Theoret. chim. Acta (Berl.) 27, 81—93 (1972)

Commentationes

Atoms-in-Molecules Treatment of Li_2^+ and Li_2 Using Optimum Gaussian Approximations of Li^+ and Li Eigenstates*

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Received November 4, 1971/July 4, 1972

Expectation energies for the Li^+, Li and Li^- ground states and for the $1s^2 2p$ Li excited state are individually minimized with respect to variation of parameters in Gaussian lobe expansions of the 1*s*, 2*s* and 2*p* AO's. A new technique is used to control $1s-2s$ orthonormality. The resulting approximate many-electron atomic eigen-functions are utilized for determining interatomic matrix elements in atoms-in-molecules (AIM) calculations on the two lowest energy $^1\Sigma_g^+$ states of Li_2 and on the lowest energy $^2\Sigma_g^+$ and $^2\Sigma_u^+$ states of Li_2^+. For R greater than 4 a.u., convergence to exact theoretical AIM limits, within about 0.001 h.u., is obtained by using three-term expansions. Three-structure Li_2 and two-structure Li_2^+ AIM energies are above experimental by 0.005 and 0.007 h.u., respectively. It is conjectured that an AIM model extended to permit scaling of valence electrons independently of inner-shell electrons would reduce significantly these energy differences.

Die Energieerwartungswerte für die Grundzustände von Li^+, Li und Li^- sowie für den angeregten Zustand $1s^2 2p$ von Li werden einzeln bezüglich der Variationsparameter einer Entwicklung der 1*s*-, 2*s*- und 2*p*-Atomorbitale nach Gaußfunktionen minimisiert. Zur Kontrolle der Orthonormalität der 1*s*- und der 2*s*-Funktion wird eine neue Technik angewandt. Die resultierenden angenäherten Atomeigenfunktionen werden bei Atom-in-Molekül (AIM)-Rechnungen für die zwei niedrigsten $^1\Sigma_g^+$-Zustände von Li_2 und die niedrigsten Zustände der Symmetrie $^2\Sigma_g^+$ und $^2\Sigma_u^+$ von Li_2^+ verwendet. Für einen Atomabstand R größer als 4 A.E. wird mit einer Entwicklung mit drei Termen eine Annäherung bis zu 0,001 A.E. an den exakten theoretischen AIM-Grenzwert erreicht. Die AIM-Energiewerte, die mit drei Resonanzstrukturen von Li_2 bzw. zwei Resonanzstrukturen von Li_2^+ erhalten werden, liegen 0,005 A.E. bzw. 0,007 A.E. über den experimentellen Werten. Es wird angenommen, daß eine Erweiterung des AIM-Modells, bei der eine Skalierung der Valenzelektronenfunktionen unabhängig von den inneren Elektronen möglich ist, diese Energiedifferenz stark herabsetzen würde.

Les énergies de l'état fondamental de Li^+, Li et Li^-, et de l'état excité $1s^2 2p$ de Li sont individuellement minimisées par rapport à la variation des paramètres dans le développement gaussien des orbitales atomiques 1*s*, 2*s* et 2*p*. Une technique nouvelle est utilisée pour contrôler l'orthonormalité $1s-2s$. Les fonctions d'onde polyélectroniques approchées résultantes sont utilisées pour des calculs du type atomes dans les molécules (ADM) pour les deux états $^1\Sigma_g^+$ de plus basse énergie de Li_2 et sur les états $^2\Sigma_g^+$ et $^2\Sigma_i^+$ de plus basse énergie de Li_2^+. Pour R supérieur à 4 u.a., la convergence vers les limites théoriques exactes ADM est obtenue avec un développement à trois termes, à 0,001 u.a. près. Les énergies ADM à trois structures pour Li_2 et à deux structures pour Li_2^+ sont respectivement à 0,005 et 0,007 a.u. au dessus des énergies expérimentales. On émet l'hypothèse qu'un modèle ADM étendu pour permettre le calibrage des électrons de valence indépendamment des électrons des couches internes réduirait d'une manière significative ces différences d'énergie.

1. Introduction

Atoms-in-molecules (AIM) theory was formally developed by Moffitt for the purpose of eliminating atomic correlation energy errors from molecular calcu-

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* Supported in part by National Science Foundation Grant GP 25415.

lations [1]. Practical modifications have been devised by Arai [2], by Hurley [3], and by Balint-Kurti and Karplus [4]. The basic approach has been reviewed and discussed by Parr [5].

The wave function basis in AIM theory consists, in the first place, of linear combinations of antisymmetrized products of atomic substate eigenfunctions. As the number of basis functions Ψ_n is increased, one would expect predicted molecular eigenvalues to converge toward experiment in accordance with the variational principle. In AIM methods, *exact* equations are used for determining, by reference to experimental atomic energies, all *intraatomic* contributions to the energy matrix elements. All other parts of these elements, as well as all overlap matrix elements, are *interatomic* in nature, and these parts are computed using previously determined *approximate* atomic eigenfunctions. Because of this dichotomy, common to all AIM methods, the variational principle is not necessarily followed; predicted molecular energies may lie above or below experiment[1]. However, as the approximate atomic functions are successively refined, a predicted molecular energy should converge toward an exact theoretical AIM limit which will satisfy the variational principle; as the number of basis functions Ψ_n is increased, results should converge to experiment.

