

Accurate Potential Curves and Properties for the  $X^2\Sigma$  and  $A^2\Pi^+$  states of LiO

by

M. Yoshimine

A Special Technical Report

for

Calculation of Physical Properties of Diatomic Molecules

Principal Investigator: Dr. P. S. Bagus

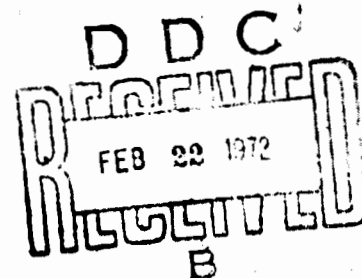
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ACCURATE POTENTIAL CURVES AND PROPERTIES FOR THE  $X^2\Pi$  AND  $A^2\Sigma^+$  STATES OF  $LiO^+$

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ABSTRACT: Ab initio calculations have been performed to determine potential curves and molecular properties for the  $X^2\Pi$  and  $A^2\Sigma^+$  states of the  $LiO$  molecule. The calculations use a conventional configuration interaction (CI) method in which the Hartree-Fock configuration is taken as reference configuration and only valence shells are correlated. The molecular orbital (MO) basis set used in the CI calculations is composed of the Hartree-Fock orbitals and additional MO's. These additional MO's are formed by truncating a set of pseudonatural orbitals (PSNO's) obtained as the natural orbitals of a CI calculation on a single pair of valence electrons. The main results are  $R_e = 1.695\text{\AA}$ ,  $D_e^0 = 3.37\text{ eV}$ ,  $\omega_e = 851.5\text{ cm}^{-1}$  ( $^7Li^{16}O$ ),  $\mu = 6.76$  Debye for the  $X^2\Pi$  state and  $R_e = 1.599\text{\AA}$ ,  $D_e^0 = 4.90\text{ eV}$ ,  $\omega_e = 866.8\text{ cm}^{-1}$  ( $^7Li^{16}O$ ),  $\mu = 5.96$

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† This research was supported by the Advanced Research Projects Agency of the Department of Defense under Contract No. DAHCO4 69 0080, monitored by U.S. Army Research Office - Durham, Box CM, Duke Station, Durham, North Carolina, 27706.

Debye for the  $\Lambda^2\Sigma^+$  state. The computed  $D_e^0(X^2\Pi) = 3.37$  eV is in good agreement with the observed value of  $3.39 \pm 0.26$  eV. The other results are also believed to be accurate to within a few percent. The computed term energy  $T_e(X^2\Pi \rightarrow \Lambda^2\Sigma^+)$  is  $2330 \text{ cm}^{-1}$  with the CI wave functions, in surprising agreement with the Hartree-Fock value of  $2342 \text{ cm}^{-1}$ .

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**ABSTRACT:** Ab initio calculations have been performed to determine potential curves and molecular properties for the  $X^2\Pi$  and  $A^2\Sigma^+$  states of the  $LiO$  molecule. The calculations use a conventional configuration interaction (CI) method in which the Hartree-Fock configuration is taken as reference configuration and only valence shells are correlated. The molecular orbital (MO) basis set used in the CI calculations is composed of the Hartree-Fock orbitals and additional MO's. These additional MO's are formed by truncating a set of pseudonatural orbitals (PSNO's) obtained as the natural orbitals of a CI calculation on a single pair of valence electrons. The main results are  $R_e = 1.695\text{\AA}$ ,  $D_e^0 = 3.37\text{ eV}$ ,  $\omega_e = 851.5\text{ cm}^{-1}$  ( ${}^7\text{Li}^{16}\text{O}$ ),  $\mu = 6.76$  Debye for the  $X^2\Pi$  state and  $R_e = 1.599\text{\AA}$ ,  $D_e^0 = 4.90\text{ eV}$ ,  $\omega_e = 866.8\text{ cm}^{-1}$  ( ${}^7\text{Li}^{16}\text{O}$ ),  $\mu = 5.96$  Debye for the  $A^2\Sigma^+$  state. The computed  $D_e^0(X^2\Pi) = 3.37\text{ eV}$  is in good agreement with the observed value of  $3.39 \pm 0.26\text{ eV}$ . The other results are also believed to be accurate to within a few percent. The computed term energy  $T_e(X^2\Pi \rightarrow A^2\Sigma^+)$  is  $2330\text{ cm}^{-1}$  with the CI wave functions, in surprising agreement with the Hartree-Fock value of  $2342\text{ cm}^{-1}$ .

