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Ab initio versus CNDO Potential Surface Calculations for Li_2O and Al_2O

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Potential surfaces for Li_2O and Al_2O have been calculated by an *ab initio* SCF–LCAO–MO method and by the semiempirical CNDO method. For both molecules the semiempirical methods incorrectly imply unreasonable structures with very acute apex angles and very long bond distances – rather more like diatomic Li_2 or Al_2 molecules with O-atoms attached to their bonds. Our *ab initio* treatment does correctly predict a symmetrical linear configuration for Li_2O with bond distances in excellent agreement with experiment. This method also predicts a linear symmetrical structure for Al_2O, in agreement with experimental gas phase measurements but in disagreement with matrix-isolation studies.

Key words: Potential surfaces – Li_2O–Al_2O – *Ab initio versus* CNDO potential surface calculations

Introduction

Although semiempirical molecular orbital methods are being used extensively for calculating various molecular properties, it is apparent that the results of such calculations may be quite misleading in certain cases [1]. However, it is generally conceded that the geometrical configuration is the most reliable molecular property calculable by semiempirical methods, and in fact, qualitative agreement of such calculations with experiment is most often obtained. For example, the semiempirical CNDO (Complete Neglect of Differential Overlap) and INDO (Intermediate Neglect of Differential Overlap) methods give quite satisfactory angular geometry predictions for a variety of molecular types, in particular, for "normal" AB_2-type molecules [2], although often the predicted bond distances are in significant error. Our CNDO energy contour diagrams (potential surfaces) for H_2O and F_2O are displayed in Fig. 1. These diagrams correctly predict C_{2v} geometries with apex angles of 104.2° and 106.8°, respectively, as compared with the observed 104.5° and 103.3° angles. Generally, as here, the CNDO calculated bond distances are somewhat in error.

In special cases where the molecules have "anomalous" structures, certain of the semiempirical methods apparently cannot cope even with the problem of geometry prediction [3]. One illustration of a simple molecule with anomalous geometry is the dilithium oxide molecule, Li_2O. It has been concluded from mass spectrometric and infrared matrix-isolation studies [4] and from electric deflection measurements [5] that Li_2O molecules in the vapor phase are linear symmetrical with $Li-O$ distances estimated to be 1.59 Å and 1.55 Å,

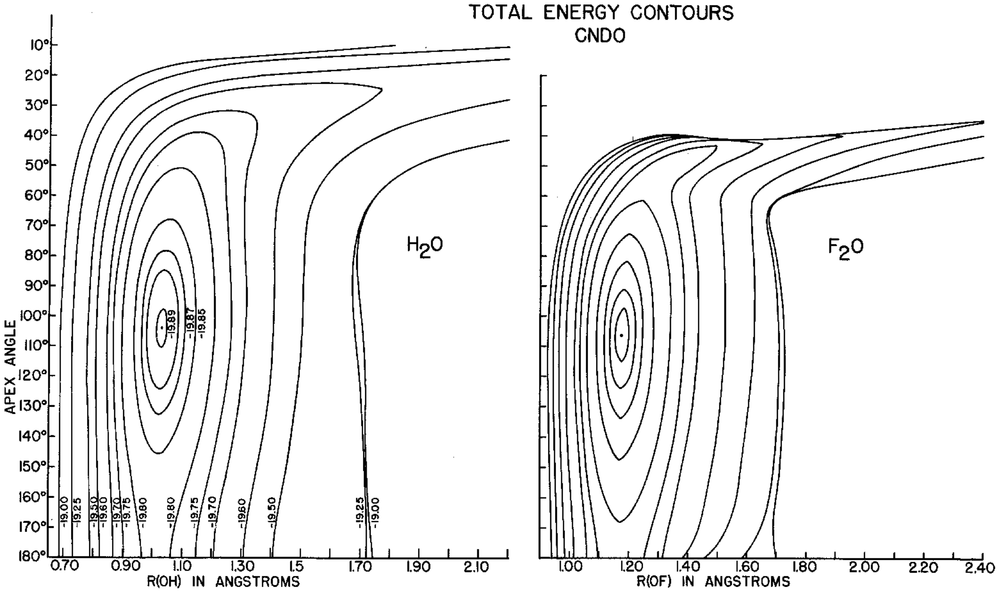

Fig. 1. CNDO energy contour diagrams for H_2O and F_2O

respectively. In a subsequent electron diffraction study of the vapor, the Li – O distance was determined to be 1.60 ± 0.02 Å [6]. This linear structure for the Li_2O molecule requires an apex angle considerably larger than the "normal" angle about an oxygen atom (H_2O, 104°27′; F_2O, 103°18′; Me_2O, 111°37′; O_3, 116°48′; etc.). Such gross differences from the normal angle have been attributed to the presence of strongly electropositive ligands [7], in which case, "ionic repulsions overcome the lone-pair repulsions". An earlier SCF calculation on Li_2O corroborated the highly ionic linear structure but predicted a bond distance of 1.65 Å [8].

Another related molecule which may also have an anomalous geometry is dialuminum oxide (aluminum suboxide), Al_2O. Electric-deflection measurements were interpreted as favoring a $D_{\infty h}$ linear structure [5], although the conclusions in this case were not considered unambiguous because of the possibly small Al – O bond moment. Infrared studies of gaseous Al_2O further indicated that the molecule was linear [9]. However, infrared spectral measurements of $Al_2{}^{16}O$ and $Al_2{}^{18}O$ vapors trapped in rare gas matrices [10, 11], seemed to establish a bent C_{2v} structure with an apex angle of about 145°. The Al – O distance was estimated to be 1.65 – 1.66 Å using the Laurie-Hershbach relation [12]. Further studies of the infrared spectra of Al_2O molecules isolated in rare gas matrices, which find the ν_2 bending mode at a quite high frequency, suggest the occurrence of a metal-metal bond resulting in a ring-type structure [13]. In any case, although the structure of gaseous Al_2O has not been well established experimentally, the apex angle is apparently considerably larger than normal, so the Al_2O molecule may be adjusted to have an anomalous geometry, again probably as a result of the presence of highly electropositive ligands.