Sometime ago, a new AIM approach called *scaled atoms-in-molecules* (SAIM) theory for predicting potential energy curves of diatomic molecules was developed [6]. In this method, each basis function Ψ_n is modified by introducing factors s_n^{A} and s_n^{B} into its component A- and B-atom eigenfunctions. Exact equations were developed for determining, again by reference to experimental atomic energies, all intraatomic contributions to the energy matrix elements. Total molecular expectation energies could be minimized with respect to the several scale factors. Thus, a principal objection to pure AIM theory is overcome: namely, that the scale factors (i.e., effective nuclear charges) appropriate to free atoms and ions simply are not favorable for fast convergence of the AIM series [2, 3, 5].

We have reported initial calculations on various electronic states of H_2, He_2^{++}, He_2^+, H_2^- and He_2 [6–8]. For the ground $X\,^1\Sigma_g^+$ and excited $E\,^1\Sigma_g^+$ states of H_2, five basis functions were considered, corresponding to the following interacting states: (1) $1s\,H + 1s\,H$; (2) $^1S\,H^- + H^+$; (3) $1s\,H + 2s\,H$; (4) $1s\,H + 2p_0\,H$; and (5) $2p_+\,H + 2p_-\,H$ [8]. Use of $1s^2$ approximation for $^1S\,H^-$, where $1s$ is the STO (Slater-type orbital) appropriate to H^-, leads to SAIM H_2 energies lower than experimental. Use of the Hylleraas-Eckart $1s\,1s'$ function [9] or the Silverman-Platas-Matsen $1s\,1s' + \lambda\,2p^2$ [10] for H^- leads to SAIM H_2 energies approaching the exact limit within 0.001 h.u. (1 Hartree unit = 27.21 eV).

It seems clear from all work done so far that the optimized STO minimal basis set is not sufficiently accurate for SAIM calculations. If this theory is to be useful for prediction and explanation of ground and excited electronic state potential energy curves (and surfaces), it is essential that approximate ground and excited state atomic eigenfunctions be developed that are both adequate to achieve the exact theoretical SAIM limit and practical from the computational viewpoint.

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[1] Our experience has shown that use of defective approximate atomic eigenfunctions usually *depress* calculated AIM molecular energies. For infinite internuclear separations, AIM predicted energies will, of course, be identical to experiment.

In this paper, we report AIM calculations on electronic states of Li_2^+ and Li_2 in which approximate Li^+, Li and Li^- substate wave functions (used to determine molecular interaction and overlap matrix elements) are constructed from orbitals varied so as to minimize the total energy of each individual many-electron atomic substate function. The orbitals are expressed as linear combinations of simple Gaussian functions. A technique slightly different from that used before is outlined for controlling $1s-2s$ orthonormality; the new method leads to shorter series for the orthogonalized $2s$ orbital. Finally, we find that three-term energy-optimized Gaussian orbitals are sufficient to obtain convergence to exact theoretical AIM limits for Li_2^+ and Li_2.

2. Least Energy Minimal Atomic Orbitals: Gaussian Lobe Functions (LEMAO-NGL's)

A) General

In this paper, we report pure atoms-in-molecules (AIM) calculations in which the approximate many-electron atomic substate wave functions (used to determine the interaction and overlap elements) are constructed from orbitals varied so as to minimize the total energy of the given many-electron atomic substate functions. These orbitals are expressed as linear combinations of simple Gaussian functions. For $1s$ and $2s$ orbitals, the Gaussians have their origin at the given nucleus. For $2p$ orbitals, we have elected to utilize "lobe" functions [11][2]; a $2pz$ orbital, for example, is represented as the difference between two identical linear combinations of Gaussian functions, one with origin located at $z=P$ and the other with origin located at $z=-P$[3]. Thus,

$$\begin{aligned} 1s &= \sum_i^N b_{1i}\exp(-a_{1i}r_0^2)\,, \\ 2s &= \sum_i^M b_{2i}\exp(-a_{2i}r_0^2)\,, \\ 2pz &= \sum_i^L b_{3i}[\exp(-a_{3i}r_1^2)-\exp(-a_{3i}r_2^2)]\,, \end{aligned} \tag{1}$$

in which r_0, r_1, and r_2 are radial coordinates from the nucleus, from $z=P$, and from $z=-P$, respectively.

For a given electron configuration $1s^q 2s^r 2p^s$, where $n_1=q$, $n_2=r$, and $n_3=s$ are the orbital occupation numbers, a manifold of atomic substates are obtained. For any one of these substates, a proper wave function, in the restricted orbital approximation, may be expressed as a linear combination of Slater determinants. If the atomic orbitals are kept orthonormal, the total electronic energy may be expressed in the form

$$E=\sum_i n_i H_i + \tfrac{1}{2}\sum_i \sum_j [n_i(n_j-\delta_{ij})J_{ij}-A_{ij}K_{ij}]\,. \tag{2}$$

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[2] It has been shown that the "lobe" Gaussian function basis is essentially equivalent to the Cartesian Gaussian basis [12, 13].