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## INTRODUCTION

Gaseous monoxides are important high temperature systems being the subject of numerous experimental investigations in recent years.<sup>1</sup> From a theoretical point of view, the LiO molecule is one of the smallest and simplest gaseous monoxides; however, very few experimental data are presently available, in fact, the dissociation energy is only property for which a reliable value is known experimentally. There is a measurement of the vibrational frequency  $\nu(1-0)$  of LiO in an inert gas matrix but its gas phase value is not known.<sup>2</sup> It has been established that there is a considerable shift in the value of  $\nu$  measured in an inert gas matrix from its gas phase value for molecules with small mass and large dipole moment, in particular for the LiF molecule.<sup>3</sup> Since the LiO molecule is similar to the LiF molecule, one would also expect a considerable difference between  $\nu$  measured in an inert gas matrix and in the gas phase.

In this work, we have determined potential curves and other properties for the two lowest states,  $X^2\Pi$  and  $A^2\Sigma^+$ , of the LiO molecule. These results have been obtained with large CI wavefunctions including  $\sim 1500$  symmetrized configurations. Techniques of quantum mechanical calculations have been improved recently and it is now possible to calculate with reasonable accuracy many properties of system like LiO. In other words, the ab initio results may be used to fill gaps in experimental data and that is the main purpose of this work.

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It is still impracticable to carry out CI calculations which give potential curves with small absolute errors even for a system of the size of LiO. However, it is only necessary to obtain a potential curve which is closely parallel to the actual curve in order to derive reliable

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spectroscopic constants and other properties. In the present calculations, we have only considered correlation effects due to interactions of the valence shell electrons with themselves. If we start from Hartree-Fock or near Hartree-Fock solutions, we expect that the contribution to the total correlation energy of interactions of the core electrons (1s in Li and O) with themselves and with the valence shell electrons will remain constant along the potential curve. We also expect that the neglect of these interactions will have a small effect on other properties. In practice, this restriction allows us to treat the valence shell correlation more accurately and in a more uniform manner along the potential curve. This is possible because we are able to include more valence shell correlating orbitals and configurations in the CI calculation than would be possible if all electrons were correlated.

In CI calculations it is of utmost importance to have a proper orbital basis and proper choice of configurations. To meet this end, the following procedure was used for the present calculations: 1) Obtain Hartree-Fock (HF) wavefunctions for various internuclear distances; 2) Obtain pseudonatural orbitals<sup>4</sup> (PSNO's) for an appropriate pair of electrons; 3) Form the MO basis for the CI calculation by adding a truncated set of the PSNO's to the Hartree-Fock occupied orbitals; 4) Perform the CI calculation using the Hartree-Fock configuration as the reference configuration and including all configurations generated by single and double substitution of the valence orbitals into all the PSNO's used. The detail of the procedure will be given in the next section.

This procedure is necessarily pragmatic in its nature. In addition to assessing the quality of the computed wavefunctions and properties, comparison of the results with known experimental data serves the purpose

of testing the general applicability of the procedure. This is another important purpose of this work.

These calculations are performed with the ALCHEMY system of programs developed by the quantum chemistry group, IBM Research Laboratory, San Jose.

### CALCULATIONS

A basis set of Slater-type functions is constructed based on the accurate atomic basis sets of P. S. Bagus et al.<sup>5</sup> for both Li and O. The atomic basis sets are supplemented with polarization functions needed for the HF calculation and also other Slater-type functions of higher angular momentum needed for describing axial correlation effects. The number and exponents of these supplementary functions are chosen so that the basis set will span an adequate space without performing optimization of exponents. The result is a rather large basis set of  $36\sigma$ ,  $22\pi$ ,  $10\delta$ ,  $4\phi$  type functions, which is listed in Table I.