We here compare the potential surfaces for Li_2O and Al_2O molecules as calculated by *ab initio* all-electron self-consistent-field methods with those surfaces calculated by the semiempirical CNDO and INDO methods of Pople *et al.* [14–16]. We find that our *ab initio* SCF procedure does correctly predict a linear structure for the Li_2O molecule with highly acceptable Li – O bond distances in agreement with experiment. On the other hand, the CNDO and INDO methods incorrectly imply stable bent structures with very acute apex angles and very long Li–O distances; rather more like Li_2 molecules and O-atoms held together by van der Waals forces than like covalently bonded molecules with conventional bonds. In the case of Al_2O, the CNDO calculations produce a very complex energy contour diagram; the stablest configuration having long bonds and an acute apex angle. Again this unlikely structure is better described as an Al_2 molecule with an O-atom attached to the Al – Al bond. The SCF calculations here also predict a linear configuration to be the most stable, this in contrast to the experimental conclusions from matrix-isolation studies. Previous *ab initio* LCAO–SCF–MO calculations on AB_2-type molecules have always given values for bond angles in excellent agreement with experiment; the differences have never been larger than 5° [17], so in this case there may be additional factors involved.

Table 1. Orbital exponents used for oxygen, lithium, and aluminum

O (^3P)		Li (^2S)		Al (^2P)	
s-type functions		s-type functions		s-type functions	
1.	18045.3	1.	1782.90	1.	55112.7
2.	2660.12	2.	267.096	2.	8204.66
3.	585.663	3.	60.0718	3.	1863.56
4.	160.920	4.	16.7798	4.	530.195
5.	51.1637	5.	5.40327	5.	174.895
6.	17.8966	6.	1.90603	6.	64.0090
7.	6.63901	7.	0.71791	7.	25.3231
8.	2.07658	8.	0.26344	8.	10.5639
9.	0.77360	9.	0.077157	9.	3.21260
10.	0.25576	10.	0.028536	10.	1.15432
				11.	0.178128
				12.	0.065885
p-type functions					
11.	49.8279			p-type functions	
12.	11.4887			13.	259.307
13.	3.60920			14.	60.9263
14.	1.32052			15.	19.3113
15.	0.48209			16.	6.99747
16.	0.16509			17.	2.66879
				18.	1.03447
				19.	0.307591
				20.	0.113877
				21.	0.041397

Methods of Calculation

In our *ab initio* method of calculation the energies and wave functions were determined by the conventional all-electron SCF–MO–LCAO procedure [18]. The molecular orbitals were expanded in terms of groups of Gaussian functions optimized for the free atoms and the computations were carried out using the computer program IBMOL [19]. We used Huzinaga's $(10s-6p)$ and $(10s)$ Gaussian orbital basis sets for the oxygen and lithium atoms, respectively [20]. For the aluminum atom we used a $(12s-9p)$ Gaussian basis [21]. The Gaussian bases were "contracted" to a smaller number of orbital functions by taking certain appropriate linear combinations of them [22]. The contractions employed in the calculations were: Li $(5-1s,\ 2-1s',\ 1-2s,\ 1-2s',\ 1-2s'')$, O $(5-1s,\ 2-1s',\ 1-2s,\ 1-2s',\ 1-2s'',\ 4-2p,\ 1-2p',\ 1-2p'')$, and Al $(6-1s,\ 2-1s',\ 1-2s,\ 1-2s',\ 1-3s,\ 1-3s',\ 3-2p,\ 3-2p',\ 1-3p,\ 2-3p')$. Thus in the molecular calculations we had a total of 48 Gaussian orbitals contracted to 24 orbital functions for Li_2O, and a total of 106 Gaussian orbitals contracted to 50 orbital functions for Al_2O. The uncontracted basis sets generate atomic energy values for oxygen (^3P), lithium (^2S), and aluminum (^2P) of: -74.806295, -7.432503, and -241.87118 a.u. as compared to the corresponding Hartree-Fock values: -74.809359, -7.4327257, and -241.87665 a.u., respectively [23]. With the contractions we used in the molecular calculations, these atomic energies became, respectively: -74.800344, -7.430840, and -241.85583 a.u.

Table 2. Contracted gaussian sets used for oxygen, lithium, and aluminum[a]

$1s$ (O)	$0.0014499\chi_1+0.0114955\chi_2+0.0621722\chi_3+0.2514504\chi_4+0.7528668\chi_5$
$1s'$ (O)	$0.5579327\chi_6+0.4851125\chi_7$
$2s$ (O)	$1.0\chi_8$
$2s'$ (O)	$1.0\chi_9$
$2s''$ (O)	$1.0\chi_{10}$
$2p$ (O)	$0.0164570\chi_{11}+0.1064213\chi_{12}+0.3493159\chi_{13}+0.6572345\chi_{14}$
$2p'$ (O)	$1.0\chi_{15}$
$2p''$ (O)	$1.0\chi_{16}$
$1s$ (Li)	$0.0012504\chi_1+0.0097322\chi_2+0.0505364\chi_3+0.1924760\chi_4+0.8751657\chi_6$
$1s'$ (Li)	$0.4890310\chi_5+0.6556144\chi_7$
$2s$ (Li)	$1.0\chi_8$
$2s'$ (Li)	$1.0\chi_9$
$2s''$ (Li)	$1.0\chi_{10}$
$1s$ (Al)	$0.0006430\chi_1+0.0050522\chi_2+0.026051\chi_3+0.1026050\chi_4+0.3084398\chi_5$ $+0.6507015\chi_6$
$1s'$ (Al)	$0.7465045\chi_7+0.2802842\chi_8$
$2s$ (Al)	$1.0\chi_9$
$2s'$ (Al)	$1.0\chi_{10}$
$3s$ (Al)	$1.0\chi_{11}$
$3s'$ (Al)	$1.0\chi_{12}$
$2p$ (Al)	$0.0270729\chi_{13}+0.2027476\chi_{14}+0.8440499\chi_{15}$
$2p'$ (Al)	$0.3422733\chi_{16}+0.4800991\chi_{17}+0.3117411\chi_{18}$
$3p$ (Al)	$1.0\chi_{19}$
$3p'$ (Al)	$0.6342460\chi_{20}+0.4364747\chi_{21}$

[a] The $\chi_1, \chi_2, \ldots$ are the Gaussian functions whose exponents are given in Table 1

The orbital exponents and contraction coefficients actually used in the calculations are exhibited in Tables 1 and 2.

