Nonnuclear Maxima in the Charge Density *

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Basis-set and electron-correlation effects on the appearance and disappearance of nonnuclear maxima in the electron density are examined in Li_2, Na_2, Na_4 and Na_5. It is shown that nonnuclear attractors can be removed in all cases except Li_2. The appearance of a pseudoatom in a lithium molecule correlates remarkably well with the size of the region, in an atomic calculation, of $\nabla^2 \varrho(\boldsymbol{r})$ for the valence shell of the atom. This and the fact that the pseudoatom is also present in the promolecule indicate that the pseudoatoms are remnants of, or in fact are portions of, atoms that are not perturbed enough in the molecule to remove an essentially atomic characteristic.

Key words: Li_2; Na_2; Topological analysis; Pseudoatoms; Charge density; Electron correlation.

1. Introduction

Besnainou et al. [1] reported in 1955 that in Li_2 there was a local maximum in the electron density at the midpoint of the bond in addition to the expected maxima at the nuclei. Although non-nuclear maxima were reported subsequently in a few systems, they remained a curiosity until the topological properties of the electron density $\varrho(\boldsymbol{r})$ were used by Bader and co-workers to develop a theory of molecular structure [2]. By using zero-flux surfaces, which satisfy the condition

$$\nabla \varrho(\boldsymbol{r}) \cdot \boldsymbol{n} = 0 \tag{1}$$

for every point on the surface of the subsystem with $\boldsymbol{n}$ as a unit vector to the surface, a molecule may be partitioned into atoms. Points on these surfaces that are saddle points in the electron density are critical points where

$$\nabla \varrho(\boldsymbol{r}) = 0. \tag{2}$$

Should a critical point fall on the path between bonded atoms along which the electron density is a maximum with respect to a lateral displacement it is known as a bond critical point.

As well, critical points may be characterized by the eigenvalues of the matrix of second derivatives (Hessian) of the electron density at the critical point with its rank equal to the number of nonzero eigenvalues and its signature equal to the excess number of positive over negative eigenvalues. There are four possible signatures of critical points of rank three. These critical points correspond to a local maximum (peak) in $\varrho(\boldsymbol{r})$, $(3, -3)$, a saddle point (pass) in $\varrho(\boldsymbol{r})$ that is a maximum in the surface it defines, $(3, -1)$, a saddle point (pale) in $\varrho(\boldsymbol{r})$ that is a minimum in the surface it defines, $(3, +1)$, and a local minimum (pit) in $\varrho(\boldsymbol{r})$, $(3, +3)$. Note that nuclei behave topologically as $(3, -3)$ critical points. Motion in any direction away from a $(3, -3)$ critical point leads to a decrease in the electron density. Since all of the gradient paths of the electron density in the neighbourhood of a particular nucleus terminate at that nucleus, the nucleus acts as an attractor in the gradient vector field of the electron density. $(3, -1)$ critical points, that is the previously mentioned bond critical points, are situated between neighbouring attractors that are linked by a unique pair of trajectories associated with the $(3, -1)$ critical points. It is through the attractor behaviour of nuclei that distinct atomic forms are created within the electron distribution [2]. Thus, $(3, -3)$ and $(3, -1)$ critical points play a crucial rôle in defining atoms in the theory of molecular structure. A nonnuclear attractor, such as that in Li_2, would define a 'pseudoatom', see Figure 1.

Cao et al. [3] found nonnuclear attractors to exist in Li_n and Na_n clusters even after the inclusion of elec-

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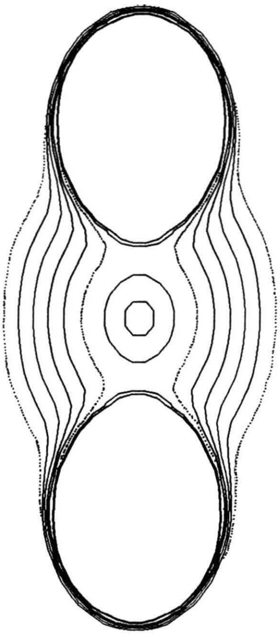

Fig. 1. Contour diagram for the charge density in Li_2 for a plane containing the lithium atoms and the pseudoatom at the bond midpoint.

tron correlation at the multi-reference configuration interaction (MRCI) level. Glaser et al. [4] investigated the origin and consequences of the pseudoatom in Li_2 and also found that inclusion of electron correlation did not remove the nonnuclear attractor at the bond midpoint. They ascribed the origin of this attractor to the shape of the valence molecular orbital and suggested that nonnuclear attractors might occur in bonds of low polarity.