[3] P is equivalent to R_0 in Ref. [12].

The indices 1, 2, and 3 refer to 1*s*, 2*s*, and 2*p*, respectively; H_i is the diagonal element of the one-electron core hamiltonian; J_{ij} and K_{ij} are the usual coulomb and exchange integrals, except that

$$\begin{aligned} J_{33} &= (J_{2pz,2pz} + 2J_{2pz,2px})/3\,, \\ K_{33} &= K_{2pz,2px}\,. \end{aligned} \tag{3}$$

The coefficients $A_{ij} = A_{ji}$ are characteristic of each atomic substate: $A_{ij} = \frac{1}{2} n_i n_j \delta_{ij}$ if $i < 3$ and $j < 3$; numerical values of A_{23} and A_{33} are listed in Ref. [14], but not needed in this work.

Eqs. (1) are used to express the integrals appearing in Eq. (2) in terms of integrals over simple Gaussian functions, all of which are easily evaluated [15]. The total electronic energy E is thus obtained as a function of the parameters a_{ni}, b_{ni}, and P of Eq. (1). The so-called *least energy minimal atomic orbitals* [16] (which we shall refer to as LEMAO-NGL orbitals, N being the number of terms in the expansion, GL standing for Gaussian lobe) will be determined if the parameters are chosen so as to minimize the total energy E of a given atomic substate.

This has been accomplished, for example, for a selection of atomic ground states using Gaussian lobe functions by Grimmelmann and Chesick [17] and using Cartesian Gaussians by Pople and coworkers [16].

In AIM theory, we have need for such LEMAO's appropriate not only to atomic ground states, but also to excited states, to positive ion states, and to negative ion states. We do not expect to require that these approximate eigenfunctions yield extremely accurate *intra-atomic* energies; they are not used for that purpose in AIM calculations. It is the principal purpose of this research to determine the expansion lengths in Eq. (1) necessary to provide acceptably accurate interatomic contributions to the AIM matrix elements.

Let us rewrite the Eqs. (1) generally as follows:

$$\psi_n = \sum_i^N b_{ni} \varphi_i\,. \tag{4}$$

For the special case $\psi_3 = 2pz$, φ_i represents a difference between two Gaussians located at $z = \pm P$. Since Eq. (2) requires that the ψ_n be orthonormal, the b_{ni} and a_{ni} are not all independent. We may take the first coefficient in each orbital to be determined by normalization:

$$\begin{aligned} \psi_n &= b_{n1} \sum_i c_{ni} \varphi_i\,, \\ c_{ni} &= b_{ni}/b_{n1}\,, \\ b_{n1} &= \Big[\sum_i \sum_j c_{ni} c_{nj} S_{ij}\Big]^{1/2}, \\ S_{ij} &= \int \varphi_i \varphi_j dv\,. \end{aligned} \tag{5}$$

We now take the c_{ni} $(i > 1)$ to be independent, c_{n1} being set equal to one.

Now, if one is minimizing E with respect to the exponents a_{1i} $(i = 1, 2, \ldots)$ or the coefficients c_{1i} $(i = 2, 3, \ldots)$ (i.e., with respect to variations in the 1*s* AO), and if $n_2 \neq 0$ (i.e., if the 2*s* AO is occupied), then the parameters c_{1i} $(i = 2, 3, \ldots)$ are not all independent; orthogonality between 1*s* and 2*s* must be preserved. We have elected to choose c_{12} so as to constrain this orthogonality:

$$c_{12} = -\left[\sum_{i\neq 2}\sum_{j} c_{1i}c_{2j}S_{ij}\right]\Big/\sum_{j} c_{2j}S_{2j}\,. \tag{6}$$

Thus, the true independent variables are c_{1i}, $i>2$; a_{1i}, $i\geqq 1$. In like manner,

$$c_{22} = -\left[\sum_{i}\sum_{j\neq 2} c_{1i}c_{2j}S_{ij}\right]\Big/\sum_{i} c_{1i}S_{i2} \tag{7}$$

if one is minimizing with respect to variations in the 2*s* AO and $n_1 \neq 0$ (which will always be the case in this work); the true independent variables are c_{2i}, $i>2$, and a_{2i}, $i\geqq 1$.

This approach for handling 1*s* – 2*s* orthogonality differs from that most often used. Usually, a 2*s* Gaussian expansion is Schmidt orthonormalized with respect to a predetermined 1*s* Gaussian expansion to yield the orthogonalized 2*s* AO, now expressed in terms of two Gaussian expansions. Our approach generally leads to a shorter series for the orthogonalized 2*s* AO.