For the semiempirical CNDO and INDO calculations we utilized the computer program CNINDO [24], slightly modified but with the original parameterization. This program calculates the CNDO or INDO energies and the corresponding molecular orbitals of Pople [14–16]. For second row elements only CNDO calculations can be made, but *d*-orbitals are taken into account. All computations were performed on the IBM 360/67 Computer at the Washington State University Computing Center.

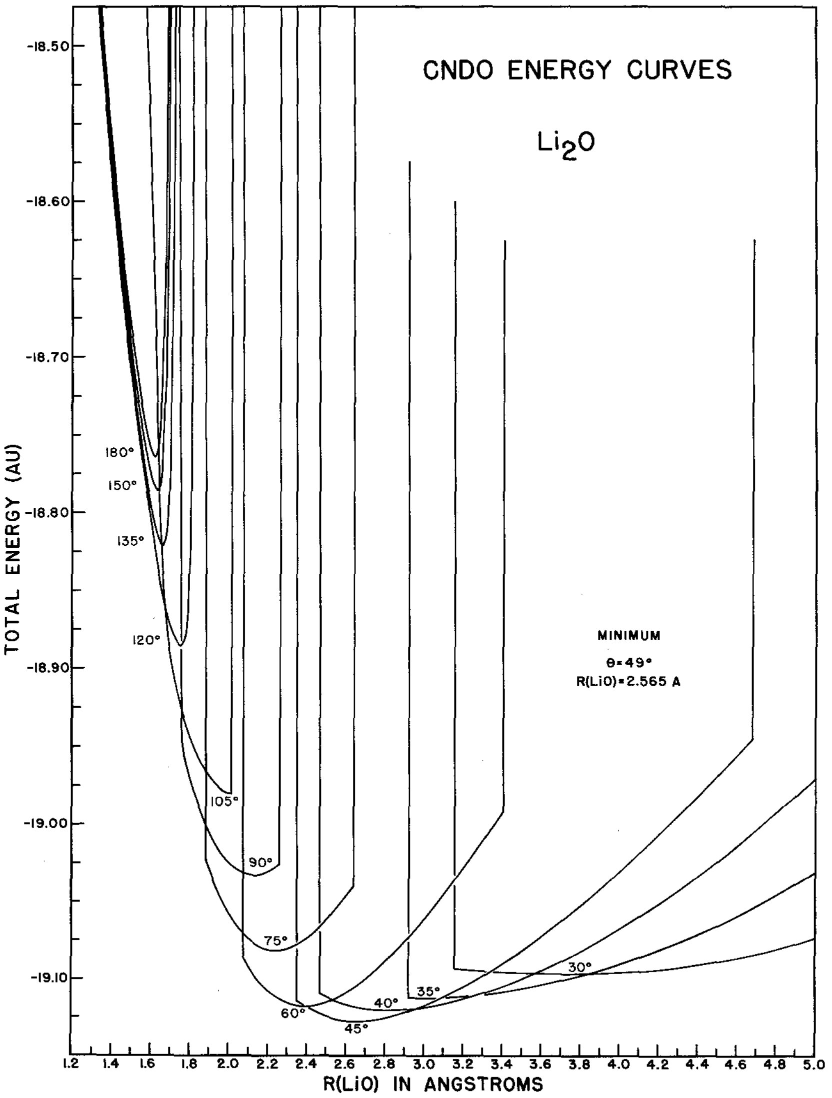

Fig. 2. CNDO total energy curves for Li_2O

Results and Discussion

In both the *ab initio* and the semiempirical treatments of Li_2O and Al_2O, total energy curves for different apex angles as functions of the bond distances were computed under the assumption of either C_{2v}, $C_{\infty v}$, or $D_{\infty h}$ symmetry. The CNDO and INDO energy curves are very complex, but a few of the CNDO energy curves for Li_2O are shown in Fig. 2. These curves represent a steep-walled valley decending to a minimum in energy at an apex angle of $\theta = 49°$ and R (LiO) = 2.565 Å. From these curves, points of equal energies were collected and the total-energy contour diagram – potential surface – was constructed and is shown in Fig. 3. The INDO potential surface of Li_2O is very similar with its minimum energy at $\theta = 50°$ and R (LiO) = 2.45 Å. These surfaces predict acute angled structures for Li_2O with long LiO distances. The Li – Li separations in these CNDO and INDO minimum energy structures are only 2.127 and 2.071 Å, respectively, compared to the experimental Li – Li distance in the Li_2 molecule of 2.5625 Å. However, CNDO and INDO methods generally give short equilibrium distances in such diatomic molecules; for Li_2 the CNDO and INDO internuclear distances are 2.180 and 2.135 Å, respectively. Thus the Li – Li separations in the CNDO and INDO Li_2O molecules are less than the Li – Li distances in the corresponding Li_2 molecules. For this reason the semiempirically calculated structures of Li_2O are described as O-atoms attached to the bonds of Li_2 molecules. This interpretation is supported by the high value calculated for

