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# Characteristics and some peculiarities of multiconfigurational self-consistent field stationary points of the $\text{Li}^-$ ground state

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We examine in detail the multiconfigurational self-consistent field (MCSCF) energy hypersurface of the ground state of  $\text{Li}^-$  using a previously reported Cartesian Gaussian basis set and several previously used different choices of complete active space (CAS). For many of the CASs we show there are many close-lying (in energy) stationary points that have the correct number of negative eigenvalues in the total Hessian with respect to real variations of the orbital and configurational parameters and correspond to the lowest energy eigenvector in the configuration interaction (CI) which uses the MCSCF orbitals and configurations. These stationary points may be obtained with any of the current, forefront MCSCF codes. More detailed examination of these stationary points shows that some of these are improper and that some do not correspond to the most "desired" stationary point. The presence of two nearby proper, desired MCSCF stationary points with the  $2-3s, 2-3p$  CAS is troubling.

## I. INTRODUCTION

In a multiconfigurational self-consistent field (MCSCF) calculation both the linear configuration state function rotational parameters and the nonlinear orbital rotational parameters are simultaneously optimized.<sup>1-3</sup> The set of MCSCF rotational parameters define a very complicated energy hypersurface, containing in general several stationary points, which may or may not be good representations of the exact eigenstates. In order to have a proper representation of the correct  $N$ th state in energy of a given symmetry, and MCSCF stationary point should fulfill a number of criteria,<sup>3-5</sup> i.e.,

(i) The stationary point must be variationally correct ( $\delta E = 0$ ).

(ii) A multiconfigurational linear response (MCLR) (also known as the multiconfigurational time-dependent Hartree-Fock and the multiconfigurational random phase approximation (MCTDHF/MCRPA)) calculation<sup>6</sup> for electronic transitions to states of the same symmetry as the MCSCF stationary point must be stable (i.e., give all real excitation energies) and have  $N - 1$  negative transition energies.

(iii) The number of negative eigenvalues (index) of the total Hessian (second derivatives matrix) with respect to real variations of both the orbital and the configurational parameters,  $\mathbf{A} - \mathbf{B}$ , must be equal to  $N - 1$ .

(iv) The index of the total Hessian with respect to imaginary variations of both the orbital and the configurational parameters,  $\mathbf{A} + \mathbf{B}$ , must be equal to  $N - 1$ . (Note that  $\mathbf{A} + \mathbf{B}$  is a matrix with all real elements.)

(v) The MCSCF approximation should be the  $N$ th state in energy of a configuration interaction (CI) calculation using the converged MCSCF orbitals and the same configuration state functions (CSFs) defining the MCSCF state expansion (i.e., the MCSCF CI), thus ensuring that the energy is an upper bound.

The close, natural relationship of criteria (i) and (ii) has been noted previously.<sup>3-7</sup> Fulfillment of (ii) also implies that there are a total of  $2N - 2$  negative eigenvalues in the total Hessians with respect to both real and imaginary variations of both the orbital and configurational parameters.<sup>4</sup> For both the lowest and the first excited state of a given symmetry fulfillment of (ii) implies that there are  $N - 1$  negative eigenvalues in each of the total Hessians with respect to real variations and also with respect to imaginary variations of both the orbital and the configurational parameters.<sup>4</sup> It should perhaps also be pointed out that the requirement (iv) for the proper MCSCF stationary point to have  $N - 1$  negative eigenvalues in the total Hessian with respect to imaginary variations of the rotational parameters of both the orbital and configurational parameters is not necessarily related to the introduction of complex orbitals or to actually allowing variations in complex space, but arises naturally from requirement (ii). In fact, for all calculations reported below the orbitals and state expansion coefficients are always real.

The use of limited basis sets and/or of a limited number of CSFs in the MCSCF may lead to cases where there may exist several stationary points [i.e., fulfill criterion (i)] which may or may not fulfill all five of the above criteria.<sup>5</sup> Stationary points which do not meet all five criteria (i.e., improper stationary points) should, in general, be discarded. Subsequent use of the orbitals obtained from an improper MCSCF stationary point in, for example, multiconfigura-

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tional linear response, large scale CI, or multireference coupled cluster can give misleading or erroneous results.<sup>5</sup> Of course, in the limit of a subsequent full CI the results are independent of the orbital choice; however, even the largest full CI calculations to date have been limited to "benchmark" studies of fairly small atoms or molecules.<sup>8-10</sup>

MCSCF stationary points reported in the literature are not examined, in general, for all five aforementioned criteria [especially, criteria (ii) and (iv) are not usually examined]. Apparently no forefront MCSCF program monitors or controls all of these criteria during or after convergence. Forefront MCSCF programs apparently monitor only criteria (i) and usually (iii) and (v). Hence, stationary points may often be obtained which upon examination would not fulfill criteria (ii) and/or (iv) and, hence, should be discarded. Of course, many stationary points are also obtained with these forefront programs which fulfill all of (i)–(v) as well.

The occurrence of stationary points which, are variationally correct [criterion (i)], have the correct number of negative eigenvalues in  $\mathbf{A} - \mathbf{B}$  [criterion (iii)], and are the correct state in the corresponding MCSCF CI [criterion (v)], but do not exhibit the correct number negative MCLR transition energies and MCLR stability [criterion (ii)] or do not have the correct number of negative eigenvalues in  $\mathbf{A} + \mathbf{B}$  [criterion (iv)] is now well documented. Several examples follow. At least one stationary point for which the examination of the index of  $\mathbf{A} + \mathbf{B}$  [criterion (iv)] was necessary in order to give a correct choice among different obtained stationary points was reported in a study of  $\text{BeO}^4$  and  $\text{C}_2$ .<sup>5</sup> Recent MCSCF calculations on the ground state of Be using a  $\langle 9s9p5d \rangle$  basis set of contracted Cartesian Gaussian function (CGTOs) and a complete active space (CAS)<sup>11</sup> including the  $2s$ ,  $2p$ ,  $3s$ ,  $3p$ , and  $3d$  orbitals led to several stationary points at higher energies with respect to the proper MCSCF ground state, which had zero negative eigenvalues in  $\mathbf{A} - \mathbf{B}$  and were the lowest states in the corresponding MCSCF CI but exhibited the incorrect (i.e., greater than 0) number of negative eigenvalues in the Hessian with respect to imaginary variations.<sup>9,12</sup> There has been at least one other case reported to us for Be atom where an alternative, higher-lying (in energy) ground state stationary point was reported (with the same basis set and CAS as in Refs. 9 and 12 but obtained with a different forefront MCSCF code which uses a different algorithm). Unfortunately, for this case<sup>13</sup> no further analysis was done with respect to the above five criteria for this stationary point. In addition, Jensen, Jørgensen, Ågren, and Olsen<sup>14</sup> report the presence of two MCSCF "ground states" for HCl. They did not examine criteria (ii) and (iv)<sup>14(b)</sup> (hence, it is possible that one or both of these stationary points may have been "improper"); however, from an overlap analysis of the MCSCF natural orbitals with canonical Hartree–Fock orbitals they determined that in their lower energy stationary point the MCSCF orbitals were correlating the  $2s$  and  $2p$  chlorine orbitals rather than the valence  $3s$  and  $3p$ . Hence, they concluded that the higher-lying MCSCF stationary point was the desired one.