It should be noted, though, that Edgecombe and Boyd [5] reported that in H_2S not only are bond critical points sensitive to the basis sets used to calculate the density and the addition of polarization functions, but also to the orbital exponent of the polarization functions. In particular, by varying the polarization function exponents in the 6-311G** basis set [6], multiple critical points could be created along the internuclear axis. These multiple critical points along the internuclear axis are converted to a single bond critical point upon energy optimization of the polarization function exponents. Edgecombe [7] noted that the minimum in the electron density along the bond path was located in a very shallow well. As a result, slight changes in the density could move the position of the critical point over relatively large distances without much change in the value of the electron density at the new critical point. These findings point to possible causes of multiple critical points and pseudoatoms in other systems.

In this paper we report on both the removal of nonnuclear attractors in Na_2, Na_4, and Na_5, but not in Li_2, and on the possible cause of the nonnuclear attractor in the latter.

2. Method

Uncorrelated wavefunctions were obtained from restricted and unresticted Hartree-Fock calculations using the HONDO 8 [8] and the GAUSSIAN 86 [9] program systems. The inclusion of electron correlation with all single and double substitutions (CISD) was performed using HONDO 8. For comparison, numerical Hartree-Fock finite-differences calculations [10] were performed on the lithium and sodium dimers. Analysis of the topological properties of the electron density was done with the AIMPAC series of programs [11]. Note that all distances, energies and electronic properties are given in atomic units (a_0, E_h, etc.).

The Li_2 and Na_2 bond lengths were set at 5.1 and 6.05 a_0, respectively. For comparison, the geometry used by Cao et al. [2] was utilized for Na_4, i.e. $(0, 0, \pm 6.1633\ a_0)$ and $(0, \pm 3.035\ a_0, 0)$. For the Na_5 geometry [12], the coordinates Na1 $(-0.0068019\ a_0, 0, 0)$, Na2 and Na3 $(0.090886\ a_0, \pm 6.8768876\ a_0, 0)$, Na4 and Na5 $(6.1253683\ a_0, \pm 3.5379788\ a_0, 0)$, i.e., C_{2v} symmetry was assumed.

3. Results

Uncorrelated:

In Table 1 are listed the basis sets, supplemental exponents (standard as well as energy-optimized) and abbreviations used in our study of the sodium compounds. For comparison, the Martin and Davidson [6s4p1d] basis set [13] that Cao et al. used [3] is included. Note that Cao et al. reported an MRCI energy of $-323.66860\ E_h$ for Na_2 using this basis set. Inspection of the energy values listed in Table 1 shows that 'B' and all the other larger basis sets used give lower energy values at the Hartree-Fock level than the Martin and Davidson basis set 'A' at the MRCI level!

Table 1. Basis sets and results for the sodium compounds examined[a, b, c].

