], [6*s*], and [10*s*] sets, abbreviated [2*s*2*p*], [2*s*4*p*], and [4*s*6*p*], respectively, were generated by simply replacing all the *2s* with *2p* functions of the same exponent. The [2*s*2*p*] set is seen to give a huge 78% error with the delta function and a large 30% error with HSF. Improvement of the *p* space description with the larger [2*s*4*p*] basis leads to a smaller −7% error with the delta function but a still large −35% error with HSF. Further improvement of the both the *s* and *p* space descriptions with the [4*s*6*p*] set, however, leads to a larger 22% error for the delta function, indicating that the better performance of [2*s*4*p*] was simply fortuitous, and to a smaller 7% error for HSF.

It is of interest to track down the reason for the poor results obtained with the small [2*s*2*p*] and [2*s*4*p*] sets. Since all the *2s* functions were converted to *2p* in those bases, it was suspected that the problem may be primarily due to an inadequate description of the s^* spin polarization orbital, which is more diffuse than the *1s* orbital that it polarizes. To test this idea, a small [3*s*2*p*] set was constructed [29] that includes one additional *s* function in the outer core-inner valence region. This leads to an essentially exact delta function result, which again is probably fortuitous, and a moderate −12% error with HSF, thus supporting the hypothesis.

The [4*s*6*p*] set was further extended to [6*s*6*p*] by including two even more diffuse *1s* functions, with exponents determined by geometric continuation [30]. This now leads to a small 3% error with the delta function and an essentially exact result with HSF. Finally, a somewhat different ($1s$, $3s$, $3s'$, $3s''$, $2p$, $4p$, $4p'$, $4p''$, $4p'''$) set [28], abbreviated [4*s*5*p*], that was constrained to satisfy the nuclear cusp condition and optimized specifically for delta function spin density calculation of the excited state, was tested. This leads to moderate errors of about −5–6% for both the delta function and HSF formulations.

Overall, the STO spin densities for the excited state range from poor to excellent agreement with the numerical result. HSF again generally performs better than the delta function, with certain accidental exceptions.

Gaussian basis sets

Results for the ^{2}S ground state with CGTO basis sets are given in Table 4. The first four bases examined were from the Pople group. Note that the *p* functions in these bases are irrelevant here, since only the *s* part is probed by ground state calculations with the simple SP–SCI wavefunction. The smallest basis examined is the standard 3-21G split valence set [31]. With this, the delta function approach shows a modest −5% error in the direct contribution but gives a near zero result for the spin polarization correction, leading to a large net −26% error in the total result. With the HSF approach the 3-21G basis shows a significant 16% error in the direct contribution and again gives a near zero result for the spin polarization correction, the former overestimate accidentally leading to a reasonably small −7% error in the total result. Adding diffuse functions to produce the 3-21+G set [32] produces only small changes in any of the results. The 6-31G set [33] is still of split valence quality, but is constructed from a larger number of primitive functions that, in particular, should give an improved description of the ROHF orbitals. However, it gives larger errors in the direct contributions, 17% for the delta function and 19% for HSF, and still essentially zero spin polarization corrections, the overestimated direct contributions again leading to fortuitously small errors of −10% in the delta function and −5% in the HSF total results.

From the near zero spin polarization contributions, it may be surmised that the CGTO basis sets described above are deficient in variational flexibility in the outer core-inner valence region needed for proper description of the s^* orbital. The 6-311G set [34] that was optimized to describe electron correlation effects has been

Table 4. Spin densities with CGTO basis sets for ^{2}S ground state of lithium atom

Basis set	$q^{\delta}(0)$			$q^{\mathrm{HSF}}(0)$		
	Direct	Spin pol	Total	Direct	Spin pol	Total
3-21G	0.1588	0.0016	0.1604	0.2019	0.0022	0.2041
3-21+G	0.1601	0.0016	0.1617	0.2035	0.0022	0.2056
6-31G	0.1954	0.0000	0.1953	0.2071	0.0004	0.2075
6-311G	0.1565	0.0621	0.2186	0.1755	0.0490	0.2245
$(9s) \to [3s]$	0.1801	0.0004	0.1806	0.1844	0.0005	0.1849
$(9s) \to [4s]$	0.1801	0.0459	0.2260	0.1844	0.0406	0.2250
$(10s) \to [4s]$	0.1732	0.0581	0.2313	0.1809	0.0483	0.2292
$(10s) \to [5s]$	0.1720	0.0559	0.2279	0.1790	0.0470	0.2260
Numerical	0.1666	0.0516	0.2182	0.1741	0.0450	0.2191

shown [35] to be of essentially double zeta quality in the s space, and so may be expected to give a better description of this region. For the delta function, it leads to a -6% error in the direct contribution and a much improved but still significant 20% error in the spin polarization correction, these errors accidentally cancelling to give a nearly exact total result. For HSF, it gives a small 1% error in the direct contribution and a modest 9% error in the spin polarization correction, leading to a small 2% error in the total result. This represents a dramatic improvement over the previously examined CGTO bases, with HSF showing somewhat greater reliability in the individual contributions than the delta function.