In this paper we will refer to stationary points which do not fulfill criteria (i)–(v) as improper and those which do not fulfill other criteria (such as the overlap criteria above

for HCl) as undesired. Unwanted stationary points can be proper but undesired (as shown below), improper but with desired characteristics (also shown below), and improper and undesired. Sought after stationary points should be both proper and desired. Other obtained stationary points should be rejected.

Different stationary points may be obtained, for example, from using different initial guesses for the orbitals. Different MCSCF algorithms may also result in convergence to different stationary points. (Note that use of different initial orbital guesses and/or different MCSCF algorithms frequently may not result with different obtained stationary points as well.) However, as noted above, no current MCSCF algorithm<sup>1-3,15-19</sup> apparently monitors or controls (ii) and (iv) so all of the current algorithms can converge to improper stationary points as well as to proper stationary points. All current forefront MCSCF codes may also converge to undesired as well as to desired stationary points.

There have been two recent methods proposed for choosing initial guess orbitals. One of these<sup>14</sup> is based on the use of second-order Møller–Plesset perturbation (MP2) theory natural orbitals (NOs). As we show below, this procedure apparently leads to an improper stationary point in  $\text{Li}^-$  for case of two active electrons in a  $2-3s$ ,  $2-3p$  complete active space. This may perhaps be expected since MP2 is inherently single configuration based. A second method uses UHF natural orbitals.<sup>20</sup> This technique has only limited applicability (e.g., it cannot be reasonably used for the  $^1\text{S}$  ground states in  $\text{Li}^-$  and Be) and may be most useful where there is simple bond breaking or formation.

The most reliable method we have found for obtaining a proper, desired stationary point is to use a systematic procedure which progresses from a proper, desired SCF point and then to a proper, desired MCSCF point that includes all important nondynamical correlation effects. Nonenergy changing orbital transformations are performed at each stationary point to define the orbitals. Larger MCSCF calculations are then undertaken using the smaller MCSCF transformed occupied and transformed virtual orbitals as initial guess orbitals.

The purpose of the present paper is to report and examine several MCSCF stationary points which may or may not fulfill all the five criteria above. All of these MCSCF stationary points have *real* orbitals and *real* state expansion coefficients. These stationary points fulfill (i), (iii), and (v) above and, hence, without a more detailed and careful examination of their other characteristics [(ii) and (iv)] may be easily mistaken to be proper MCSCF stationary points. We find that in addition to the five criteria listed above a simple analysis of the orbital size, i.e.,  $\langle r^2 \rangle$ , will eliminate most of the remaining undesired stationary points. In order to perform the  $\langle r^2 \rangle$  orbital analysis we use a physically relevant, nonenergy changing transformation on the MCSCF orbitals. Transformations such as described below are necessary to uniquely define the MCSCF orbitals within arbitrary, energy conserving rotations. This  $\langle r^2 \rangle$  analysis is similar to the criteria previously used by Jensen *et al.*<sup>14</sup> as noted above who instead examined the overlap of the MCSCF natural orbitals with canonical Hartree–Fock orbitals to elimi-

nate one of their ground state stationary points in  $\text{HCl}$ .<sup>14</sup>

$\text{Li}^-$  has been recently the object of a great deal of interest, due especially to the strong multiconfigurational nature of the system, whose ground state shows a mixing of the  $(1s)^2(2s)^2$  and  $(1s)^2(2p)^2$  configurations even greater than for the isoelectronic Be atom. Until the very recent paper by Ågren, Olsen, Jensen, and Jørgensen,<sup>23</sup> a reliable value of the static electronic dipole polarizability of  $\text{Li}^-$  could not be found in the literature. Ågren *et al.* performed a MCLR study of both the static and dynamic polarizabilities of  $\text{Li}^-$  and compared their results with the corresponding full CI (FCI) numbers. Their final value for the static electric dipole polarizability ( $798 \pm 5$  a.u.) is by far the most accurate value to date, and their work confirms the ability of MCLR, in most cases, to accurately mimic FCI results with comparatively limited computational efforts. Canuto, Duch, Geertsen, Müller-Plathe, Oddershede, and Scuseria<sup>24</sup> calculated the polarizability of  $\text{Li}^-$  in the coupled cluster polarization propagator approximation (CCSDT-1a PPA) as 547 a.u. and estimated this value was 50–100 a.u. too low (i.e., that the “correct”  $\alpha$  was 597–647 a.u.). Since Ågren *et al.*<sup>23</sup> in their FCI calculations ( $\alpha = 798$  a.u.) use the best basis set of Ref. 24 this shows the difficulty in doing reliable energy and property calculations for certain highly correlated atoms and molecules even with coupled cluster approaches. Perhaps a difficulty is that the coupled cluster method is inherently single configuration based, i.e., coupled cluster uses SCF orbitals and only one principal configuration (although initial multiconfigurational coupled cluster programs and results are starting to become available).

While independently carrying out some of the same calculations, using the basis sets introduced by Canuto *et al.*<sup>24</sup> and adopted by Ågren *et al.*,<sup>23</sup> we noticed some peculiarities for a certain number of the obtained MCSCF stationary points for “ground state”  $\text{Li}^-$ . For some well defined choices of the CAS for the MCSCF optimization, convergence was obtained to stationary points which, upon characterization, proved to be variationally correct [criterion (i)], to exhibit the expected number of negative eigenvalues in the Hessian with respect to real variations [criterion (iii)], and to correspond to the lowest energy MCSCF CI eigenvector [criterion (v)] but would not satisfy the above mentioned criteria (ii) and (iv) showing several instabilities in the MCLR calculation for the ground state, symmetry, i.e.,  $^1S$ , and an incorrect number of negative eigenvalues in the Hessian with respect to imaginary variations of the orbital and configurational parameters. These same stationary points may be obtained by all of the current, high quality modern MCSCF codes and, in fact, one was reported by Ågren *et al.*<sup>18,23</sup> as a good MCSCF ground state stationary point in their successive series of MCSCF CAS spaces leading to FCI. Furthermore, we obtained several stationary points which had all the characteristics (i)–(v) above for being a proper representation of the ground state but were not the “desired” stationary points since some of the correlating orbitals at convergence correlated primarily the core rather than the valence space as desired. For one CAS choice we even obtain two different proper, desired MCSCF ground state stationary points.