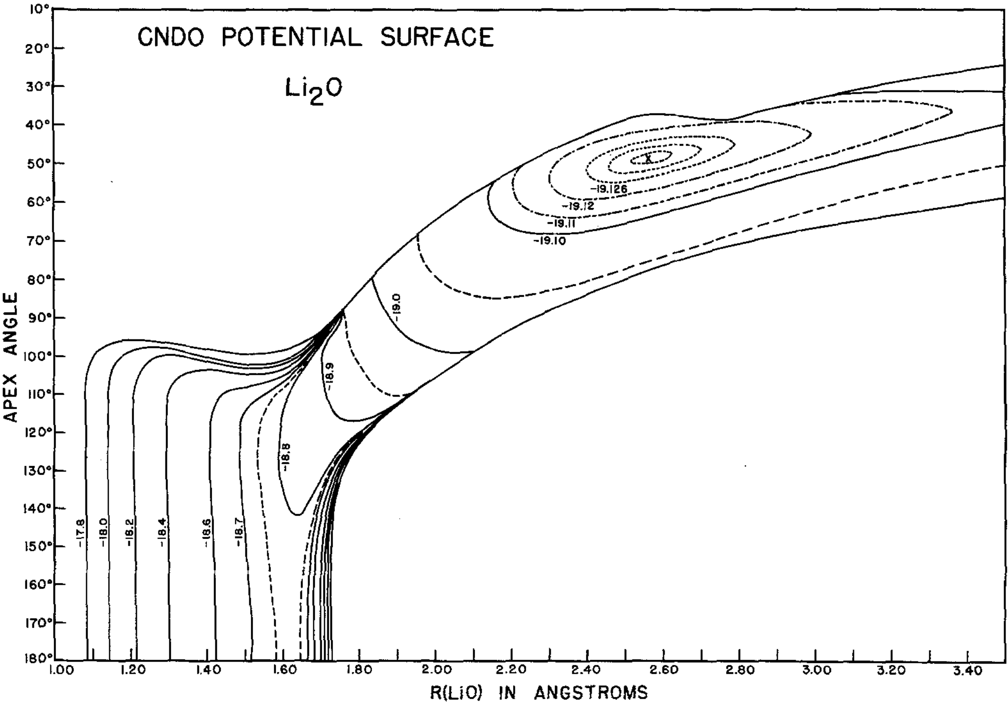

Fig. 3. CNDO potential surface for Li_2O

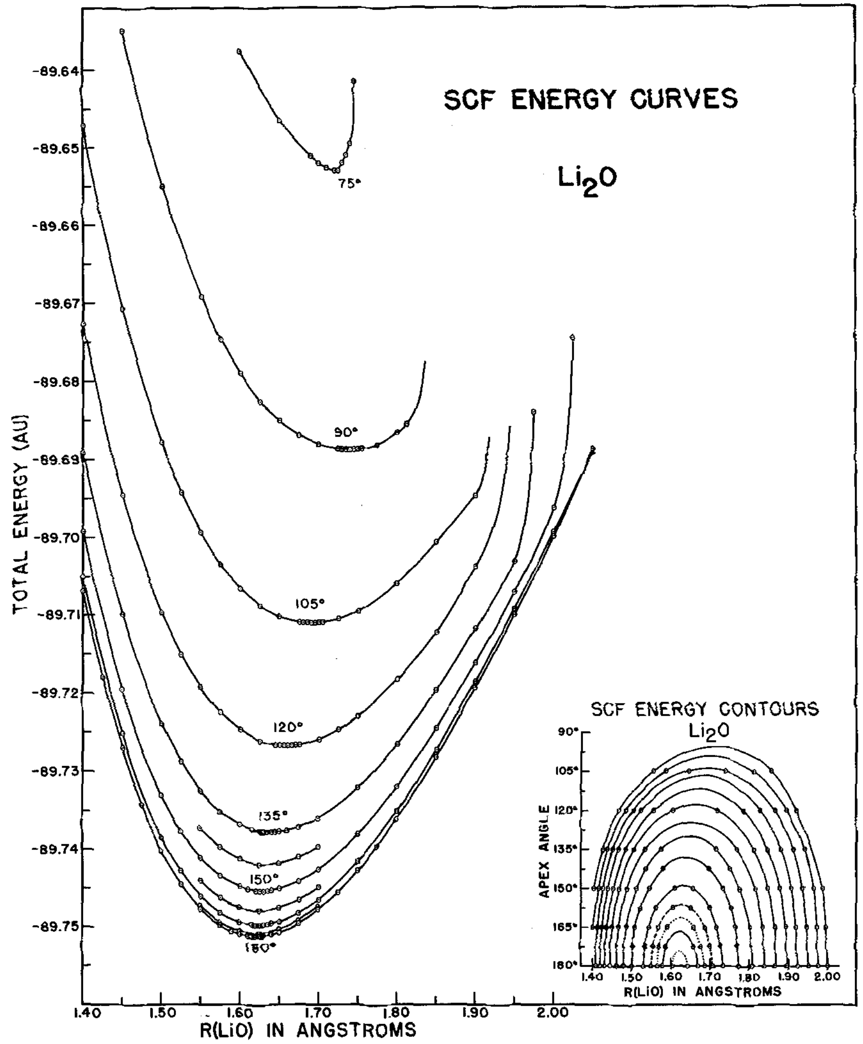

Fig. 4. *Ab initio* SCF energy curves and potential surface for Li_2O

the bending frequency of the acute-angled CNDO Li_2O molecule, namely 619.6 cm^{-1}, as compared to the corresponding stretching frequency calculated for the CNDO Li_2 molecule, 638.5 cm^{-1}.

The *ab initio* SCF energy curves and the resulting potential surface for Li_2O are shown in Fig. 4 and the calculated total energies are listed in Table 3. This potential surface unambiguously predicts a linear configuration for Li_2O with a bond distance of 1.620 Å, in excellent agreement with the experimental value of 1.60 ± 0.02 Å [6]. In addition, from the symmetrical stretching, bending, and asymmetrical stretching potential curves (Tables 3 and 4), this surface predicts vibrational frequencies for Li_2O within about 10% of the observed values (see Table 5).