B) LEMAO-NGL'*s for* Li^+ *and* Li

In Table 1, we list parameters for Gaussian expansions of the 1*s* AO chosen so as to minimize the total electronic energy of $1s^2\,{}^1S\,Li^+$; the energies are listed in Table 2. For comparison, we list also in Table 2 Li^+ energies calculated with an

Table 1. Orbital exponents and expansion coefficients for $1s^2\,{}^1S\,Li^+$

N	a_{1i}	b_{1i}	N	a_{1i}	b_{1i}
2	1.388532	0.7513883	5	0.6818738	0.2156861
	10.11372	1.130360		2.318487	0.6496735
				8.464990	0.7436694
3	1.015169	0.4701795		37.17722	0.5505841
	4.993060	0.9747399		248.8885	0.3114376
	33.64526	0.7669813			
			6	0.5323748	0.1161647
4	0.8190934	0.3184732		1.586883	0.4959026
	3.254383	0.8049811		5.161091	0.7114812
	14.83208	0.7783552		18.93839	0.6067729
	98.15334	0.4812371		85.20426	0.3834520
				547.6970	0.2069751

Table 2. Energies (h.u.) for $1s^2\,{}^1S\,Li^+$

N		1*s*-STO-NG	1*s*-LEMAO-NG
2			−6.9804
3		−7.1673	−7.1797
4		−7.2092	−7.2224
5		−7.2191	−7.2326
6			−7.2353
STO	−7.2227		
Hartree-Fock	−7.2364		
Experimental	−7.2799		

Table 3. Orbital exponents and expansion coefficients for $2s$ orbital in $1s^2 2s\ ^2S$ Li

$N(1s)$	$M(2s)$	a_{2i}	b_{2i}	$N(1s)$	$M(2s)$	a_{2i}	b_{2i}
2	3	0.015819661	0.005736902	3	4	0.02776284	0.02312028
		0.04855379	0.06446754			0.06563349	0.05461865
		1.240164	−0.1628947			0.9753701	−0.1378904
						7.421443	−0.1628015
2	4	0.01700869	0.007848712				
		0.05755439	0.07048959	4	3	0.008535179	0.001434313
		1.031532	−0.1346667			0.04155497	0.06373754
		8.040977	−0.1420034			1.322863	−0.1819831
2	5	0.02705561	0.02075375	4	4	0.01358333	0.004907548
		0.06614091	0.05877351			0.05168967	0.06906989
		1.027527	−0.1363496			1.104849	−0.1521092
		8.052362	−0.1423947			8.545282	−0.1708829
		25.00000	−0.0008272647				
3	3	0.02232988	0.01140161				
		0.04800623	0.05601393				
		1.267782	−0.1739216				

Table 4. Energies (h.u.) for $1s^2 2s\ ^2S$ Li

$N(1s)$	$M(2s)$	E	$N(1s)$	$M(2s)$	E	$N(1s)$	$M(2s)$	E
2	3	−7.1693	3	3	−7.3641	4	3	−7.4046
2	4	−7.1782	3	4	−7.3742	4	4	−7.4159
2	5	−7.1783						
STO		−7.4179						
Hartree-Fock		−7.4327						
Experimental		−7.4779						

appropriately scaled ($Z_{\text{eff}} = 2.6875$) $1s$-STO-NG. Our work here overlaps to some extent that presented by Chesick and coworkers [18]. Gaussian expansions of the STO's $1s$ and $2s$ used in this research were obtained from Huzinaga [19]; Gaussian lobe expansions of the STO $2p$ were obtained from Sambe [20].

In Tables 3 and 4, we list results for Gaussian expansions of the $2s$ AO in $1s^2 2s\ ^2S$ Li. We first appropriated a $1s$-LEMAO-NG determined previously for $1s^2\ ^1S$ Li$^+$; independent parameters for the $2s$-LEMAO-MG (a_{2i}, $i = 1, 2, 3, \ldots, M$, and c_{2i}, $i = 3, 4, \ldots, M$) were determined by minimizing the total electronic energy of $1s^2 2s\ ^2S$ Li. Then, the independent parameters for the $1s$-LEMAO-NG (a_{1i}, $i = 1, 2, 3, \ldots, N$ and c_{1i}, $i = 3, 4, \ldots, N$) were revaried to seek a still lower energy for Li. Never were we able to gain as much as 0.001 h.u. by this revariation of the inner-shell. Consequently, the $1s$-LEMAO-NG parameters listed in Table 1 are used not only in Li$^+$ but also in $1s^2 2s\ ^2S$ Li.

In Tables 5 and 6, we list results for excited $1s^2 2p\ ^2P$ Li. Again, it was found that revariation of the inner $1s$-shell made little difference in the final total energy. Furthermore, we found that an optimized $2p$-LEMAO-NGL function with given N can be used arbitrarily in conjunction with $1s$-LEMAO-MG functions with

Table 5. Orbital exponents and expansion coefficients for $2p$ orbital in $1s^2 2p\ ^2P$ Li[a]

N	a_{3i}	b_{3i}
2	0.0332337	0.2015516
	0.1535016	0.1251251
3	0.03081741	0.1756399
	0.1167678	0.1365198
	0.688099	0.03659062
4	0.02265422	0.1090897
	0.06546205	0.1517314
	0.2240412	0.07309883
	1.702588	0.02239308

[a] $P = 0.6$ for $N = 2, 3, 4$.