With this set, single configuration SCF calculations,  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^3$  for the  $X^2\Pi$  state and  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 1\pi^4$  for the  $A^2\Sigma^+$  state, are performed at a number of points around the equilibrium internuclear distance  $R_e$ . The same basis set is used for both states and for all separations. These single configurations do not dissociate to the proper states of the separated atoms for either the  $X^2\Pi$  or  $A^2\Sigma^+$  state. However, for the range of  $R$  (around  $R_e$ ) of interest, we believe that the single Hartree-Fock configuration is sufficiently dominant to be suitable as the "reference state" in subsequent CI calculations. The configurations in the CI calculations are constructed and described as zero, one, two, etc. replacements from the reference configuration(s). If several configurations



have large weights in a CI wavefunction, it may be important to include these configurations as part of the "reference state." We have verified that this is not the case in our calculations by examining the weights of configurations and the occupation numbers of the natural orbitals.

The results of SCF calculations indicate that our choice of the basis set is a reasonable one so far as the total SCF energy is concerned. Further, there were no problems of basis set linear dependence for the SCF calculations. However, the basis set was redundant for the CI calculations. This redundancy is manifested by several virtual Hartree-Fock orbitals with large ( $\sim 50-100$ ) positive and negative coefficients, causing a substantial loss of accuracy in the four index transformation of electron repulsion integrals from integrals over STO's to integrals over molecular orbitals. It was thus necessary to reduce the space spanned by the orthogonal complement of the occupied Hartree-Fock orbitals. This was done in the following way. First, the overlap matrix of the STO basis functions was diagonalized. The eigenvectors associated with eigenvalues less than a certain threshold were deleted. The SCF calculation was then performed in the space spanned by the remaining eigenvectors of the overlap matrix. (The SCF energies for LiO of these calculations differed only in the fifth decimal place from those obtained using the full STO basis set.) The virtual Hartree-Fock orbitals of this new calculation are well behaved,<sup>6</sup> and were orthogonalized to the occupied Hartree-Fock orbitals obtained without truncating the space spanned by the STO basis set. (This orthogonalization introduced only very small changes in the virtual orbitals.) These orbitals plus a set of orthogonalized  $\delta$  and  $\phi$  type STO's formed a molecular orbital basis set for PSNO calculations; the sets are denoted by  $\phi_A(2\Pi)$  and  $\phi_A(2\Sigma^+)$ . The sets  $\phi_A$  consisted of  $31\sigma$ ,  $20\pi$ ,  $10\delta$ ,

and 4s type orbitals for  $2.3 \leq R \leq 3.1$  a.u. and 32s, 20p, 10d, and 4f type for  $3.2 \leq R \leq 3.9$  a.u.

Since LiO is ionic in the vicinity of its equilibrium internuclear separation ( $R_e$ ) and the correlation effect of valence shell electrons alone is considered here, the problem reduces essentially to correlating the valence electrons in  $O^-$ . Weiss' work<sup>7</sup> on the first row atoms shows that the pseudonatural orbital transformation on any single pair of valence electrons yields a rapidly converging and variationally optimum set of virtual orbitals. We have calculated several of the pair correlation energies for the valence shells of both the  $X^2\Pi$  and  $A^2\Sigma^+$  states; angular limits as well as total pair correlation energies have been obtained. We have chosen the 1s-1s pair for the calculation of all but one set of PSNO's. This was done because the pair correlation energy, more precisely the appropriate angular limit of the pair correlation energy, was largest for this pair. The one exception is the set of  $\sigma$  PSNO's for the  $X^2\Pi$  state; here the 4s-4s pair has been used since the  $\sigma$ -limit of the pair correlation energy for this pair is larger than for the 1s-1s pair.

The configurations along with the coupling schemes used in the PSNO calculations are listed below:

For the  $^2\Pi$  state

$$(1\sigma^2 2\sigma^2 3\sigma^2 1\pi^3)^2_{\Pi(m\sigma n\sigma)} 1\Sigma^+,$$

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$$(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi)^2_{\Pi(m\lambda n\lambda)} 1\Sigma^+, \quad \lambda \neq \sigma,$$

Consider Alternative

For  $\lambda \neq \sigma$

and for the  $^2\Sigma^+$  state

$$(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 1\pi^2)^2_{\Sigma^+(m\lambda n\lambda)} 1\Sigma^+,$$

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where  $m, n = 4, \dots, 31$  for  $\lambda = 0$ ,  $m, n = 2, \dots, 20$  for  $\lambda = 1$ ,

$m, n = 1, \dots, 10$  for  $\lambda = 2$ , and  $m, n = 1, \dots, 4$ , for  $\lambda = 3$ .