Table 3. Calculated total SCF energies (a.u.) for $C_{2v}Li_2O$

$\theta = 180°$		$\theta = 165°$		$\theta = 150°$		$\theta = 135°$		$\theta = 120°$		$\theta = 105°$		$\theta = 90°$		$\theta = 75°$	
R (Å)	E (a.u.)	R (Å)	E (a.u.)	R (Å)	E (a.u.)	R (Å)	E (a.u.)	R (Å)	E (a.u.)	R (Å)	E (a.u.)	R (Å)	E (a.u.)	R (Å)	E (a.u.)
1.40	−89.706912	1.40	−89.705025	1.40	−89.699291	1.40	−89.689107	1.40	−89.672665	1.40	−89.646713	1.40	−89.607824	1.60	−89.637707
1.425	.717921	1.45	.725149	1.45	.719597	1.45	.709888	1.45	.694559	1.45	.670771	1.45	.634987	1.65	.646472
1.45	.726987	1.50	.738354	1.50	.733057	1.50	.723895	1.50	.709671	1.50	.687901	1.50	.655038	1.69	.651212
1.475	.734322	1.525	.742817	1.525	.737669	1.525	.728799	1.525	.715123	1.525	.694310	1.55	.669365	1.70	.652147
1.50	.740113	1.55	.746060	1.55	.741070	1.55	.732502	1.55	.719369	1.55	.699485	1.575	.674740	1.71	.652678
1.525	.744530	1.575	.748217	1.575	.743393	1.575	.735134	1.575	.722538	1.575	.703552	1.60	.679085	1.72	.653005
1.55	.747722	1.60	.749405	1.60	.744755	1.60	.736811	1.60	.724746	1.60	.706629	1.625	.682508	1.725	.653004
1.575	.749824	1.615	.749700	1.61	.745057	1.615	.737405	1.625	.726100	1.625	.708825	1.65	.685101	1.73	.651964
1.59	.750611	1.62	.749734	1.62	.745228	1.625	.737641	1.645	.726630	1.65	.710231	1.675	.686950	1.735	.651062
1.60	.750954	1.625	.749736	1.625	.745266	1.63	.737714	1.65	.726691	1.675	.710934	1.70	.688106	1.74	.649573
1.61	.751161	1.63	.749708	1.63	.745275	1.635	.737757	1.655	.726726	1.68	.710997	1.725	.688734	1.75	.643514
1.615	.751215	1.635	.749650	1.635	.745254	1.64	.737771	1.66	.726734	1.685	.711035	1.73	.688788	1.80	.551292
1.62	.751236	1.64	.749563	1.64	.745204	1.645	.737757	1.665	.726716	1.69	.711050	1.735	.688821		
1.625	.751227	1.65	.749305	1.65	.745020	1.65	.737716	1.67	.726672	1.695	.711040	1.74	.688831		
1.63	.751186	1.675	.748200	1.675	.744102	1.66	.737554	1.675	.726604	1.70	.711002	1.745	.688821		
1.64	.751017	1.70	.746498	1.70	.742589	1.675	.737121	1.70	.725914	1.705	.710953	1.75	.688792		
1.65	.750735	1.75	.741577	1.75	.738051	1.70	.735931	1.725	.724689	1.725	.710519	1.755	.688734		
1.675	.749566	1.80	.735032	1.80	.731887	1.75	.732037	1.75	.722989	1.75	.709517	1.775	.688213		
1.70	.747800	1.85	.727262	1.85	.724487	1.80	.726490	1.80	.718358	1.80	.706010	1.80	.686644		
1.725	.745507	1.90	.718578	1.90	.716127	1.85	.719696	1.85	.712350	1.85	.700673	1.8125	.685558		
1.75	.742750	1.95	.709258	1.95	.707051	1.90	.711789	1.90	.703814	1.90	.694701	1.85	.584990		
1.775	.739590	2.00	.699381	2.00	.696207	1.95	.703175	1.95	.627725						
1.80	.736077	2.05	.688956	2.025	.674560	1.975	.683926								
1.85	.728179														
1.90	.719352														
1.95	.709936														
2.00	.699909														
2.05	.688650														

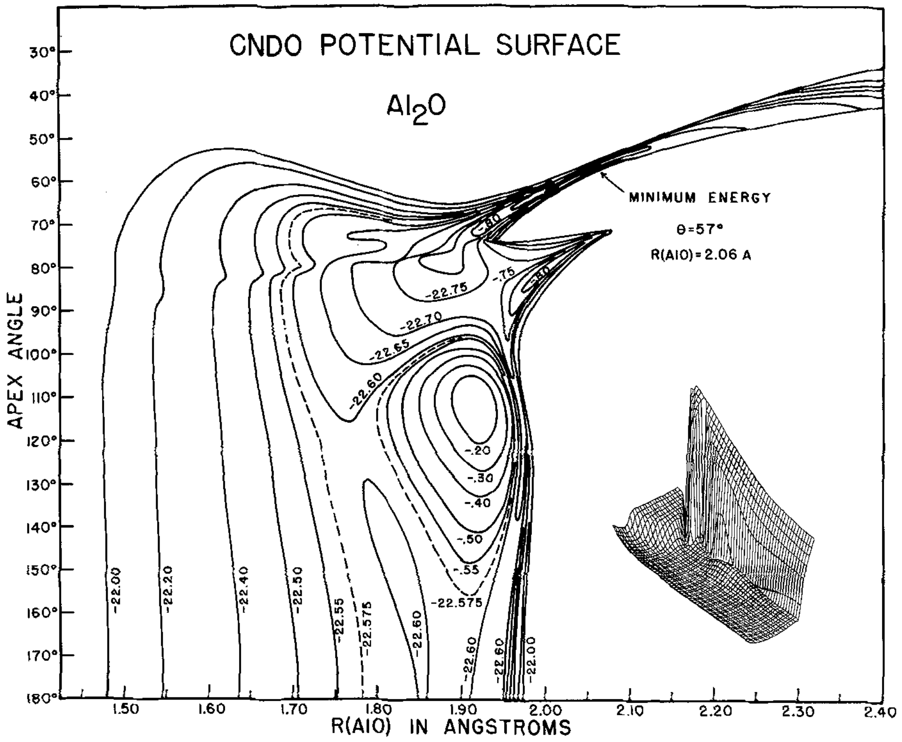

Fig. 5. CNDO potential surface for Al_2O

Table 4. Calculated total SCF energies for $C_{\infty v}$ Li_2O

$R_1(LiO)/R_2(LiO)$	E (a.u.)
1.62/1.62	−89.751236
1.61/1.63	.751173
1.60/1.64	.750982
1.59/1.65	.750664
1.575/1.665	.749948
1.55/1.69	.748104
1.525/1.715	.745429