Table 6. Energies (h.u.) for $1s^2 2p\ ^2P$ Li

$N(1s)$	$M(2p)$	STO-GL	LEMAO-GL
2	2		−7.1051
2	3		−7.1073
2	4		−7.1078
3	2		−7.3046
3	3	−7.2942	−7.3071
3	4	−7.2946	
STO	−7.3504		
Experimental	−7.4100		

Table 7. Orbital exponents, expansion coefficients, and energies (h.u.) for $1s^2 2s^2\ ^1S$ Li^-

$N(1s)$	$M(2s)$	a_{2i}	b_{2i}	$-E$
2	3	0.008381412	0.01056586	
		0.04016744	0.03681205	7.1664
		1.257558	−0.1110685	
3	3	0.008047178	0.01013226	
		0.03700817	0.03462523	7.3602
		1.290961	−0.1187769	
Hartree-Fock			$E = -7.4282$	
Experimental			$E = -7.5054$	

various different M. That is, suppose we are initially given two different $2p$-LEMAO-2GL functions: the first yields an optimum energy $E = -7.1051$ h.u. for $1s^2 2p\ ^2P$ Li using $1s$-LEMAO-2G; the second yields an optimum energy $E = -7.3046$ h.u. for $1s^2 2p\ ^2P$ Li using $1s$-LEMAO-3G. It turns out that both of these $2p$-LEMAO-2GL functions will give the same energy $E = -7.1051$ h.u. if they are used with $1s$-LEMAO-2G or $E = -7.3046$ h.u. if they are used with $1s$-LEMAO-3G. Thus in Tables 5 and 6, only one $2p$-LEMAO-NGL for each N is needed. Such transferability of $2s$-LEMAO's with different $1s$-LEMAO's was not possible because of the orthogonality requirement.

In Table 7, results are given for the ground electronic state $1s^2 2s^2\ ^1S$ Li^-. Again, it was found that revariation of the inner $1s$-shell made no significant difference in the final total energy. Consequently, the 1s-LEMAO-NG parameters listed in Table 1 are used in $1s^2\,{}^1S$ Li$^+$, $1s^2 2s\,{}^2S$ Li, $1s^2 2p\,{}^2P$ Li, as well as in $1s^2 2s^2\,{}^1S$ Li$^-$.

3. AIM Calculations on Li_2^+ and Li_2

A) General

The following correlation of lower states of Li$^+$, Li, and Li$^-$ with states of Li$_2$ and Li$_2^+$ can be obtained:

$$1s^2 2s\,\mathrm{Li} + 1s^2 2s\,\mathrm{Li} \rightarrow {}^1\Sigma_g^+ + {}^3\Sigma_u^+\,\mathrm{Li}_2\,, \tag{8}$$

$$1s^2 2s\,\mathrm{Li} + 1s^2 2p\,\mathrm{Li} \rightarrow {}^1\Sigma_g^+ + {}^3\Sigma_u^+ + {}^1\Pi_g + {}^3\Pi_u\,\mathrm{Li}_2\,, \tag{9}$$

$$1s^2\,\mathrm{Li}^+ + 1s^2 2s^2\,\mathrm{Li}^- \rightarrow {}^1\Sigma_g^+ + {}^1\Sigma_u^+\,\mathrm{Li}_2\,, \tag{10}$$

$$1s^2\,\mathrm{Li}^+ + 1s^2 2s\,\mathrm{Li} \rightarrow {}^2\Sigma_g^+ + {}^2\Sigma_u^+\,\mathrm{Li}_2^+\,, \tag{11}$$

$$1s^2\,\mathrm{Li}^+ + 1s^2 2p\,\mathrm{Li} \rightarrow {}^2\Sigma_g^+ + {}^2\Sigma_u^+ + {}^2\Pi_g + {}^2\Pi_u\,\mathrm{Li}_2^+\,. \tag{12}$$

The total energies (relative to a state of all electrons and nuclei infinitely separated), in h.u., of the reactants are -14.956, -14.888, -14.785, -14.758, and -14.690 for reactions (8)–(12), respectively. Actually, there are a number of separated atom states, $1s^2 2s$ Li + $1s^2$ nl Li, $n = 3$ and 4, the energies of which lie between levels (9) and (10); i.e., between -14.888 h.u. and -14.785 h.u. If we were interested, for example, in the second excited ${}^1\Sigma_g^+$ state of Li$_2$ (i.e., the third lowest energy ${}^1\Sigma_g^+$ state), then at least some of these omitted separated-atom states would be extremely important. In the present study of the lowest two singlet states, it is asserted that the ionic interaction (10) should be included at the expense of these lower energy neutral atom interactions.