Out of the full set of PSNO's,  $11\sigma$ ,  $10\pi$ ,  $5\delta$  and  $2\epsilon$  virtual orbitals, all of which have the occupation number greater than  $10^{-6}$ , are selected and combined with the Hartree-Fock orbitals to produce orthonormalized orbital sets,  $\psi_B(^2\Pi)$  and  $\psi_B(^2\Sigma^+)$ . The composition of  $\psi_B$  is  $15\sigma$ ,  $11\pi$ ,  $5\delta$  and  $2\epsilon$  type orbitals. The effect on the total energy of truncation in this method of selecting virtual orbitals has been studied and will be discussed later in this section.

Configuration wavefunctions are constructed with the orbital set  $\psi_B$ . All configurations are included which have formally non-vanishing Hamiltonian matrix elements with the single HF reference configuration, and which could be constructed by single and double excitations from the valence shell orbitals in the reference configuration (in this system, the  $3\sigma$ ,  $4\sigma$ , and  $1\pi$  orbitals) into all virtual orbitals. We have included all single excitations even though many of them have numerically zero matrix elements with the reference configuration because of Brillouin's theorem.<sup>8</sup> This was done to ensure a proper wavefunction for the evaluation of one electron property such as the dipole moment.<sup>9</sup>

It should be noted that for some orbital configurations which result from double excitations, the orbital and spin angular momentum coupling give more than two linearly independent states of the desired total symmetry. [For example, a  $1\pi^2 - n\pi^2$  excitation for the  $^2\Pi$  state gives rise to three states:

(1)  $4\sigma^2 1\pi(^2\Pi) n\pi^2(^3\Sigma^-)$  ,

(2)  $4\sigma^2 1\pi(^2\Pi) n\pi^2(^1\Delta)$  ,

(3)  $4\sigma^2 1\pi(^2\Pi) n\pi^2(^1\Sigma^+)$  .]

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All of these states may have non-vanishing Hamiltonian matrix elements with the reference configuration. However, these matrix elements are all expressed in terms of only two different two-electron integrals. [For example, above they are  $K^0(1\pi, 1\pi)$  and  $K^2(1\pi, 1\pi)$ .] For these cases a reduction of the number of configurations can be accomplished by taking proper linear combinations of these configurations so that only two resultant configurations have non-vanishing Hamiltonian matrix elements with the reference configuration. This is done whenever applicable in the present calculations resulting in a considerable reduction of the number of configurations to be included. The actual numbers of configurations used are 1632 and 1458 for the  $X^2\Pi$  and  $A^2\Sigma^+$  states, respectively. The same set of configurations is used for all values of  $R$  except  $R = 50$  a.u.

In order to estimate the dissociation energy, a similar calculation for the  $X^2\Pi$  state, but with a different reference configuration, was carried out at  $R = 50$  a.u. where for practical purposes the system is in the separated atom limit. The reference configuration used here is  $1s^2 2s^2 2p^2 4s^2 1\pi^3$  which dissociates properly to  $Li:2S$  and  $O:3P$ . At this distance all orbitals are necessarily atomic like and atomic symmetry can be taken into account; this reduces the number of configurations for a given set of orbitals. To be consistent with the calculations at other values of  $R$  it is only necessary to consider the correlation effect of the valence electrons in the oxygen atom. We used the Hartree-Fock orbitals plus all virtual orbitals belonging to the oxygen atom; thus the set  $\phi_A(^2\Pi)$  at  $R = 50$  a.u. consists of  $18\sigma$ ,  $10\pi$ ,  $5\delta$  and  $2\phi$  type orbitals. A PSNO calculation was not carried out here since the set  $\phi_A(^2\Pi)$  is small enough that all orbitals can be included in the final CI. The error due to the truncation of orbitals at <sup>11</sup> other values of  $R$  turned out to be

negligible for estimating the dissociation energy (see the discussion below). The configurations for the final CI calculation at  $R = 50$  a.u. were selected in a manner similar to that described above except that the set  $\phi_A$  is used instead of  $\phi_B$ . However, for the cases where more than two states can be obtained by angular momentum coupling from a given orbital configuration, the reduction of the number of these states was not completely carried out. The total number of configurations used was 1431.