The Huzinaga $(9s)$ set primitive set [36] was first used as contracted by Dunning to a split valence $[3s]$ basis [37], i.e., $(9s) \to [3s]$. As with the split valence bases examined above, the direct contribution is described reasonably well, with the delta function error being 8% and the HSF error being 6%, but near zero spin polarization contributions are again obtained, leading to errors of -16–17% in the total results. This basis was altered to $(9s) \to [4s]$ by removing the outermost s member from the inner group contraction and allowing it instead to float freely in order to provide additional variational flexibility in the outer core-inner valence region that should allow for a better description of the s^* polarizing orbital. This modification had essentially no effect on the direct contributions but drastically improved the spin polarization corrections to show much improved errors of -10–11%, leading to total results having only 3–4% errors, with HSF performing slightly better than the delta function.

Using Huzinaga's larger $(10s)$ primitive set [36] as contracted by Dunning [38] to form a double zeta $[4s]$ basis, i.e., $(10s) \to [4s]$, improves the direct contributions to have errors of 4% and now overestimates the spin polarization corrections by 12% for the delta function and 7% for HSF, leading to net results having a 6% error for the delta functions and 5% for HSF. Finally, a $(10s) \to [5s]$ basis was constructed by altering the $[4s]$ contraction to remove the outermost s member from the inner group contraction and allowing it instead to float freely. This reduces the direct contribution errors to 3%, the spin polarization correction errors to 8% for the delta function and 5% for HSF, and the errors in the total result to 4% for the delta function and 3% for HSF.

Overall, the CGTO spin densities for the ground state with split valence and related basis sets give unreliable results, especially for the spin polarization contri-

Table 5. SP–SCI spin densities with CGTO basis sets for ^{2}P excited state of lithium atom

Basis set	$q^{\delta}(0)$	$q^{\mathrm{HSF}}(0)$
3-21G	−0.0053	−0.0063
3-21+G	−0.0052	−0.0064
6-31G	−0.0046	−0.0048
6-311G	−0.0172	−0.0162
$(9s4p) \to [3s2p]$	−0.0053	−0.0060
$(9s4p) \to [4s2p]$	−0.0186	−0.0178
$(10s4p) \to [4s2p]$	−0.0181	−0.0168
$(10s4p) \to [5s2p]$	−0.0169	−0.0162
Numerical	−0.0161	−0.0163

bution, but agree well with numerical results with double zeta and larger sets. There are generally only small differences in performance between the delta function and HSF, with HSF being consistently slightly better.

Results for the ^{2}P excited state with CGTO basis sets are given in Table 5. Based on the experience with STO basis sets, *s* functions representing the valence region were retained when treating the excited state, following the usual specifications of these CGTO sets. As with the ground state, the 3-21G, 3-21G+ and 6-31G bases show very large errors in the spin polarization contributions, with HSF being slightly better than the delta function. And again the errors are considerably smaller with 6-311G, being 7% for the delta function and only −1% for HSF.

The Huzinaga $(9s4p)$ set primitive set [36] as contracted by Dunning to a split valence $[3s2p]$ basis [37], i.e., $(9s4p) \to [3s2p]$, also gives very large errors. Altering the *s* space contraction as described above to produce a $(9s4p) \to [4s2p]$ double zeta basis considerably improves the results, with a 16% error in the delta function and a 9% error in HSF. Another $[4s2p]$ double zeta basis was constructed by using *s* functions from Huzinaga's $(10s)$ primitive set [36] as contracted to $[4s]$ by Dunning [38], and including the same *p* functions as just discussed above. This $(10s4p) \to [4s2p]$ set does even better, with a 13% error in the delta function and only a 3% error in HSF. Finally, altering the *s* space contraction of this as previously described to give a basis with more flexibility in the outer core-inner valence region produces a $(10s4p) \to [5s2p]$ set that gives very good results for both formulations, with a 5% error for the delta function and only −0.5% error for HSF.

Overall, the CGTO spin densities for the excited state again give unreliable results with split valence and related basis sets and show moderate to very good agreement with numerical results with double zeta and larger sets. HSF here performs considerably better than the delta function with all the basis sets that are capable of providing reasonable results.