Basis set	Supplement (exponents)	Symbol	E_{total}/E_h	Type	r/a_0	$\varrho(\boldsymbol{r}_c)$	$\nabla^2\varrho(\boldsymbol{r}_c)$
Na_2							
[6s4p1d]	d (0.09)	A [13]	−323.641821	(3, −3)	0.0	0.007885	−0.00405
				(3, −1)	0.4006	0.007834	−0.00023
[6s5p]		B [6]	−323.690819	(3, −1)	0.0	0.007691	−0.00205
[6s5p]+d	d (0.175)	B1	−323.691343	(3, −1)	0.0	0.008486	−0.00378
	d (0.4)	B2	−323.693061	(3, −1)	0.0	0.007941	−0.00251
	d (0.69)	B3	−323.695058	(3, −1)	0.0	0.007890	−0.00256
(24s12p)		C [14]	−323.714772	(3, −3)	0.0	0.0080724	−0.00416
				(3, −1)	0.0831	0.0080723	−0.00402
(24s12p)+d	d (0.3)	C1	−323.715028	(3, −3)	0.0	0.0085586922	−0.004927
				(3, −1)	0.01936	0.0085586920	−0.004921
Numerical HF ($r_{\max} = 45\ a_0$)	121 × 137	D1	−323.717454	(3, −3)	0.0	0.00862227	
				(3, −1)	0.01294	0.00862084	
	145 × 169	D2	−323.717320	(3, −3)	0.0	0.00862226	
				(3, −1)	0.00899	0.00862079	
Na_4					Atoms		
[6s5p]		B	−647.386330	(3, +1)	ring	0.005698	+0.00068
				(3, −1)		0.006315	+0.00171
[6s5p]+d	d (0.175)	B1	−647.387870	(3, +1)	ring	0.005904	+0.00041
				(3, −1)		0.006841	+0.00196
	d (0.4)	B2	−647.391011	(3, +1)	ring	0.005757	+0.00048
				(3, −1)		0.006498	+0.00245
	d (0.93)	B4	−647.401714	(3, +1)	ring	0.005770	+0.00064
				(3, −1)		0.006369	+0.00152
Na_5							
[6s5p]+d	d (0.4)	B2	−809.248973	(3, −3)	4,5	0.005224	−0.00209
				(3, +1)	1,4,5	0.003296	+0.00082
				(3, −1)	1,3 and 1,2	0.005763	+0.00231
				(3, −1)	2,4 and 3,5	0.005741	+0.00186
				(3, −1)	4,ps and 5,ps	0.005223	−0.00200
	d (0.93)	B4	−809.262162	(3, +1)	all	0.003276	+0.00073
				(3, −1)	4,5	0.004873	−0.00166
				(3, −1)	1,2 and 1,3	0.005780	+0.00222
				(3, −1)	2,4 and 3,5	0.006005	+0.00143

[a] r is the distance from the midpoint of the internuclear axis to the critical point.

[b] (3, −3) critical points at nuclei are not included.

[c] Pseudoatoms are represented by a 'ps', while 'ring' indicates that all atoms are associated with that (3, +1) critical point.

The use of the McLean and Chandler basis set (B) removes the (3, −3) critical point in electron Na_2. Basis set 'C' [14] retains the (3, −3) critical point, but it is debatable whether it is real, as its size (net elevation) is $2 \times 10^{-9}\ a_0^{-3}$ after the addition of polarization functions. Our basis-set-free numerical Hartree-Fock calculations do not clarify the issue as they retain a 'bump' that is $1.5 \times 10^{-6}\ a_0^{-3}$ in size. Calculations on Na_4 and Na_5 show that energy optimization of the supplemental exponent removes any nonnuclear (3, −3) critical points.

Table 2 lists the basis sets and supplemental basis function exponents as well as the abbreviations used for the lithium dimer. Note that the supplemental exponents have been at least partially energy-optimized. Use of the Partridge (18s) basis set [15] yields a pseudoatom at the bond midpoint. Augmenting the basis set with one set of p-type functions increases the charge density along the bond. The supplemented basis set also yields an energy that is lower by 0.0082 E_h.

Addition of the (10p) component of the Partridge Li (14s10p) basis set [15] to the (18s) basis set produces perhaps the best sp basis set in that placement of two supplementary s-type functions midway between each nucleus and the bond midpoint yields the lowest Hartree-Fock energy found in this study for Li_2 at a bond length of 5.1 a_0. Note, however, that so six places after the decimal, the (18s10p) basis set supplemented with one set of d-type functions is calculated to give the same energy, but is in fact higher in energy if another digit is considered. For comparison, a much larger basis set, (23s11p6d3f) [16], gave an energy that

Table 2. Basis sets and results for lithium[a].