Corresponding to a given component of any molecular state shown on the right of Eqs. (8)–(12), an AIM basis function may be written as a known linear combination of antisymmetrized products of atomic substate functions from the left of Eqs. (8)–(12). For example, the AIM basis function corresponding to ${}^1\Sigma_g^+$ Li$_2$ in Eq. (9) can be written as follows:

$$\Omega_1 = \Psi_1 - \Psi_2 \tag{13}$$

where

$$\Psi_1 = a'(\Phi_1^A\Phi_4^B - \Phi_2^A\Phi_3^B), \qquad \Psi_2 = a'(\Phi_3^A\Phi_2^B - \Phi_4^A\Phi_1^B)\,; \tag{14}$$

here, Φ_1^X to Φ_4^X represent Li atom eigenfunctions corresponding to lowest energy states ${}^2S\,(M_S = 0.5)$, ${}^2S\,(M_S = -0.5)$, ${}^2P\,(M_L = 0, M_S = 0.5)$, and ${}^2P\,(M_L = 0, M_S = -0.5)$, respectively ($z$-axes on the two atoms A and B are taken to lie along the internuclear axis, and both have the same positive directions). Electrons 1–3 are initially assigned to the Φ_i^A eigenfunction and electrons 4–6 to the Φ_i^B eigenfunctions; a' is a partial antisymmetrization operator which causes Ψ_1 and Ψ_2 to obey the Pauli principle.

Calculations on ${}^1\Sigma_g^+$ Li$_2$ were done with: (1) the one function from Eq. (8); (2) the resonance of two functions from Eqs. (8)–(9); and (3) the resonance of three functions from Eqs. (8)–(10). Calculations on ${}^2\Sigma_g^+$ and ${}^2\Sigma_u^+$ Li$_2^+$ were done with: (1) the one function from Eq. (11); and (2) the resonance of two functions from Eqs. (11)–(12).

B) Results

In all cases, we carried out AIM calculations using Gaussian expansions of appropriately scaled Slater-type orbitals (i.e., 1*s*-STO-NG, 2*s*-STO-NG, and 2*p*-STO-NGL) [19, 20] in addition to our own newly developed LEMAO-NGL's. AIM predicted energies for $^2\Sigma_g^+$ Li_2^+, $R = 6.0$ a.u., and $^1\Sigma_g^+$ Li_2, $R = 5.05$ a.u., are listed in Table 8.

Table 8. AIM ground state energies (h.u.) for Li_2^+ and Li_2 using 1*s*, 2*s*, and 2*p* Gaussian expansions of lengths (N, M, L)

N	M	L	Li_2^+ ($R = 6$ a.u.)		Li_2 ($R = 5.05$ a.u.)	
			STO	LEMAO	STO	LEMAO
One-structure calculations						
2	3			−14.776		−14.976
3	3		−14.774	−14.773	−14.987	−14.973
3	4		−14.774	−14.774	−14.986	−14.972
4	3		−14.773		−14.986	
4	4		−14.773			
5	3		−14.772		−14.986	
Two-structure calculations						
2	3	2		−14.798		−14.985
2	3	3		−14.799		−14.985
3	3	2		−14.795		−14.980
3	3	3	−14.796	−14.796	−15.021	−14.980
3	3	4	−14.796		−15.020	
4	3	3	−14.795			
4	4	3	−14.795			
Three-structure calculations						
2	3	2				−14.993
3	3	2				−14.989
Expt'l			−14.803[a]		−14.994	

[a] Based upon estimated $D_e = 1.24$ eV.

Results for a given number of structures should converge toward an exact theoretical AIM limit as the Gaussian expansion lengths (N, M, L denote lengths of the 1*s*, 2*s* and 2*p* expansions, respectively) are increased; it appears that $(N, M, L) = (3, 3, 2)$ is nearly sufficient to give results within 0.001–0.002 h.u. from this limit. As the number of structures is increased, we expect the exact theoretical AIM limit to approach experiment.

Initial investigations made use of STO-NGL expansions. Results for the two-structure calculation on ground state Li_2 at $R = 5.05$ were below experiment; this was consistent with our previous experience with the STO-basis as described in Sect. 1 above. It was for this reason, of course, that we began developing the LEMAO-NGL expansions. In Table 8, we see that AIM energies using these new functions are not depressed below experimental. The three-structure Li_2 energy appears to be about 0.005 h.u. above the experimental result. For Li_2^+, our com-

Table 9. AIM energies (h.u.) and projection numbers for Li_2^+ using LEMAO-(3, 3, 3)

R	$^2\Sigma_g^+$				$^2\Sigma_u^+$			
	w_1	w_2	$-E_{AIM}$	$-E_{PP}$[a]	w_1	w_2	$-E_{AIM}$	$-E_{PP}$[a]
4	0.650	0.350	14.757		0.201	0.799	14.617	
5	0.661	0.339	14.786	14.799	0.515	0.485	14.657	14.670
5.7	0.680	0.320	14.794		0.702	0.298	14.678	
6	0.688	0.312	14.796	14.803	0.768	0.232	14.685	14.696
7	0.714	0.286	14.796	14.799	0.934	0.066	14.706	14.716
8	0.738	0.262	14.791		1.015	−0.015	14.723	
Inf.	1.000	0.000	14.758	14.758	1.000	0.000	14.758	14.758

[a] We have added the experimental energy of $2Li^+$ to the valence-electron energies for Li_2^+ calculated by a pseudopotential model in Ref. [21].

puted two-structure energy appears 0.007 h.u. above the estimated experimental value.