For a given choice of MCSCF configurations these different improper and proper stationary points can be obtained, for example, by simply choosing different initial guesses. Since no current forefront MCSCF program monitors or controls criteria (ii) and (iv) above improper stationary points can be frequently (and usually unknowingly) obtained by all of these programs. Furthermore, only a detailed  $\langle r^{-2} \rangle$ , overlap, or similar orbital analysis can aid in differentiating desired from undesired proper (i.e., that fulfill all five criteria) stationary points.

In the following section we discuss our methods, including the MCSTEP and MCIVO orbital transformations, and we present several of these proper and improper stationary points [all of which, however, fulfill criteria (i), (iii), and (v) above]. In Sec. III we analyze the results. In the final section we conclude and summarize.

## II. CALCULATIONS

In this section we report our observations in the study of some of the MCSCF stationary points of the “ground state” energy hypersurface of  $\text{Li}^-$  using one of the CGTO basis sets introduced by Canuto *et al.*<sup>24</sup> and used by Ågren *et al.*<sup>23</sup> The results we report here uses the basis set called V by Canuto *et al.* and GIII by Ågren *et al.* It is a  $\langle 16s12p4d \rangle$  (76CGTO) fully uncontracted set and information on it may be obtained from Refs. 23 and 24. We have also studied the characteristics of MCSCF stationary points of basis sets GI and GII of Ref. 23 (basis sets I and IV of Ref. 24). However, since the results are analogous for brevity we report only the results from GIII.

Our MCSCF code uses a complete second-order Newton–Raphson algorithm<sup>1–3</sup> which gives rapid convergence to a stationary point with “guaranteed” convergence<sup>25</sup> to the “lowest state” of each symmetry. Convergence (as always) is guaranteed to a stationary point with no negative eigenvalues in  $\mathbf{A} - \mathbf{B}$  (the Hessian with respect to real variations of both the orbital and configurational parameters). All calculations with this code involve only *real* orbitals and *real* state expansion coefficients. The variational correctness of our stationary point and the existence of the correct number of negative eigenvalues in  $\mathbf{A} - \mathbf{B}$  are automatically assured with our MCSCF procedure, i.e., we cannot converge to stationary points which do not fulfill those two requirements [i.e., (i) and (iii)]. The MC linear response [criterion (ii)], the number of negative eigenvalues of  $\mathbf{A} + \mathbf{B}$  [criterion (iv)], and the relative position in energy of the stationary point in a CI calculation within the configuration space defined by the MCSCF configuration state functions [criterion (v)] are monitored after convergence.

Since the first complete second-order MCSCF calculations<sup>1,2</sup> there have been several alternative complete second-order MCSCF schemes developed and used.<sup>3,15–19</sup> Each of these demonstrates quadratic convergence near a stationary point. Apparently none of these procedures monitors or controls the number of negative eigenvalues of the Hessian with respect to imaginary variations [criterion (iv)], the MC linear response [criterion (ii)] or related criteria. All of these MCSCF procedures are expected to be able to converge to the stationary points listed in the tables and there is no valid reason to expect that one certain MCSCF procedure will

preferentially only converge to stationary points which are proper (i.e., fulfill *all* of the five criteria above). However, it is expected that each of these MCSCF procedures may have somewhat different convergence characteristics in the non-local region (i.e., when far from convergence).

The stationary points we obtained are given in Tables I–VIII. Different stationary points for a given configuration choice may be obtained by choosing different initial guesses of orbitals. Of course, different initial guesses may also converge to the same stationary point as well. Also different MCSCF algorithms may, in addition, converge to different stationary points even given the same choice of initial orbital guess. (In addition we have previously shown how it is possible to “walk” from one MCSCF stationary point to another on the energy hypersurface.<sup>5</sup>)

Since a purpose of this paper is to report on and examine the characteristics of the different stationary points in  $\text{Li}^-$  and *not* to compare the effectiveness of different MCSCF algorithms or initial orbital guesses we do not list here in detail our various initial guesses. They were all obtained in a common, straightforward, and simple manner. Many of the same MCSCF stationary points were obtained using several different initial orbital guesses. If desired, these initial guesses may be obtained by contacting one of the authors. A

typical initial guess would be to use the orbitals obtained from an original (smaller) MCSCF and then to choose additional orbitals from the virtual MCSCF space without additional transformations on the original occupied, partially occupied, and virtual MCSCF orbitals.

The procedure we have found to be the most consistently reliable to obtain a proper, desired MCSCF stationary point is to first perform an SCF calculation and then subsequently the simplest MCSCF calculation (using appropriately transformed SCF occupied and virtual orbitals as an initial guess) where all important nondynamical correlation effects are included. More complicated MCSCF calculations can then be carried out using the orbitals from this “simple” MCSCF. It may sometimes be necessary to increase the MCSCF CAS sizes gradually in a stepwise manner. In each step of this process appropriate “defining” orbital transformations are performed.<sup>21,22</sup>

These are separate MCSTEP transformations<sup>21,22</sup> in the original CAS inactive and active subblocks and an MCIVO transformation<sup>22</sup> in the original virtual space. In addition, at each obtained stationary point an analysis is performed to determine that the point is both proper (i.e., fulfill the five above criteria) and desired (fulfill other criteria such as certain orbital  $\langle r^{-2} \rangle$  values). Improper and/or undesired sta-

TABLE I. Analysis of the “ground state”  $\text{Li}^-$  stationary points obtained also by Ågren *et al.* (Ref. 23).