Table 5. Vibrational frequencies of Li_2O and Al_2O

Vibrational	Li_2O		Al_2O	
Mode	Matrix-isolation [4]	SCF Calculation	Matrix-isolation [13]	SCF Calculation
ν_1 Sym. stretch	760 cm^{-1}	804 cm^{-1}	716 cm^{-1}	527 cm^{-1}
ν_2 Bend	140 cm^{-1}	129 cm^{-1}	503 cm^{-1}	102 cm^{-1}
ν_3 Asym. stretch	987 cm^{-1}	1100 cm^{-1}	992 cm^{-1}	1057 cm^{-1}

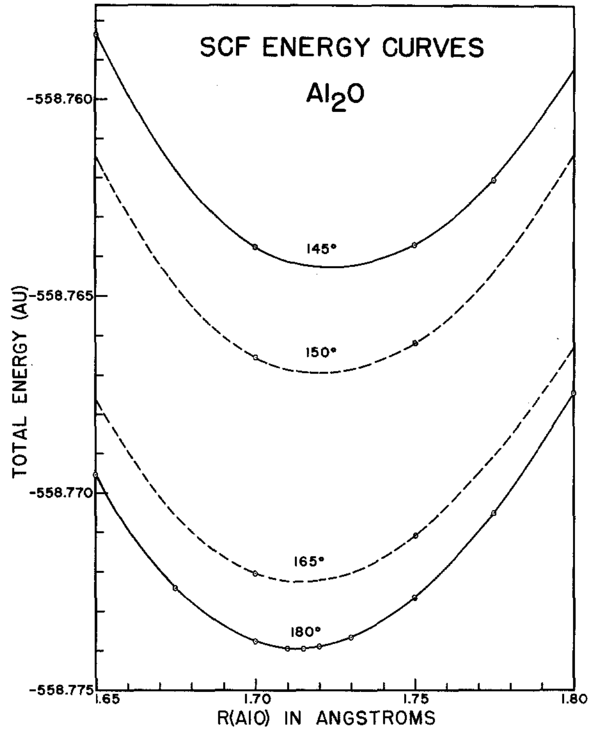

Fig. 6. *Ab initio* SCF energy curves for Al_2O

Table 6. Calculated total SCF energies (a.u.) for Al_2O

R (Al – O) (Å)	Apex Angle 180°	165°	150°	145°
1.65	−558.76954			−558.75837
1.675	.77241			
1.70	.77377	−558.77203	−558.76654	.76376
1.71	.77393			
1.715	.77394			
1.72	.77389			
1.73	.77366			
1.75	.77266	.77110	.76619	.76370
1.775	.77050			.76203
1.80	.76744			

The CNDO energy curves for Al_2O are very complex often with several peaks and valleys and are not shown, but the potential surface constructed from these curves is exhibit in Fig. 5. This is a very complex surface and obviously absurd. It predicts the same type of unreasonable structure as the CNDO calculation did for Li_2O. Here the minimum energy configuration occurs when

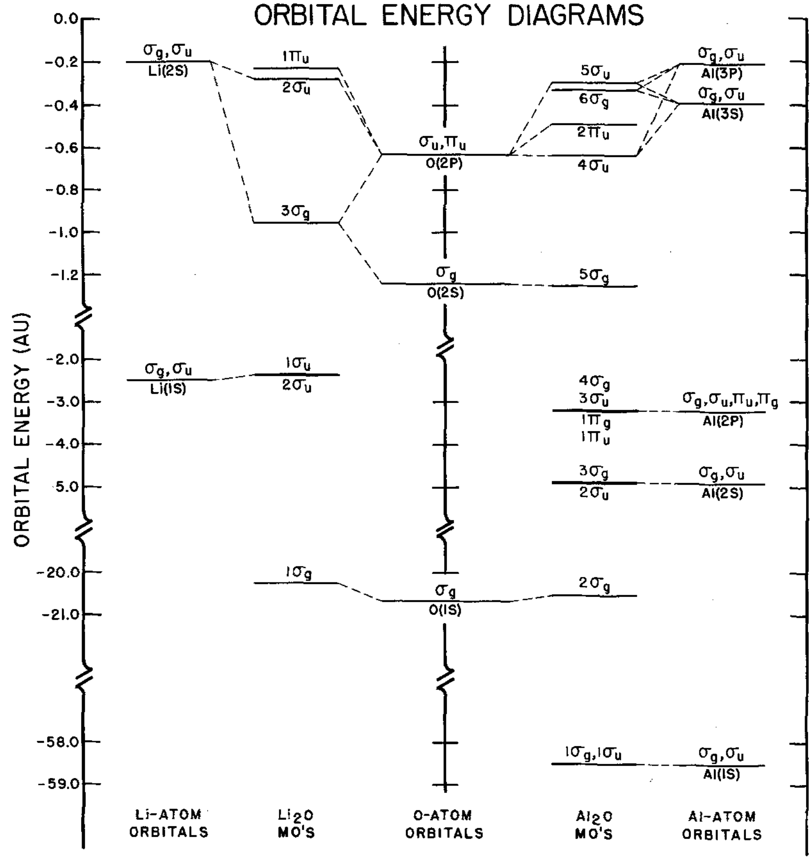

Fig. 7. *Ab initio* SCF orbital energy diagrams for Li_2O and Al_2O

R (AlO) = 2.06 Å and the apex angle is 57°. The Al – Al distance in this acute-angled structure is predicted to be 1.966 Å, which is again shorter than the CNDO calculated Al – Al distance in the Al_2 molecule, 2.007 Å, so again this corresponds to an Al_2 molecule with attached O-atom.