The present *scaled* atoms-in-molecules (SAIM) theory provides for scaling of each individual many-electron atom in a molecule [6]; such scaling does not discriminate between inner- and outer-shell electrons. Most of the electronic energy of a molecule is inner-shell energy, and this is primarily affected by the scaling process. On the other hand, the interatomic binding energy in a molecule is largely outer-shell energy, and this is affected least by scaling. Therefore, the scaling feature of present SAIM theory is most important only for molecules containing one- and two-electron atoms, for which inner-shell-outer-shell discrimination is usually not significant. We are presently working upon an extension of the SAIM model which will allow for this discrimination; that is, it will permit scaling of valence electrons independently of inner-shell electrons. It is our opinion that the gap between present AIM results and experiment, for Li_2^+ and Li_2, may be nearly closed in an extended SAIM model which allows for such valence-electron scaling.

In Table 9, we list AIM results for $^2\Sigma_g^+$ and $^2\Sigma_u^+$ Li_2^+ as a function of R. We include, for comparison, energies computed by Bardsley using the pseudopotential model [21]; his values should be very close to experimental. A Rydberg series of three Li_2 states leads to predicted ionization potential of 4.99 eV [22], which gives $D_e(Li_2^+) \simeq 1.45$ eV, or $E = -14.811$ h.u. relative to all electrons and nuclei infinitely separated. Most theoretical calculations indicate $D_e(Li_2^+) \simeq 1.24$ eV [23–26], $E = -14.803$ h.u. The ground state potential energy curve is very broad and quite shallow.

Given a wave function

$$\Omega_0 = \sum_i C_i \Psi_i \tag{15}$$

like Eq. (13), the projection numbers

$$w_i = C_i \sum_j C_j \int \bar{\Psi}_i \Psi_j dv \tag{16}$$

may be defined. For Li_2^+, w_1 and w_2 correspond to structures derived from separated atom states indicated in Eqs. (11) and (12), respectively. We see that ground state Li_2^+ contains a significant fraction of the structure $1s_A^2 1s_B^2(2pz_A + 2pz_B)$;

Table 10. Comparison of Li_2^+ results

Method	R	$-E_R$	$-E_{\text{inf}}$	$E_{\text{inf}}-E_R$		R_{eq}
	a.u.	h.u.	h.u.	h.u.	eV	a.u.
$1s_A^2 1s_B^2(2s_A+2s_B)$	5.6	14.6517	14.6405	0.0112	0.30	5.96
LCAO-MO-SCF	6.5	14.6692	14.6405	0.0287	0.78	6.5
$1s_A^2 1s_B^2(\varphi_A+\varphi_B)$	5.6	14.6874	14.6418	0.0456	1.24	5.96
SCF	6.0	14.7139	14.6691	0.0448	1.22	5.7
AIM-1[a]	6.0	14.772	14.758	0.014	0.38	~6.5
AIM-2	6.0	14.795	14.758	0.037	1.01	~6.5
Pseudopot.	6.0	14.803	14.758	0.045	1.23	5.9

[a] AIM-n = Atoms-inMolecules calculation including n structures.

that is, the Li^+ ion induces considerable polarization in the oncoming Li atom[4].

In Table 10, results for ground state Li_2^+ are compared with those of other calculations. The first and third lines refer to work done by James [23]; the LCAO-MO-SCF calculation was done by Fraga and Ransil [24] using the AO basis ($1s_{\text{Li}}, 2s_{\text{Li}}, 2p_{\text{Li}}$) with optimized orbital exponents; the SCF result is by Fischer and Kemmy using a basis of Gaussian orbitals [25]; and, the pseudopotential result is by Bardsley [21].

In Table 11, we list AIM results for the ground and first excited $^1\Sigma_g^+$ states of Li_2 as a function of R. Experimental results are taken from a tabulation in Ref. [31]. We see that results based upon the less accurate LEMAO-(2, 3, 2) expansions are depressed below results based upon the more accurate LEMAO-(3, 3, 2) expansions by 0.001, 0.004, and 0.006 h.u. at $R = 7.0$, 5.05 and 3 a.u., respectively. At $R = 4.0$ a.u., one finds $E_1 = -14.982$ h.u. using LEMAO-(3, 3, 2), by interpolation; experimental is $E = -14.981$ h.u. Thus results for $R \leq 4.0$ a.u. are depressed below experiment; longer Gaussian expansions would be required to obtain exact AIM results which, in theory, would provide upper bounds to experiment.

Finally, results for ground state Li_2 are compared in Table 12 with results of other calculations. The first line refers to an LCAO-MO-SCF calculation by Ransil [32] using the AO basis ($1s_{\text{Li}}, 2s_{\text{Li}}, 2p_{\text{Li}}$) with optimized orbital exponents. The next two lines refer to calculations performed by James [33]. The SCF and ODC ("optimized double configuration") are given by Das and Wahl [34] and the 7-CI (seven configuration calculation using optimized orbitals) is by Das [31]. The most recent experimental value is by Velasco and coworkers [35].