|  | Stationary point |            |            |            |            |
|--|------------------|------------|------------|------------|------------|
|  | A                | B          | C          | E          | F          |
| CAS  | SCF              | 2s2p       | 2–3s,2–3p  | 1–4s,2p    | 1–4s,2–3p  |
| Active Electrons                                   | 0                | 2          | 2          | 4          | 4          |
| MCSCF energy (a.u.)                                | –7.427 947       | –7.452 481 | –7.454 958 | –7.469 792 | –7.491 346 |
| $\Delta(E_{\text{MCSCF}} - E_{\text{SCF}})$ (a.u.) | ...              | –0.024 534 | –0.027 011 | –0.041 845 | –0.063 399 |
| MCLR $^1S$   | 0                | 0          | 0          | 0          | 0          |
| neg. transition energies <sup>a</sup>              |                  |            |            |            |            |
| MCLR $^1S$   | 0                | 0          | 6          | 0          | 0          |
| instabilities <sup>a</sup>                         |                  |            |            |            |            |
| A–B  | 0                | 0          | 0          | 0          | 0          |
| negative eigenvalues <sup>b</sup>                  |                  |            |            |            |            |
| A + B  | 0                | 0          | 6          | 0          | 0          |
| negative eigenvalues <sup>c</sup>                  |                  |            |            |            |            |
| Position in energy                                 | 1                | 1          | 1          | 1          | 1          |
| in MCSCF CI <sup>d</sup>                           |                  |            |            |            |            |
| Proper?  | Yes              | Yes        | No         | Yes        | Yes        |
| MCLR $^1P^0$                                       | 0                | 0          | 0          | 0          | 0          |
| neg. transition energies                           |                  |            |            |            |            |
| MCLR $^1P^0$                                       | 0                | 0          | 10         | 0          | 0          |
| instabilities                                      |                  |            |            |            |            |
| $S_0$ (sum rule) <sup>e</sup> (MCLR)               | 4.0002           | 4.0260     | 4.0242     | 4.0238     | 4.0247     |
| $\alpha$ (a.u.) <sup>f</sup> (MCLR)                | 1198.39          | 622.97     | 804.21     | 805.54     | 803.90     |
| % $1s^2 2s^2$ s                                    | 100              | 87.01      | 86.56      | 86.47      | 86.39      |
| % $1s^2 2p^2$ s                                    | 0                | 12.99      | 11.33      | 11.45      | 11.32      |

<sup>a</sup>To fulfill criterion (ii) the value should be 0.

<sup>b</sup>To fulfill criterion (iii) the value should be 0.

<sup>c</sup>To fulfill criterion (iv) the value should be 0.

<sup>d</sup>To fulfill criterion (v) the value should be 1.

<sup>e</sup>The exact value is 4.

<sup>f</sup>Static polarizability. The full-CI value in this basis set is 797.77 a.u. (see Ref. 23).

<sup>g</sup>Using MCSTEP transformed (Refs. 21 and 22) MCSCF orbitals.

TABLE II. Values of  $\langle r^{-2} \rangle$  (in a.u.<sup>2</sup>) for the orbitals<sup>a</sup> of the stationary points of Table I.

|                  | Stationary point |       |           |         |                    |
|------------------|------------------|-------|-----------|---------|--------------------|
|                  | A                | B     | C         | E       | F                  |
| CAS              | SCF              | 2s2p  | 2-3s,2-3p | 1-4s,2p | 1-4s,2-3p          |
| Active Electrons | 0                | 2     | 2         | 4       | 4                  |
| 1s               | 0.45             | 0.45  | 0.45      | 0.45    | 0.45               |
| 2s               | 43.64            | 33.59 | 40.20     | 40.18   | 40.17              |
| 3s               | ...              | ...   | 70.71     | 70.84   | 70.54              |
| 4s               | ...              | ...   | ...       | 3.05    | 3.04               |
| 2p               | ...              | 31.58 | 35.96     | 32.14   | 31.85              |
| 3p               | ...              | ...   | 47.75     | ...     | 0.72               |
| Desired?         | Yes              | Yes   | Yes       | Yes     | Maybe <sup>b</sup> |

<sup>a</sup> The orbitals used are the MCSTEP transformed (Refs. 21 and 22) MCSCF orbitals (see the text). The SCF orbitals are the canonical Hartree-Fock.

<sup>b</sup> An alternative desired stationary point would perhaps have  $\langle r^{-2} \rangle_{sp}$  in the valence rather than the core region (see the text).

tionary points are rejected and the orbitals are not used as initial guess orbitals in any subsequent MCSCF calculations.

MCSTEP (the multiconfigurational spin tensor electron propagator method)<sup>21</sup> is an *ab initio* technique for efficiently and very accurately directly calculating ionization potentials and electron affinities.<sup>26</sup> The MCSTEP orbital transfor-

mation<sup>21</sup> involves separately diagonalizing the  $\langle 0 | \{a_i^\dagger, H, a_j\} | 0 \rangle$  (where  $|0\rangle$  is the MCSCF stationary point) subblocks for inactive and active orbitals. New orbitals are defined from the eigenvectors. Rotations can separately be performed within a CAS MCSCF inactive orbital and within a CAS MCSCF active orbital space without

TABLE III. Analysis of the "ground state"  $\text{Li}^-$  stationary points: two electrons in a 2-3s, 2-3p CAS.

|  | Stationary point |            |            |            |                 |
|--|------------------|------------|------------|------------|-----------------|
|  | C                | C'         | C''        | C'''       | C <sup>iv</sup> |
| MCSCF energy (a.u.)                                | -7.454 958       | -7.454 965 | -7.454 959 | -7.454 447 | -7.465 922      |
| $\Delta(E_{\text{MCSCF}} - E_{\text{SCF}})$ (a.u.) | -0.027 011       | -0.027 018 | -0.027 012 | -0.026 500 | -0.037 975      |
| MCLR 'S  | 0                | 0          | 0          | 0          | 0               |
| neg. transition energies <sup>a</sup>              |                  |            |            |            |                 |
| MCLR 'S  | 6                | 0          | 0          | 0          | 0               |
| instabilities <sup>a</sup>                         |                  |            |            |            |                 |
| A - B  | 0                | 0          | 0          | 0          | 0               |
| negative eigenvalues <sup>b</sup>                  |                  |            |            |            |                 |
| A + B  | 6                | 0          | 0          | 0          | 0               |
| negative eigenvalues <sup>c</sup>                  |                  |            |            |            |                 |
| Position in energy in MCSCF CI <sup>d</sup>        | 1                | 1          | 1          | 1          | 1               |
| Proper?  | No               | Yes        | Yes        | Yes        | Yes             |
| MCLR 'P <sup>o</sup>                               | 0                | 0          | 0          | 0          | 0               |
| neg. transition energies                           |                  |            |            |            |                 |
| MCLR 'P <sup>o</sup>                               | 10               | 5          | 5          | 3          | 1               |
| instabilities                                      |                  |            |            |            |                 |
| $S_0$ (sum rule) <sup>e</sup> (MCLR)               | 4.0242           | 4.0318     | 4.0436     | 4.3075     | 4.0012          |
| $\alpha$ (a.u.) <sup>f</sup> (MCLR)                | 804.21           | 825.09     | 991.19     | 723.59     | 1199.69         |
| % $1s^2 2s^2 s$                                    | 86.56            | 86.67      | 86.67      | 86.88      | 99.69           |
| % $1s^2 2p^2 s$                                    | 11.33            | 10.85      | 10.84      | 10.45      | 0.16            |

<sup>a</sup> To fulfill criterion (ii) the value should be 0.