As mentioned above, the effect of the truncation of orbitals was studied at  $R = 3.2$  a.u. for the  ${}^2\Pi$  state by computing pair energies separately with orbital sets  $\phi_A({}^2\Pi)$  and  $\phi_B({}^2\Pi)$ . The pair energy is defined here as the energy improvement obtained in a CI calculation using single and double excitation from one pair of HF space orbitals at a time. The results are shown in Table II. Truncation errors are given in magnitude and in percentage. As expected, the  $3\sigma$  pair energy is the worst case and gives a 3% error. The error in the sum of all pair energies is, however, 1.4% indicating our method of selecting orbitals is satisfactory. No investigation was made for the  ${}^2\Sigma^+$  state but it is expected that the magnitude of the errors should be the same as for the  ${}^2\Pi$  state.

## RESULTS AND DISCUSSION

The SCF and CI results for the  $X^2\Pi$  and  $A^2\Sigma^+$  states of LiO computed at internuclear distances very close to their respective equilibrium internuclear distances are listed in Table III. The CI energies, the energy improvements in CI, and selected molecular properties computed at various internuclear distances are shown in Tables IV and V for the  $X^2\Pi$  and  $A^2\Sigma^+$  states, respectively. The CI potential curves are also shown in Figure 1.

The previously calculated SCF energy at  $R = 3.184$  a.u. for the  $X^2\Pi$  state is  $-82.3111$  a.u.<sup>10</sup> and our value is  $-82.3115$  a.u., an improvement of  $.0004$  a.u. The SCF energies obtained in the present calculations should be close to the exact Hartree-Fock values; at least within  $.0001$  a.u. Our SCF wavefunctions satisfy the virial theorem very well and the computed net forces on the nuclei are very small. These observations also support our claim of having reached the Hartree-Fock limit. The same observations also hold for the CI wavefunctions although the actual agreements are slightly worse than those for the SCF wavefunctions.

The non-relativistic total energy of LiO in the  $X^2\Pi$  state is about  $-82.666$  a.u., estimated from the experimental dissociation energy of  $.1247$  a.u.<sup>1</sup> and atomic energy data.<sup>11</sup> The correlation energy of LiO is  $-.355$  a.u. out of which we estimated that  $-.250$  a.u. is the valence electron correlation energy ( $E_{VC}$ ). This estimate for  $E_{VC}$  is obtained as follows: first taking  $E_{VC}$  of atomic oxygen to be  $-.193$  a.u.,<sup>12</sup> the rest of the correlation energy for the separated atom system is determined to be  $-.115$  a.u., and assuming that this part of the correlation energy remains the same in the molecular system,  $E_{VC}$  of LiO is obtained. The energy improvement obtained at  $R_e$  is  $-.223$  a.u. for both states. This is 89% of  $E_{VC}$  and 63% of the total correlation energy. It may be of interest to point out that the sum of pair energies shown in Table II overestimates  $E_{VC}$  by about 5%. The molecular properties presented in Table III show remarkable agreement between the SCF and CI results. For example, the change in dipole moment is less than 2% indicating that there is practically no shift of the charges from the SCF to the CI wavefunctions. The changes in the expectation values of electronic coordinates are also small; the largest is the 1% change in  $\langle \rho \rangle$ .<sup>-13-</sup> This is also reflected in a relatively

small change of .059 a.u. in the nuclear attraction energy. Since the change in the potential energy is -.426 a.u. and the kinetic energy is .203 a.u., the energy improvement in CI comes essentially from a substantial decrease in  $1/r_{ij}$  terms.

The  $X^2\Pi$  state of LiO dissociates to the ground states of separated atoms, namely to  $Li:2S + O:3P$ ; the  $A^2\Sigma^+$  state dissociates to excited state  $Li:2P$  and ground state  $O:3P$ . Another possible dissociation for the  $A^2\Sigma^+$  state is to  $Li:2S + O:1D$ ; however the atomic transition energy for  $Li:2S \rightarrow Li:2P$ , .0679 a.u.,<sup>13</sup> is less than that for  $O:3P \rightarrow O:1D$ , .0719 a.u.<sup>13</sup> For the  $X^2\Pi$  state SCF and CI calculations have been performed at  $R = 50$  a.u. For the  $A^2\Sigma^+$  state the energy at  $R = 50$  a.u. was obtained by adding the Hartree-Fock transition energy, .0677 a.u.,<sup>14</sup> for the  $2S \rightarrow 2P$  transition of atomic Li to the SCF and CI energies of the  $X^2\Pi$  state at this same separation of 50 a.u. The results are shown in Table VI together with computed dissociation energies and transition energies for  $X^2\Pi \rightarrow A^2\Sigma^+$ . The dissociation energy  $D_e$  for the  $X^2\Pi$  state computed using CI wavefunctions, 3.37 eV, is in excellent agreement with the experimental value of  $3.39 \pm .26$  eV.<sup>1</sup> This almost exact agreement may be fortuitous since we did not get all of the correlation energy. However, the good agreement strongly suggests (1) that the computed  $D_e$  for the  $A^2\Sigma^+$  state should also be quite accurate, and (2) that the procedure used in the present calculations is successful in giving wavefunctions of the same level of accuracy along the potential curve. The analysis of the computed potential curves, which will be given below, also supports the latter assertion.