Basis set	Supplement (exponents)	Symbol	E_{total}/E_h	Type	r/a_0	$\varrho(\boldsymbol{r}_c)$	$\nabla^2\varrho(\boldsymbol{r}_c)$
18s		E [15]	−14.861590	(3, −3)	0.0	0.00826	−0.00594
				(3, −1)	0.6637	0.00782	+0.00722
18s+s	s (0.015)	E1	−14.861613	(3, −3)	0.0	0.00825	−0.00592
				(3, −1)	0.6638	0.00782	+0.00723
18s+p	p (0.13)	E2	−14.869843	(3, −3)	0.0	0.01310	−0.01303
				(3, −1)	0.8064	0.01178	+0.01608
18s 10p		E3	−14.871614	(3, −3)	0.0	0.01323	−0.01177
				(3, −1)	0.7592	0.01243	+0.00769
18s 10p+1d	d (0.2)	E4	−14.871705	(3, −3)	0.0	0.01367	−0.01293
				(3, −1)	0.7744	0.01277	+0.00843
18s 10p+ghost[b]	p (0.5)	E5	−14.871614	(3, −3)	0.0	0.01323	−0.01176
				(3, −1)	0.7588	0.01243	+0.00764
18s 10p+ghost[b]	s (0.2)	E6	−14.871699	(3, −3)	0.0	0.01374	−0.01322
				(3, −1)	0.7760	0.01281	+0.00845
18s 10p+2 ghosts[c]	s (0.15)	E	−14.871700	(3, −3)	0.0	0.01363	−0.01277
				(3, −1)	0.7719	0.01273	+0.00832
18s 10p+2 ghosts[c]	s (0.15, 0.6)	E8	−14.871705	(3, −3)	0.0	0.01374	−0.01315
				(3, −1)	0.7721	0.01286	+0.00753
18s 10p 1d+ghost[c]	d (0.2)	E9	−14.871705	(3, −3)	0.0	0.01370	−0.01300
				(3, −1)	0.7752	0.01249	+0.00846
23s 11p 6d 3f		F1 [16]	−14.871699	(3, −3)	0.0	0.01372	
				(3, −1)	0.8	0.01284	
Numerical HF ($r_{\text{max}} = 45\ a_0$)	121 × 137 grid	D	−14.871701	(3, −3)	0.0	0.01372	
				(3, −1)	0.2242	0.01284	

[a] See Table 1.

[b] Extra basis functions are centred at the midpoint of the internuclear axis.

[c] Extra basis functions are centred halfway between the atoms and the midpoint of the internuclear axis.

is 0.000006 E_h higher. As well, our numerical Hartree-Fock calculation, using a 121 × 137 grid, resulted in an energy 0.000004 E_h higher.

Despite the high quality of the best basis sets and the use of a basis-set-free numerical method, in all cases a (3, −3) critical point is found at the bond midpoint of Li_2.

Correlated:

Table 3 lists the results with the inclusion of electron correlation with all singles and doubles. Such correlation with our best Li_2 Hartree-Fock wavefunction does not remove the (3, −3) critical point at the bond midpoint. Cao et al. [3] reported that inclusion of electron correlation using the MRCI method with the Martin and Davidson basis set does not remove the (3, −3) critical point in Na_2. Similarly, we find that using the CISD method with this basis set does not do so either. However, electron correlation (CISD) does remove the (3, −3) critical point in Na_2 with our best basis sets ('C' and 'C1').

4. Discussion and Conclusions

Although first reported in 1955, the lithium dimer pseudoatom question is still unanswered. Spackman and Maslen [17] showed that a nonnuclear attractor could be created by adding the atomic electron densities of two lithium atoms to form the Li_2 promolecule. This observation of a (3, −3) critical point at the midpoint of the internuclear axis of the promolecule is startling. Could it mean that reorganization of the density in the formation of the dimer does not overcome what is essentially an atomic property? The lithium promolecule pseudoatom can be reproduced with the basis sets used in this study [18]. In an attempt to mimic the Spackman and Maslen observation of the Li_2 promolecule we calculated atomic densities for sodium with the 'A', 'C' and 'B3' basis sets (see Table 1). Only nuclear (3, −3) critical points were found in the Na_2 promolecule density.

The observations by Gatti et al. [19] that the pseudoatoms in Li_2 disappears upon bond shortening and by Cioslowski [20] that a second pseudoatom appears upon bond lengthening are clues to the cause of

Table 3. Energies and critical-point data from CISD wavefunctions. See Tables 1 and 2 for the basis sets.