<sup>b</sup> To fulfill criterion (iii) the value should be 0.

<sup>c</sup> To fulfill criterion (iv) the value should be 0.

<sup>d</sup> To fulfill criterion (v) the value should be 1.

<sup>e</sup> The exact value is 4.

<sup>f</sup> Static polarizability. The full-CI value in this basis set is 797.77 a.u. (see Ref. 23).

<sup>g</sup> Using MCSTEP transformed (Refs. 21 and 22) MCSCF orbitals.

TABLE IV. Values of  $\langle r^2 \rangle$  (in a.u.<sup>2</sup>) for the orbitals<sup>a</sup> of the stationary points of Table III: two electrons in a 2-3s, 2-3p CAS.

|          | Stationary point |       |       |        |                 |
|----------|------------------|-------|-------|--------|-----------------|
|          | C                | C'    | C''   | C'''   | C <sup>iv</sup> |
| 1s       | 0.45             | 0.45  | 0.45  | 0.45   | 0.76            |
| 2s       | 40.20            | 40.46 | 40.63 | 41.13  | 43.35           |
| 3s       | 70.71            | 83.84 | 74.66 | 450.30 | 2.08            |
| 2p       | 35.96            | 24.69 | 24.89 | 31.96  | 0.34            |
| 3p       | 47.75            | 38.20 | 37.95 | 43.85  | 0.70            |
| Desired? | Yes              | Yes   | Yes   | No     | No              |

<sup>a</sup>The orbitals used are the MCSTEP transformed (Refs. 21 and 22) MCSCF orbitals (see the text).

changing the MCSCF energy; hence, the MCSCF total energy is conserved with this transformation. The eigenvalues of this diagonalization provide a rough (multiconfigurational Koopmans' theorem-like) approximation to the ionization potentials.<sup>21,22</sup> These orbitals become the canonical Hartree-Fock orbitals and the MCSTEP orbital transformation eigenvalues become the Koopmans' theorem orbital energies in the limit of the single configuration SCF.

We use the MCSTEP transformation to define the MCSCF orbitals. Otherwise there is an arbitrariness since the orbitals may be rotated among themselves within the inactive and within active CAS spaces. We use these

MCSTEP transformed MCSCF orbitals whenever properties such as orbital  $\langle r^2 \rangle$  or configurational % are determined. The five criteria defining a proper stationary point are invariant to this MCSTEP transformation of the MCSCF orbitals (or similar rotations separately within the inactive and active orbital spaces). We also may use the MCSTEP transformed orbitals as initial guess orbitals in subsequent MCSCF calculations for fairly reliable convergence to a proper, desired stationary point.

We also perform a multiconfigurational improved virtual orbital (MCIVO) transformation in the original MCSCF virtual space whenever additional orbitals are need-

TABLE V. Analysis of the "ground state"  $\text{Li}^-$  stationary points: two electrons in a 2-3s, 2-3p, 3d CAS.

|  | Stationary point |            |                 |
|--|------------------|------------|-----------------|
|  | D                | D'         | D <sup>iv</sup> |
| MCSCF energy (a.u.)                                | -7.455 002       | -7.455 016 | -7.466 627      |
| $\Delta(E_{\text{MCSCF}} - E_{\text{SCF}})$ (a.u.) | -0.027 055       | -0.027 070 | -0.038 680      |
| MCLR <sup>1</sup> S                                | 0                | 0          | 0               |
| neg. transition energies <sup>a</sup>              |                  |            |                 |
| MCLR <sup>1</sup> S                                | 6                | 0          | 0               |
| instabilities <sup>a</sup>                         |                  |            |                 |
| A-B  | 0                | 0          | 0               |
| negative eigenvalues <sup>b</sup>                  |                  |            |                 |
| A + B  | 6                | 0          | 0               |
| negative eigenvalues <sup>c</sup>                  |                  |            |                 |
| Position in energy in MCSCF CI <sup>d</sup>        | 1                | 1          | 1               |
| Proper?  | No               | Yes        | Yes             |
| MCLR <sup>1</sup> P <sup>o</sup>                   | 0                | 0          | 0               |
| neg. transition energies                           |                  |            |                 |
| MCLR <sup>1</sup> P <sup>o</sup>                   | 5                | 1          | 1               |
| instabilities                                      |                  |            |                 |
| $S_0$ (sum rule) <sup>e</sup> (MCLR)               | 4.0249           | 4.0248     | 4.0018          |
| $\alpha$ (a.u.) <sup>f</sup> (MCLR)                | 802.42           | 802.00     | 1200.05         |
| % $1s^2 2s^2$ <sup>g</sup>                         | 86.80            | 86.89      | 99.68           |
| % $1s^2 2p^2$ <sup>g</sup>                         | 11.08            | 10.66      | 0.15            |

<sup>a</sup>To fulfill criterion (ii) the value should be 0.

<sup>b</sup>To fulfill criterion (iii) the value should be 0.

<sup>c</sup>To fulfill criterion (iv) the value should be 0.

<sup>d</sup>To fulfill criterion (v) the value should be 1.

<sup>e</sup>The exact value is 4.

<sup>f</sup>Static polarizability. The full-CI value in this basis set is 797.77 a.u. (see Ref. 23).

<sup>g</sup>Using MCSTEP transformed (Refs. 21 and 22) MCSCF orbitals.

TABLE VI. Values of  $\langle r^2 \rangle$  (in a.u.<sup>2</sup>) for the orbitals<sup>a</sup> of the stationary points of Table V: two electrons in a 2-3s, 2-3p, 3d CAS.

|          | Stationary point |       |                 |
|----------|------------------|-------|-----------------|
|          | D                | D'    | D <sup>iv</sup> |
| 1s       | 0.45             | 0.45  | 0.74            |
| 2s       | 40.13            | 40.13 | 43.38           |
| 3s       | 70.77            | 71.13 | 2.08            |
| 2p       | 36.15            | 24.82 | 0.33            |
| 3p       | 48.19            | 37.61 | 0.69            |
| 3d       | 36.94            | 37.97 | 1.19            |
| Desired? | Yes              | Yes   | No              |

<sup>a</sup>The orbitals used are the MCSTEP transformed (Refs. 21 and 22) MCSCF orbitals.

ed as initial guess orbitals in a subsequent MCSCF calculation. An electron in an  $n$  electron system in an MCIVO virtual orbital "sees"  $n-1$  rather than  $n$  other electrons. The transformation is obtained by choosing a strongly occupied active orbital as the "hole" orbital, setting the **B** matrix equal

to zero in an MCLR calculation, and allowing all possible single excitations only from the hole orbital to the virtual orbitals. The resulting MCLR vectors define the (MCIVO) virtual orbital transformation. In the limit of an SCF stationary point, the MCIVO reduces to an ordinary IVO calculation.<sup>27</sup> The MCIVO orbitals are, in a sense, the optimal orbitals for describing transitions which are predominantly single excitations.