Conclusion

Theoretical considerations show that there is no difference between delta function and HSF results of spin density calculations carried out with either the UHF wavefunction or the exact wavefunction. Numerical results presented in this work further show that they perform almost equally well for lithium atom with ROHF and SP–SCI wavefunctions, HSF being slightly better.

With STO sets, HSF performs consistently better overall than the delta function in both ^2S ground state and ^2P excited state calculations on lithium. With CGTO sets, HSF performs slightly better than the delta function in the ground state and considerably better in the excited state. Although the HSF formulation is clearly no panacea for the difficult problem of spin density determination, these results are sufficiently encouraging that further studies on other first-row atoms in progress, and subsequent studies on molecular free radicals are planned as well.

In conclusion, this study provides a comprehensive comparison of delta function and HSF approaches to contact spin density calculations with spin polarization wavefunctions for lithium atom. The results give some support to the possibility that the HSF formulation will provide a significant advantage over the traditional delta function approach.

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References

1. Hiller J, Sucher J, Feinberg G (1978) Phys Rev A 18:2399
2. Sucher J, Drachman RJ (1979) Phys Rev A 20:424
3. Harriman JE (1980) Int J Quant Chem 17:689
4. Bhatia AK, Sucher J (1980) J Phys B: Atom Molec Phys 13:L409
5. Larsson S (1981) Chem Phys Lett 77:176
6. Ishida K (1986) Int J Quant Chem 30:543 and erratum (1988) in Int J Quant Chem 34:195
7. Ishida K (1989) Chem Phys Lett 158:217
8. Ishida K (1990) Chem Phys Lett 175:133
9. Cioslowski J, Challacombe M (1992) Theor Chim Acta 83:185
10. Bagus PS, Liu B, Schaefer HF (1970) Phys Rev A 2:555
11. Chipman DM (1992) Theor Chim Acta 82:93
12. Schaefer HF, Klemm RA, Harris F (1968) Phys Rev 176:49
13. Chipman DM (1989) Phys Rev A 39:475
14. Chipman DM (1989) J Chem Phys 91:5455
15. Chipman DM (1994) in: Langhoff SR (ed) Quantum mechanical electronic structure calculations with chemical accuracy. Kluwer, Dordrecht, in press
16. Harriman JE (1978) in: Theoretical foundations of electron spin resonance. Academic, New York
17. Sundholm D, Olsen J (1990) Phys Rev A 42:2614
18. Roothaan CCJ (1960) Rev Mod Phys 32:179
19. McConnell HM, Chesnut DB (1958) J Chem Phys 28:107
20. Brilloun L (1934) in: Les Champs 'self-consistents' de Hartree et de Fock. Hermann & Cie, Paris, p 19
21. Fischer CF (1972) Comp Phys Comm 4:107
22. Pendergast P, Hayes EF, Liedtke RC, Schwartz ME, Rothenberg S, Kollman PA (1976) Int J Quant Chem S10:77
23. Beckmann A, Böklen KD, Elke D (1974) Z Phys 270:173; recalculated with improved conversion factors in reference 24
24. King FW (1989) Phys Rev A 40:1735
25. Orth H, Ackermann H, Otten EW (1975) Z Phys A 273:221; recalculated with improved conversion factors in reference 24
26. Clementi E (1964) J Chem Phys 40:1944

27. Clementi E, Roothaan CCJ, Yoshimine M (1962) Phys Rev 127:1618
28. Goddard WA (1968) Phys Rev 176:106
29. The additional *1s* exponent of 0.557 was adjusted to fit the numerically determined s^* polarization orbital. The *2p* exponents of 2.0 and 0.509 that were used are similar to those in the $[2s2p]$ set
30. Additional *1s* exponents of 0.66 and 0.35 were used
31. Binkley JS, Pople JA, Hehre WJ (1980) J Am Chem Soc 102:939
32. Clark T, Chandrasekhar J, Spitznagel GW, Schleyer PvR (1983) J Comp Chem 4:294
33. Dill JD, Pople JA (1975) J Chem Phys 62:2921
34. Krishnan R, Binkley JS, Seeger R, Pople JA (1980) J Chem Phys 72:650
35. Grev RS and Schaefer HF (1989) J Chem Phys 91:7305
36. Huzinaga S (1965) J Chem Phys 42:1293
37. Dunning TH, Hay PJ (1977) in: Schaefer HF (ed) Methods of electronic structure theory. Plenum, New York, p 1
38. Dunning TH (1971) J Chem Phys 55:716