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[4] In the first approximation, Pauling long ago argued that the one-electron homopolar bond energy should be about one-half of the two-electron bond energy. However, an additional contribution would be derived from polarization of the atom in the ion field [21]. For H_2^+, the first part is said to account for (4.74 eV)/2 = 2.37 eV of the observed 2.78 eV bond energy, and polarization is said to account for most of the remaining 0.41 eV. The $s-p$ separation energies in H and Li are 10.2 eV and 1.85 eV, respectively. Hence, induced polarization should be more important in Li_2^+ than in H_2^+. A number of years ago, a theoretical approximate predecessor of SAIM theory, called modified atoms-in-molecules theory [28, 29], was used to calculate the potential energy curve for Li_2^+ using but one structure, that one derived from Eq. (11). The result $D_e(Li_2^+) = 0.65$ eV, which is about one-half of $D_e(Li_2) = 1.03$ eV, was considered reasonable (by FOE) at that time for the one-electron bond. The reason was wrong; there is an additional contribution of about 0.6 eV due to ion-atom polarization. Incidentally, the subsequent Diatomics-in-Molecules energy predictions for Li_3^+ and Li_2H^+ were too high because of the incorrect Li_2^+ potential used in those calculations [29, 30].

Table 11. AIM ground state energies E_1 (h.u.), ground state projection numbers w_i, and excited $^1\Sigma_g^+$ state energies E_2 for Li_2[a]

R	$-E_{exp}$	$-E_1$	w_1	w_2	w_3	$-E_2$
2.5		14.914	0.051	0.387	0.562	
3.0		14.954	0.182	0.330	0.489	14.778
		(14.948)	(0.120)	(0.354)	(0.525)	(14.790)
3.5		14.976	0.301	0.280	0.419	
4.0	14.981	14.987	0.402	0.240	0.358	
4.5		14.992	0.483	0.208	0.309	
5.05	14.994	14.993	0.552	0.179	0.269	14.868
		(14.989)	(0.542)	(0.175)	(0.283)	(14.871)
5.5	14.993	14.990	0.597	0.157	0.247	
6.0	14.989	14.987	0.637	0.133	0.231	
7.0	14.979	14.977	0.707	0.084	0.209	14.894
		(14.976)	(0.719)	(0.081)	(0.199)	(14.895)
8.0	14.971	14.969	0.784	0.040	0.175	

[a] Results in parentheses calculated with the more accurate LEMAO-(3, 3, 2); all other results calculated with LEMAO-(2, 3, 2).

Table 12. Comparison of Li_2 results

Method	R a.u.	$-E_R$ h.u.	$-E_{inf}$ h.u.	$E_{inf}-E_R$ h.u.	eV	R_{eq} a.u.
$1s_A^2 1s_B^2(2s_A 2s_B)$	5.05	14.845	2(7.4179)	0.009	0.24	~6.0
LCAO-MO-SCF	5.34	14.8422	2(7.4179)	0.006	0.17	5.34
$1s_A^2 1s_B^2(\varphi_A \varphi_B)$	5.63	14.866	2(7.4192)	0.028	0.76	
SCF	5.07	14.8716	2(7.4327)	0.006	0.16	5.26
ODC	5.0	14.8796	2(7.4327)	0.014	0.38	5.43
7-CI	5.07	14.9026	2(7.4327)	0.037	1.01	5.09
AIM-1[a]	5.05	14.972	2(7.4779)	0.016	0.43	~5.2
AIM-2	5.05	14.980	2(7.4779)	0.024	0.65	~5.2
AIM-3	5.05	14.989	2(7.4779)	0.033	0.90	~5.0
Pseudopot.	5.0	14.989	2(7.4779)	0.033	0.90	~5.0
Expt'l	5.05	14.994	2(7.4779)	0.038	1.03	5.05

[a] AIM-n = Atoms-in-Molecules calculation including n structures.

4. Conclusions

There are two important characteristics of Atoms-in-Molecules (AIM) theory which make it an especially attractive model in quantum chemistry. First, the basis set need not be as large as in an *ab initio* calculation of comparable accuracy; much of the configuration interaction required in the latter is accounted for by exact determination of intra-atomic energy in AIM theory. Second, the AIM method is conceptually satisfying since explanation of molecular properties is couched directly in terms of interacting exact atomic eigenfunctions.

In AIM theory, interatomic contributions to matrix elements are calculated with approximate many-electron atomic eigenfunctions. We have shown in this paper that if these approximate eigenfunctions are built from Gaussian lobe functions, parameters of which are chosen by individually minimizing the given atomic substate expectation energies, practical AIM results can be achieved. For

Li_2^+ and Li_2, convergence to exact theoretical AIM limits within about 0.001 h.u., is achieved by using three-term expansions for $R > 4$ a.u.; longer expansions would be required for smaller internuclear distances.

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