We choose the additional active initial guess orbitals from the MCIVO orbitals of the desired symmetry with  $\langle r^2 \rangle$  as close as possible but slightly larger than the  $\langle r^2 \rangle$  of the strongly occupied initial guess MCSTEP orbital(s) we primarily wish to correlate. When wishing to correlate primarily the valence space, choosing the additional MCSCF initial guess (MCIVO) orbitals in this way (i.e.,  $\langle r^2 \rangle$  slightly larger than the orbitals we primarily wish to correlate) helps avoid their collapse into the core region on convergence. In practice we use singlet rather than triplet MCIVO orbitals for the additional initial guess orbitals, although experience indicates there is little practical difference in convergence properties.

In a previous paper<sup>22</sup> we noted that the MCSTEP and

TABLE VII. Analysis of the "ground state" Li<sup>-</sup> stationary points with four active electrons.

|   | Stationary Point |            |                |                   |
|---|------------------|------------|----------------|-------------------|
|   | E                | F          | F <sup>v</sup> | F <sup>vi</sup>   |
| CAS   | 1-4s, 2p         | 1-4s, 2-3p | 1-4s, 2-3p     | 1-4s, 2-3p        |
| MCSCF energy (a.u.)                                   | -7.469 792       | -7.491 346 | -7.489 711     | -7.474 133        |
| $\Delta(E_{\text{MCSCF}} - E_{\text{SCF}})$ (a.u.)    | -0.041 845       | -0.063 399 | -0.061 764     | -0.046 186        |
| MCLR <sup>1</sup> S                                   | 0                | 0          | 0              | 0                 |
| neg. transition energies <sup>a</sup>                 |                  |            |                |                   |
| MCLR <sup>1</sup> S instabilities <sup>a</sup>        | 0                | 0          | 0              | 0                 |
| <b>A</b> - <b>B</b> negative eigenvalues <sup>b</sup> | 0                | 0          | 0              | 0                 |
| <b>A</b> + <b>B</b> negative eigenvalues <sup>c</sup> | 0                | 0          | 0              | 0                 |
| Position in energy in MCSCF CI                        | 1                | 1          | 1              | 1                 |
| Proper?   | Yes              | Yes        | Yes            | Yes               |
| MCLR <sup>1</sup> P <sup>0</sup>                      | 0                | 0          | 0              | 0                 |
| neg. transition energies                              |                  |            |                |                   |
| MCLR <sup>1</sup> P <sup>0</sup> instabilities        | 0                | 0          | 0              | 2                 |
| $S_0$ (sum rule) <sup>e</sup> (MCLR)                  | 4.0238           | 4.0247     | 4.0269         | 3.4398            |
| $\alpha$ (a.u.) <sup>f</sup> (MCLR)                   | 805.54           | 803.90     | 619.16         | 2503.06           |
| % 1s <sup>2</sup> 2s <sup>2</sup> s                   | 86.47            | 86.39      | 86.84          | 91.02             |
| % 1s <sup>2</sup> 2p <sup>2</sup> s                   | 11.45            | 11.32      | 10.72          | 0.14 <sup>h</sup> |

<sup>a</sup>To fulfill criterion (ii) the value should be 0.

<sup>b</sup>To fulfill criterion (iii) the value should be 0.

<sup>c</sup>To fulfill criterion (iv) the value should be 0.

<sup>d</sup>To fulfill criterion (v) the value should be 1.

<sup>e</sup>The exact value is 4.

<sup>f</sup>Static polarizability. The full-CI value in this basis set is 797.77 a.u. (see Ref. 23).

<sup>g</sup>Using MCSTEP transformed (Refs. 21 and 22) MCSCF orbitals.

<sup>h</sup>The % 1s<sup>2</sup>4s<sup>2</sup> is 8.21.



TABLE VIII. Values of  $\langle r^2 \rangle$  (in a.u.<sup>2</sup>) for the orbitals<sup>a</sup> of the stationary points of Table VII: four active electrons.

|          | Stationary point |                    |                |                 |
|----------|------------------|--------------------|----------------|-----------------|
|          | E                | F                  | F <sup>v</sup> | F <sup>vi</sup> |
| CAS      | 1-4s, 2p         | 1-4s, 2-3p         | 1-4s, 2-3p     | 1-4s, 2-3p      |
| 1s       | 0.45             | 0.45               | 0.45           | 0.45            |
| 2s       | 40.18            | 40.17              | 33.54          | 68.49           |
| 3s       | 70.84            | 70.53              | 0.85           | 170.87          |
| 4s       | 3.05             | 3.04               | 3.03           | 3.27            |
| 2p       | 32.14            | 31.85              | 31.37          | 0.45            |
| 3p       | ...              | 0.72               | 0.73           | 0.79            |
| Desired? | Yes              | Maybe <sup>b</sup> | No             | No              |

<sup>a</sup>The orbitals used are the MCSTEP transformed (Refs. 21 and 22) MCSCF orbitals (see the text).

<sup>b</sup>An alternative desired stationary point would perhaps have  $\langle r^2 \rangle_{3p}$  in the valence rather than the core region (see the text).

MCIVO orbital transformations together have the effect of concentrating the transition amplitudes in an MCLR/MCTDHF calculation to primarily one amplitude for each vector corresponding to an excitation. However, these orbital transformations do not change the MCLR/MCTDHF transition energies or other response properties (as noted above the MCSCF energy of the reference state is invariant to these orbital transformations as well). Thus these transformed orbitals are, in a sense, optimal for describing low-lying excitations (which are primarily single excitations).

### III. DISCUSSION

In our calculations on  $\text{Li}^-$  we would, in general, like the converged 1s and 2s orbitals to be strongly occupied with  $\langle r^2 \rangle_{1s} \ll \langle r^2 \rangle_{2s}$  and the converged 2p orbital to provide non-dynamical correlation with  $\langle r^2 \rangle_{2p}$  similar to  $\langle r^2 \rangle_{2s}$ . We would like the converged "3s" and the converged "4s" to provide "in-out" correlation for the 2s (i.e.,  $\langle r^2 \rangle_{3s}$  similar to but slightly larger than  $\langle r^2 \rangle_{2s}$ ) and the 1s (i.e.,  $\langle r^2 \rangle_{4s}$  similar to but slightly larger than  $\langle r^2 \rangle_{1s}$ ), respectively.