Basis set	Orbitals[a]	E_{total}/E_h	Type	r/a_0[b]	$\varrho(\boldsymbol{r}_c)$	$\nabla^2\varrho(\boldsymbol{r}_c)$
Li_2						
E4	50	−14.905472				
E4	80	−14.974897	(3, −3)	0.0	0.01398	
			(3, −1)	0.75	0.01308	
E4	90	−14.984896	(3, −3)	0.0	0.01399	−0.013
			(3, −1)	0.77	0.01308	+0.008
Na_2						
A	48	−323.900818	(3, −3)	0.0	0.007882	
			(3, −1)	0.37	0.007846	
B2	54	−323.977219	(3, −1)	0.00	0.007971	
B3	50−2	−323.940515	(3, −1)	0.00	0.007836	
C	90	−323.985366	(3, −1)	0.00	0.0081628	
C1	80−2	−323.993600	(3, −1)	0.00	0.0088358	−0.005
Na_4						
B4	66	−647.496127	(3, +1)	Atoms ring	0.00583	+0.0008
			(3, −1)		0.00624	+0.0004
Na_5						
B4	120−25	−809.316368	(3, +1)	all	0.00357	+0.0005
			(3, −1)	4,5	0.00476	−0.0013
			(3, −1)	1,2 and 1,3	0.00547	+0.0011
			(3, −1)	2,4 and 3,5	0.00575	+0.0001

[a] The negative numbers represent the number of core orbitals that are frozen.

[b] Distance from the nonnuclear attractor to the critical point.

Table 4. Critical point data for the Li_2 bond lengthening process with the E4 basis set at the Hartree-Fock level.

Bond length	Type	r_{Li}/a_0[a]	$\varrho(\boldsymbol{r})$	$\nabla^2\varrho(\boldsymbol{r})$	r'/a_0[b]	r''/a_0[c]
6.1	(3, −3)	3.0500	0.00986	−0.00641	1.98	2.531
	(3, −1)	1.8890	0.00920	+0.00393		
6.5	(3, −3)	3.2500	0.00855	−0.00472	2.02	2.500
	(3, −1)	1.9467	0.00815	+0.00204		
6.7	(3, −1)	3.3500	0.007954	−0.00403	2.01	2.494
	(3, −3)	3.0982	0.007955	−0.00414		
	(3, −1)	1.9792	0.00769	+0.00115		
6.9	(3, −1)	3.4500	0.00739	−0.00344	2.03	2.491
	(3, −3)	2.7700	0.00742	−0.00412		
	(3, −1)	2.0158	0.00727	+0.00030		
7.1	(3, −1)	3.5500	0.00687	−0.00292	2.05	2.492
	(3, −3)	2.5988	0.00696	−0.00400		
	(3, −1)	2.0588	0.00688	−0.00054		
7.3	(3, −1)	3.6500	0.00638	−0.00248	2.07	2.494
	(3, −3)	2.4599	0.00655	−0.00374		
	(3, −1)	2.1166	0.00653	−0.00141		

[a] Distance from the critical point to the nearest lithium.

[b] Distance from the nucleus to the point where the Laplacian becomes negative in the valence region along the internuclear axis.

[c] Distance from the nucleus to the nearest maximum in $-\nabla^2\varrho(\boldsymbol{r})$, that is, where $\nabla(-\nabla^2\varrho(\boldsymbol{r}))=0$ and is a (3, −3) critical point in that field $(-\nabla^2\varrho(\boldsymbol{r}))$, along the internuclear axis.

the anomaly. We look to the atoms for possible answers to our molecular problem. Sodium was the most logical candidate with its appearance/disappearance behaviour. In particular, we have used the ‘A’, ‘B3’ and ‘C’ basis sets to look at the atomic electron densities and Laplacian $\nabla^2\varrho(\boldsymbol{r})$ distributions of Na_2. The resulting analysis shows that although a promolecule calculation gives no pseudoatom for either basis set, examination of the Laplacian gives some interesting correlations. Negative values of the Laplacian indicate where charge is locally concentrated, $\nabla^2\varrho<0$ [21], and are thus of special interest in this problem. Although caution must be used when comparing Laplacian values calculated with different basis sets, the trend is clear using the three basis sets described. The distance between the start of the negative region of the Laplacian and the end for the valence shell [22] is 1.26, 0.71 and 0.64, respectively, for the ‘A’, ‘C’, and ‘B3’ basis sets. The minimum values of the Laplacian in this region are −0.000352, −0.000134, and −0.000088 a_0^{-5}, respectively, for the ‘A’, ‘C’, and ‘B3’ basis sets. The correspondence between regions and values of $\nabla^2\varrho$ is striking, given that basis 'A' has a large pseudoatom in the molecule, 'C' has a very small pseudoatom, while 'B3' has none.