The *ab initio* energy curves for Al_2O are shown in Fig. 6, and the energy values are given in Table 6. The minimum energy structure is the linear symmetric $D_{\infty h}$ configuration with Al – O distances of 1.715 Å. Although there are fewer points and fewer energy curves here than in the Li_2O treatment, the calculated energy for the linear configuration is certainly significantly less than for the experimentally deduced configuration, $\theta = 145°$, R (AlO) = 1.65 Å, and it is unlikely that the calculated linear structure is in significant error. One might suggest that the inclusion of *d*-orbitals in the treatment would give a stable bent structure [17], but in this case, the *d*-orbital energies on the relevant atoms and ions are much too high to have any significant contributions. Another possibility is that the "Renner Effect" is operating in this molecule. Our SCF Hamiltonian does not include the quadratic vibration-electronic interaction,

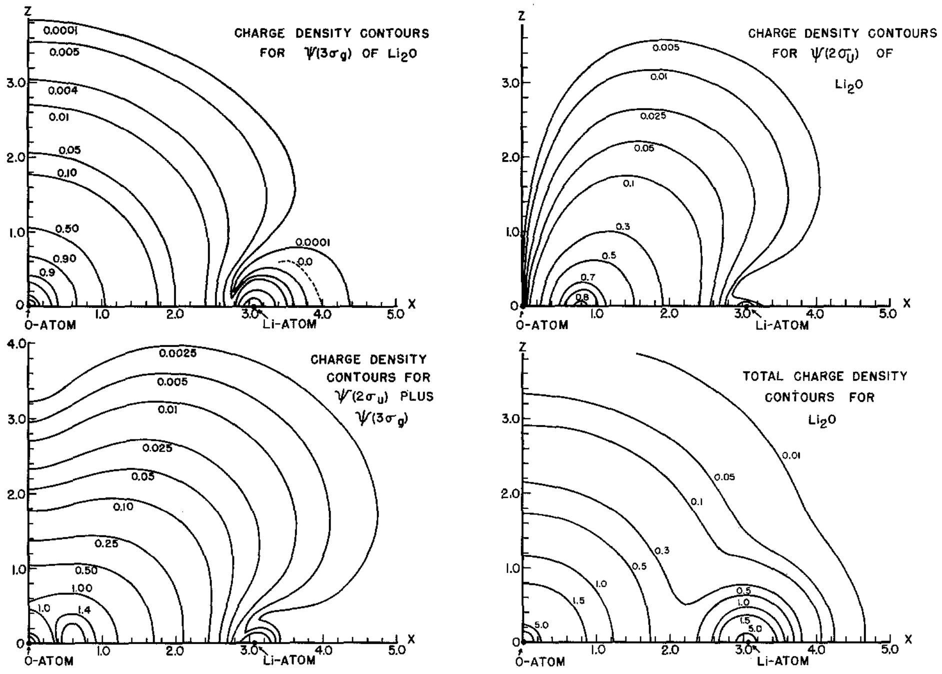

Fig. 8. *Ab initio* SCF electron density diagrams for Li_2O

but even so, such large Renner distortions as required here have not been reported or anticipated for molecules such as Al_2O. Although some AB_2-type molecules, such as CH_2, NH_2, BH_2, have been treated as extreme Renner effect molecules with such large distortions [25], conventional SCF treatments of these molecules do give the bent structures directly without additional terms in the Hamiltonians [26]. It is probably just as likely that the experimental interpretations are in error in that the matrix-isolated molecules do not have the gas phase structure, or that impurities give spurious absorptions. It has previously been observed that matrix and gas phase structures may differ. In any case, the calculated vibrational frequencies for Al_2O from our SCF potential surface do not agree with the experimentally deduced values from the matrix-isolation infrared studies as shown in Table 5.

It is evident from these results that the semiempirical CNDO and INDO treatments with standard parameterization will not correctly predict the geometries of these "anomalous" molecules. Thus, one must conclude that these semiempirical treatments are unreliable even for such "safe" predictions as geometrical configurations.

We can get some idea of the bounding in these compounds from our *ab initio* SCF results. According to these calculations, the occupied ground state molecular orbitals for the linear $D_{\infty h}$ Li_2O molecules occur in the sequence

$$(1\sigma_g)^2(2\sigma_g)^2(1\sigma_u)^2(3\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4 .$$

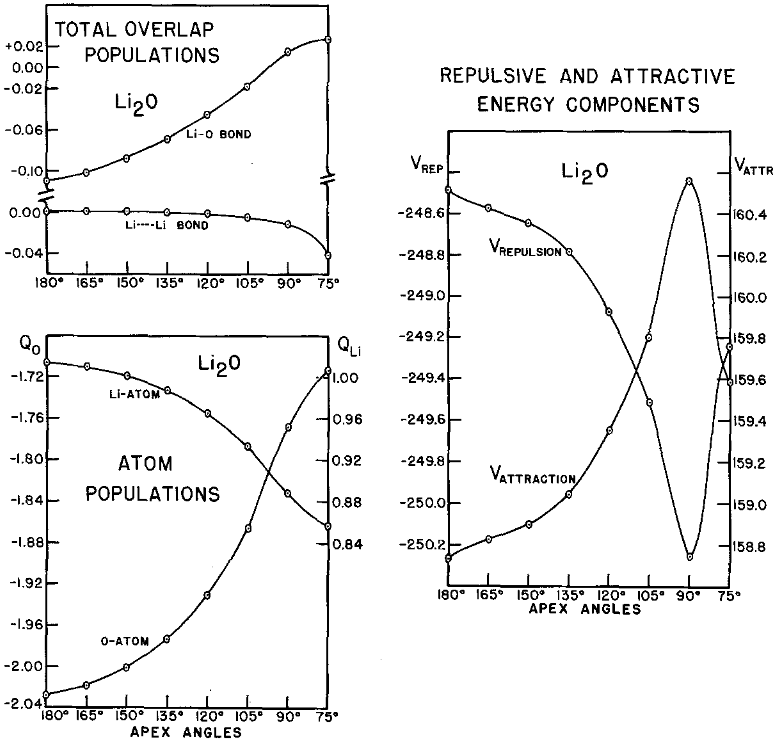

Fig. 9. Variations with apex angle of the atom populations, overlap populations, and energy components of Li_2O