The "3p" orbital should provide either in-out correlation for the 2p (i.e.,  $\langle r^2 \rangle_{3p}$  similar to but slightly larger than  $\langle r^2 \rangle_{2p}$ ) or "angular" correlation for the 1s (i.e.,  $\langle r^2 \rangle_{3p}$  about the same as  $\langle r^2 \rangle_{1s}$ ). Since in  $\text{Li}^-$  ground state the 2p orbital has an occupation number around 0.1 (i.e., fairly large) it may perhaps be more desired to have the former. Alternatively, it has been argued that the former case is not "balanced" and that instead the 3p should angularly correlate the 1s, e.g., in the 1-4s, 2-3p CAS<sup>28</sup> [for each strongly occupied active orbital a "balanced" CAS has one weakly occupied active orbital of the same symmetry in about the same spatial region (to provide in-out correlation) and has one weakly occupied active orbital with the next higher angular momentum and with about the same  $\langle r^2 \rangle$  value (to provide angular correlation)]. When the 3d is present it should provide angular correlation effects for the 2s and, in particular, the 2p orbitals. Again it has been argued that such

a CAS with a 3d included is not "balanced".<sup>28</sup> We note, however, that the presence of a 3d orbital in the MCSCF CAS for Be was necessary to give the most (and very) accurate MCLR singlet and triplet excitation energies<sup>9</sup> and response properties.<sup>12</sup> In fact, the 2-3s, 2-3p, 3d CAS MCLR results in Be are extraordinarily accurate and mimic the full CI results in the same basis set extremely well.<sup>9,12</sup>

However, it is not the purpose of this paper to debate these possible CAS choices. Instead we wish to focus on characteristics, properties, and peculiarities for  $\text{Li}^-$  ground state stationary points obtained using previously chosen CASs for  $\text{Li}^-$ <sup>23</sup> and  $\text{Be}$ <sup>9,12,13,29</sup> as well.

The MCSCF stationary points A-F in Table I were originally obtained by Ågren *et al.* by using the MCSCF algorithm described first in Ref. 18. They apparently did no further analysis of the stationary points characteristics. We also easily obtained these stationary points by the methods described in the previous section. They all have the correct number of negative eigenvalues (i.e., 0) in the Hessian with respect to real variations, A-B, and the correct position in energy (i.e., lowest) in the CI using the MCSCF configurations and orbitals (MCSCF CI). Thus these stationary points could also be obtained by all other forefront MCSCF codes as well.

The number of negative eigenvalues in the Hessian with respect to imaginary variations, A + B, is correct [i.e., 0; criteria (iv)] in all the stationary points in Table I except for stationary point C (2s-3s, 2p-3p CAS). Stationary point C has six negative eigenvalues in A + B and also six instabilities in the <sup>1</sup>S MCLR. Hence it is an improper MCSCF stationary point since neither criteria (ii) nor (iv) are fulfilled.

Stationary point C also has ten MCLR instabilities in excitations to <sup>1</sup>P<sup>0</sup> states. Contributions from these instabilities are not included in the summations which give the polarizability.<sup>6,23</sup> Hence the C static polarizability,  $\alpha$ , calculated by us and by Ågren *et al.*<sup>23</sup> is too small for this CAS even though the value is fairly close to the full CI result.

We found four stationary points (C'-C<sup>iv</sup> in Table III) with a 2s-3s, 2p-3p CAS which fulfill all the five criterion for being a proper representation of the exact state. By examin-

ing  $\langle r^2 \rangle$  values for these stationary points (Table IV) and comparing with the  $\langle r^2 \rangle$  values for the SCF stationary point A (Table II) all but stationary points C' and C'' can be eliminated as undesired.

The 3s orbital in C''' is very diffuse. For stationary point C<sup>iv</sup> the "3s", "2p", and "3p" are tight and correlate primarily the core. Hence C<sup>iv</sup> has the lowest MCSCF energy of these five points even though it is not the desired point. Since C<sup>iv</sup> has no correlating orbitals in the valence region and is 99.69% composed of the SCF configuration, its static polarizability is nearly the same as that of the SCF stationary point (A).

Stationary points C' and C'' are both proper and have desired values of orbital  $\langle r^2 \rangle$ . The 2s and 2p and correlating 3s and 3p orbitals for C' and C'' have  $\langle r^2 \rangle$  values in the valence region of space. All other calculated properties (see Table III) are similar except the MCLR static polarizabilities are 825.09 and 991.19 a.u., respectively. Without knowing beforehand the full CI limit (or at least very large CI or very large MC linear response) static polarizability it would be impossible to choose between these two MCSCF stationary points as to which is probably the better representation of the exact state. However, since the full CI value in this basis set has already been calculated, i.e., 797.77 a.u.,<sup>23</sup> it is apparent that C' is probably the better representation.

Stationary point C' also has a slightly lower MCSCF total energy than C'', -7.454 965 vs -7.454 959 a.u., respectively. Hence, it may at first appear that C' should be chosen from the two as more desired solely on (MCSCF) energetic grounds. However, we previously showed that choosing between two proper MCSCF stationary points with desired characteristics based on energy alone is not sufficient for determining which is the more desired stationary point.<sup>4,5</sup>

In Tables V and VI we compare the properties of stationary points we obtained with a 2-3s, 2-3p, 3d CAS. Ågren *et al.*<sup>23</sup> did not use this CAS in their  $\text{Li}^-$  calculations. This CAS was used in Be to give the most (and very) accurate MCLR excitation energies<sup>9</sup> and response properties.<sup>12</sup> We obtained  $\text{Li}^-$  stationary points D, D', and D<sup>iv</sup> which are analogous (i.e., have very similar characteristics) to C, C', and C<sup>iv</sup>, respectively, in the 2-3s, 2-3p, CAS. Hence, D' is the proper, desired stationary point. We have been so far unable to obtain a stationary point in the 2-3s, 2-3p, 3d CAS corresponding to C''.

In contrast to Ågren *et al.*<sup>23</sup> we note that the presence of the 3d orbital in the CAS is significant since  $\alpha$  is lowered from 825.09 to 802.00 a.u. when comparing the static polarizability of the proper, desired stationary points C' and D'. (As noted above the polarizability calculated for stationary point C is too small for its CAS since there are ten  $^1P^0$  instabilities). Since C' has five  $^1P^0$  instabilities the calculated static polarizability is again too small for this CAS. D' has only one MCLR  $^1P^0$  instability so nearly all allowed MCLR transitions are included in the polarizability summations.<sup>6</sup>

In Tables VII and VIII we list properties of the four active electron CASs we used. Stationary point E (1-4s, 2p CAS) is both proper and desired. Stationary points F, F<sup>v</sup>, and F<sup>vi</sup> (1-4s, 2-3p CAS) are all proper stationary points,

fulfilling all five criteria. Stationary points F<sup>v</sup> and F<sup>vi</sup> are not desired.