The correlation observed between features of the Laplacian and the presence of pseudoatoms in Na_2 prompted a closer look at the Laplacian in Li_2 and, of course, Li. For the lithium atom with basis 'E4', the distance between the start and the end of the negative region of the Laplacian for the valence shell is 1.5 a_0. The observation of a second nonnuclear maximum by Cioslowski [20] upon lengthening the Li_2 bond length led us to examine the Laplacian during this process. The results of six calculations are given in Table 4 for bond lengths between 6.1 and 7.3 a_0. The second nonnuclear attractor appears at a bond length of 6.7 a_0 for this set. Perhaps indicative of what is happening is the change in the difference between the value of the charge density at the (3, −1) critical point closest to the nucleus and at the pseudoatom closest to the nucleus. When the bond length increases from 6.1 to 7.3 a_0, the charge density difference decreases from 6.6×10^{-4} to 2×10^{-5} a_0^{-3}. Note that with our best basis set, 'E4', at an internuclear distance of 5.1 a_0, the difference is 9×10^{-4} a_0^{-3}. Also, the Laplacian is positive at the (3, −1) critical point closest to the nucleus until the internuclear distance of 7.1 a_0 is reached. Note as well that the distance from the nucleus to the point at which the Laplacian becomes negative (in the valence shell) changes very little during this process, increasing slightly from 1.98 a_0 at $R = 6.1$ a_0 to 2.07 a_0 at $R = 7.3$ a_0.

Table 4 also contains data from a critical-point analysis of the negative of the Laplacian of the charge density in the internuclear region. That is, we look for points where

$$\nabla(-\nabla^2 \varrho(\boldsymbol{r})) = 0 . \tag{3}$$

We see that the maximum is at a distance of 2.531 a_0 from Li with an internuclear distance of 6.1 a_0, but rapidly declines to 2.494 a_0 at an internuclear distance of 6.7 a_0. From this point on it remains relatively unchanged for further increases in the internuclear distance. At the internuclear distance used in the earlier part of this study, $R = 5.1$ a_0, the maximum in the negative of the Laplacian is located at the bond midpoint, 2.55 a_0 from the lithium nucleus. For comparison, the maximum in the negative of the Laplacian for atomic lithium with this basis set is calculated at the SCF level to be 2.49 a_0 from the nucleus, thus indicating the source of charge accumulation in the diatomic molecule. Note that as a test of the quality of the 'E4' basis set, the Li_2 bond length was energy-optimized at the HF level with the 'E4' basis set. This yields a bond length of 5.2463 a_0 with a final Hartree-Fock energy of -14.871909 E_h. This is 0.08×10^{-5} E_h lower than that obtained by Freeman and Karplus [23] with a large STO basis set (regarded as the Hartree-Fock limit [4]) with an optimized bond length of 5.25 a_0. As the d-function exponent used in this study was optimized at a bond length of 5.1 a_0, it is possible that a slight lowering of the total energy would be possible if the exponent and bond length were jointly optimized. See reference [18] for further details.

It should be noted that using Ruedenberg's atomic valence 'promotion' arguments [24], Politzer [25] concluded that the difference in bond energies between H_2 and Li_2 could be attributed to the 'promotion' and sharing of valence electrons in the formation of H_2 and the lack of 'promotion' and sharing in the case of Li_2. That is, in the formation of Li_2 the atoms do not undergo enough 'promotion' to allow for significant sharing.

Although the presence of nonnuclear attractors in sodium complexes appears to be a basis-set or method dependent effect, the pseudoatom in the lithium dimer cannot be described by normal means. In fact, the term "atoms in a molecule" perhaps describes the situation best. That is, it would appear from the data presented here that the lithium atoms retain much of their atomic character upon formation of the dimer. Put in other words, the molecular environment does not appear to be strong enough to overcome atomic characteristics.

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