The $3\sigma_g$ and $2\sigma_u$ orbitals are possible bonding orbitals as suggested in the orbital energy diagram of Fig. 7. In the case of Li_2O, the energies corresponding to all of these orbitals vary only moderately with Li–O–Li angle as illustrated in Table 7 and they do not follow Walsh's rules. Only the bonding molecular orbital $2\sigma_u$ has its minimum energy coincident with the linear configuration. The bonding MO's, which combine primarily the Li $(2s)$ and the O $(2s+2p)$ atomic orbitals, are very polar, concentrating their electron densities nearer the oxygen atom. The charge distributions of some of these orbitals are adumbrated in the electron density contour diagrams of Fig. 8. As expected the bonds are very ionic; a population analysis [27] generating atom charges of $-2.027787e$ on the oxygen and $+1.013904e$ on the lithium atoms. This means that one may well write the linear structure of Li_2O as $Li^+O^=Li^+$. These charges decrease with decreasing apex angle as shown in Fig. 9 which also shows the variation with apex angle of the overlap populations, as well as the attractive (V_{Ne}) and repulsive $(V_{NN}+V_{ee}+T)$ components of the total energy, the latter of which are summarized in Table 8. From these data it is seen that the O-atom becomes less negative and the Li-atoms less positive as the molecule is bent. At the same time the Li – Li interaction changes little with angle and the Li – O bonding actually increases slightly with decreasing apex angle. Thus the

Table 7. Total and orbital SCF energies (a.u.) for the minimum energy configurations of Li_2O

$D_{\infty h}$	Minimum energy configuration								C_{2v}
orbitals	180°, 1.62Å	1.65°, 1.625Å	150°, 1.63Å	135°, 1.64Å	120°, 1.66Å	105°, 1.69Å	90°, 1.74Å	75°, 1.72Å	orbitals
$1\sigma_g$	−20.257243	−20.258052	−20.260336	−20.264495	−20.270218	−20.279170	−20.293173	−20.122027	$1a_1$
$2\sigma_g$	− 2.3535357	− 2.3557216	− 2.3607675	− 2.3691637	− 2.3815787	− 2.3985496	− 2.4218368	− 2.4488741	$2a_1$
$1\sigma_u$	− 2.3534186	− 2.3555863	− 2.3605662	− 2.3688597	− 2.3811425	− 2.3979048	− 2.4207539	− 2.4450490	$1b_2$
$3\sigma_g$	− 0.95316376	− 0.95348827	− 0.95579827	− 0.95945332	− 0.96364719	− 0.96912026	− 0.97554729	− 0.91486390	$3a_1$
$2\sigma_u$	− 0.27466516	− 0.27334282	− 0.27117803	− 0.26795480	− 0.26348845	− 0.25919520	− 0.25581506	− 0.19809118	$2b_2$
$1\pi_u$	− 0.22503893	− 0.22516120	− 0.22671462	− 0.22911692	− 0.23165463	− 0.23523787	− 0.24213251	− 0.19014165	$1b_1$
		− 0.22504262	− 0.22628329	− 0.22834859	− 0.23093161	− 0.23491121	− 0.23842897	− 0.19451169	$4a_1$
Total	−89.751236	−89.749736	−89.745275	−89.737771	−89.726734	−89.711050	−89.688831	−89.653005	

Table 8. Energy components for minimum energy configurations of Li_2O

Configuration $\theta°$	R (Å)	Total Energy	One-electron $V_{Ne}+T$	Two-electron V_{ee}	Nuclear-nuclear V_{NN}	Attraction V_{Ne}	Repulsion $V_{NN}+V_{ee}+T$
180°	1.620	−89.751236	−160.51612	53.615958	17.148931	−250.267356	160.51612
165°	1.625	−89.749736	−160.42430	53.565755	17.108809	−250.174036	160.42430
150°	1.630	−89.745275	−160.35778	53.517244	17.095257	−250.103055	160.35778
135°	1.640	−89.737771	−160.21962	53.422415	17.059249	−249.957391	160.21962
120°	1.660	−89.726734	−159.92338	53.239032	16.957620	−249.650114	159.92338
105°	1.690	−89.711050	−159.48519	52.968504	16.805632	−249.196240	159.48519
90°	1.740	−89.688831	−158.74851	52.526568	16.533112	−248.437341	158.74851
75°	1.72	−89.653005	−159.76099	53.066329	17.041657	−249.413995	159.76099

stability of the linear configuration does not appear to be due to Li – Li repulsion alone. In fact, the total nuclear-nuclear repulsions (V_{NN}) are not at a minimum in the linear configuration because the Li_2O molecule stretches as it is bent. In support of this, the overall attraction and repulsion energy components have opposing phase relations, but, near the stable linear configuration, the attractive energy component changes more rapidly than does the repulsive component, so it would be regarded as "attractive dominant" in relation to which energy term leads to the stable configuration [28].

For Al_2O the calculated occupied ground state configuration is

$$(1\sigma_u)^2(1\sigma_g)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^4(3\sigma_u)^2(4\sigma_g)^2(5\sigma_g)^2(4\sigma_u)^2(2\pi_u)^4(6\sigma_g)^2(5\sigma_u)^2$$

Here the bonding molecular orbital, $5\sigma_u$, incorporates mainly only the oxygen $2p\sigma$ with the aluminum $3s$ and $3p\sigma$ orbitals. This again leads to a very polar charge distribution, but the orbital energy diagram (Fig. 8) suggests the bonding may be qualitatively different from that in Li_2O. However, this is a difference in degree rather than in kind. A population analysis on the minimum energy linear configuration of Al_2O again supports a strongly ionic structure; the atom charges on the Al- and O-atoms being calculated as $+0.671804e$ and $-1.343435e$, respectively, not as ionic as Li_2O and more nearly like $Al^{+2/3}$ $O^{-4/3}Al^{+2/3}$. The atom and overlap populations for Al_2O vary with apex angle in a manner similar to those for Li_2O, but here the molecule apparently stretches only slightly as it bends so that the nuclear-nuclear repulsion energy is a minimum in the linear configuration. The total repulsion energy component here changes more rapidly than the attractive energy component, so for Al_2O the stable linear configuration is "repulsive dominant".

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