For stationary point F<sup>v</sup> the 3s, 4s, and 3p are all fairly tight (i.e.,  $\langle r^2 \rangle = 0.85, 3.03, \text{ and } 0.73 \text{ a.u.}^2$ , respectively) correlating primarily the core. The 2s and 2p have  $\langle r^2 \rangle$  values close to the 2s2p CAS MCSCF (point B), i.e.,  $\langle r^2 \rangle_{2s} = 33.54 \text{ a.u.}^2$ ,  $\langle r^2 \rangle_{2p} = 31.37 \text{ a.u.}^2$  for F<sup>v</sup> and  $\langle r^2 \rangle_{2s} = 33.59 \text{ a.u.}^2$ ,  $\langle r^2 \rangle_{2p} = 31.58 \text{ a.u.}^2$  for B. Hence, the static polarizability  $\alpha$  for F<sup>v</sup> is approximately that of B, i.e., 619.16 and 622.97 a.u., respectively.

In stationary point F<sup>vi</sup> only the 2s orbital has an  $\langle r^2 \rangle$  value in the valence region. The 4s, 2p, and 3p are tight, correlating primarily the core. The 3s is fairly diffuse with  $\langle r^2 \rangle_{3s} = 170.87 \text{ a.u.}^2$ . The static polarizability  $\alpha$  for F<sup>vi</sup> is 2503.06 a.u.

Stationary point F is proper and is a desired one. The 3s orbital is largely in the valence region (i.e.,  $\langle r^2 \rangle_{3s} = 70.53 \text{ a.u.}^2$ ) and, hence, it correlates primarily valence electrons. The 4s orbital is fairly tight ( $\langle r^2 \rangle_{4s} = 3.04 \text{ a.u.}^2$ ), thus correlating primarily the core. The 2p has approximately the same  $\langle r^2 \rangle$  as the 2s2p CAS 2p, i.e., 31.85 and 31.58 a.u.<sup>2</sup>, respectively. The 3p orbital is tight ( $\langle r^2 \rangle_{3p} = 0.72 \text{ a.u.}^2$ ), so it provides angular correlation for the core. An alternative desirable result would be for the converged 3p to have  $\langle r^2 \rangle$  in the valence region (see above). Stationary point F was also obtained and reported by Ågren *et al.*<sup>23</sup> They did not report an alternative desired point. We have been unable as well to locate this alternative point.

The results for stationary points F may indicate that perhaps a more reasonable CAS for  $\text{Li}^-$  may be 1-4s, 2-4p so that at convergence the 3s and 3p will have  $\langle r^2 \rangle$  values in the valence region and the 4s and 4p will have  $\langle r^2 \rangle$  values in the core region. (Although this CAS may be "unbalanced", see above.) We have performed an MCSCF calculation for the ground state of Be with this CAS.<sup>29</sup> The resulting stationary point, while proper, had tight 4s, 4p, and 3p correlating orbitals (i.e., in the core region). This indicates the difficulty in obtaining truly desired MCSCF stationary points in some cases.

#### IV. SUMMARY AND CONCLUSIONS

We have examined the MCSCF energy hypersurface of the ground state of  $\text{Li}^-$  in a fair amount of detail using several different CASs and a large Cartesian Gaussian basis set previously used in two other studies.<sup>23,24</sup> For these studies we restricted our calculations so that only real orbitals and state expansion coefficients were allowed. We obtained a plethora of previously unreported stationary points as well as several previously reported<sup>23</sup> points. All of these stationary points we obtained were variationally correct [i.e.,  $\delta E = 0$ , criterion (i)]; had no negative eigenvalues in the full Hessian with respect to real variations in both the orbital and configurational parameters [i.e., the number of negative eigenvalues of  $\mathbf{A} - \mathbf{B}$  is 0, criterion (iii)], and were the lowest in energy in the MCSCF configuration CI [i.e., criterion (v)]. Several of these obtained stationary points were not proper since they did not fulfill criteria (ii) (i.e., they had instabilities in an MCLR calculation on excitations to the  $^1S$

states) and (iv) (i.e., they had negative-end eigenvalues in the full Hessian with respect to imaginary variations in both the orbital and configurational parameters,  $\mathbf{A} + \mathbf{B}$ ). For every choice of CAS we were able to obtain at least one proper stationary point. In most cases (i.e.,  $2-3s$ ,  $2-3p$ ;  $2-3s$ ,  $2-3p$ ,  $3d$ ; and  $1-4s$ ,  $2-3p$ ) we obtained several proper stationary points which fulfilled all five criteria.

By utilizing an MCSTEP<sup>21,22</sup> transformation which conserves the MCSCF total energy we defined new occupied and partially occupied orbital sets for analysis. Examination of these orbital  $\langle r^{-2} \rangle$  values allowed us to further eliminate many of the "undesired" stationary points from the list of proper stationary points. However, for the  $2-3s$ ,  $2-3p$  CAS two obtained stationary points,  $\text{C}'$  and  $\text{C}''$ , were both proper and desired. It was only by knowledge of the full CI static polarizability that we were able to choose  $\text{C}'$  as being the best representation with this CAS of the exact state.

For the  $1-4s$ ,  $2-3p$  CAS (previously reported<sup>23</sup>) stationary point F was a desired one with the  $3p$  orbital correlating primarily the core rather than the valence space. An alternative desired stationary point would perhaps have the  $3p$  orbital correlating the valence region.

Since all current forefront MCSCF codes apparently monitor or control only criteria (i), (iii), and (v) above (at most) during or after convergence, it is expected that all of them may at times obtain improper stationary points [i.e., do not fulfill criteria (ii) and (iv) above] as well as obtain proper stationary points. Unfortunately, criteria (ii) and (iv) are apparently not controlled during convergence or monitored after convergence with these codes. It is only by more detailed examination of the obtained stationary points that the improper points can be easily eliminated. Further analysis (by looking at appropriately transformed orbital  $\langle r^{-2} \rangle$  values) is then required to determine if a proper MCSCF stationary point is truly desired.

Caution and careful analysis is urged for users of MCSCF codes. Even though this problem in  $\text{Li}^-$  may seem to be somewhat esoteric and rare, it is obviously not so (as discussed above). Use of improper and/or undesired MCSCF stationary points for the determination of molecular properties can give incorrect results. Subsequent use of improper, undesired MCSCF orbitals in, e.g., a large scale multireference CI may give very slow convergence (as a function of the number of configurations) to the full CI results. Energy and properties calculated with, e.g., multireference coupled cluster or multireference CI which use these improper and/or undesired orbitals may be erroneous or misleading.<sup>3-5</sup>

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