Table VII gives spectroscopic constants calculated by a Dunham analysis of the CI and HF curves. <sup>14-</sup> The available experimental data are the

vibrational frequency  $\nu(1-0) = 745 \text{ cm}^{-1}$  for  ${}^7\text{Li}^{16}\text{O}$  and  $789 \text{ cm}^{-1}$  for  ${}^6\text{Li}^{16}\text{O}$  measured in a krypton matrix for the  $X^2\Pi$  state.<sup>2</sup> It is known that there is a shift in  $\nu$  measured in an inert gas matrix from its gas phase value particularly for molecules with small mass and large dipole moment. For example, for LiF, which is similar to LiO in mass and dipole moment, the value of  $\nu$  measured in a krypton matrix is  $820 \text{ cm}^{-1}$  while its gas phase value is  $890 \text{ cm}^{-1}$ , with a shift of  $70 \text{ cm}^{-1}$ .<sup>15</sup> The computed values of  $\nu(1-0)$  for the  $X^2\Pi$  state of LiO, using the CI wavefunctions, are  $825 \text{ cm}^{-1}$  and  $870 \text{ cm}^{-1}$  for  ${}^7\text{Li}$  and  ${}^6\text{Li}$ , respectively. These values are shifted from those measured in a krypton matrix by  $80 \text{ cm}^{-1}$  and  $81 \text{ cm}^{-1}$ , respectively. Considering that LiO has less mass and a slightly larger dipole moment (6.76 Debye) than LiF (6.33 Debye),<sup>16</sup> this shift of  $80 \text{ cm}^{-1}$  is reasonable. Thus, at least, the computed value of  $\omega_e$  should be accurate to within a few wave numbers. The other higher derivatives are inevitably less accurate but they also should not be too far from the true values. It is of interest to note that the HF results for spectroscopic constants shown in Table VII are in reasonable agreement with the CI results which are believed to be very close to the true values. This agreement is rather surprising since the HF results for other ionic molecules, LiF and BeO for example, are usually significantly poorer.<sup>10</sup> The CI value of  $R_e$  is slightly larger than the SCF value. Our CI value of  $1.695\text{\AA}$  for the  $X^2\Pi$  state differs considerably from the value of  $R_e = 1.62\text{\AA}$  which has been estimated from experimental data. The following observations can be made in assessing the accuracy of computed  $R_e$ .

Firstly, the value of  $R_e = 1.62\text{\AA}$  may not be reliable since it is estimated by an empirical formula using a value of the force constant obtained by a matrix isolation technique.<sup>2</sup> The second observation is that for LiF and



BeO molecules the HF values of  $R_e$  are 1.555Å and 1.29Å and the observed values are 1.564Å and 1.33Å, respectively.<sup>17</sup> Since LiO is similar to these molecules, its HF value is expected to be smaller than the actual value. Thus, the CI value of  $R_e$  should be reliable within at least .01Å.

As mentioned in a previous section, because of the method employed for deleting unwanted virtual orbitals, the number of  $\sigma$  type virtual orbitals used in the PSNO calculations is different for  $R \leq 3.2$  and  $R > 3.2$  a.u. The effect of this difference on the computed results is generally negligibly small. However, the net force on the nuclei,  $\mathcal{F}_{Li} + \mathcal{F}_O$ , listed in Tables IV and V exhibits a small but distinct discontinuity at  $R = 3.2$  a.u. Therefore, other means of deleting unwanted virtual orbitals should be employed. Perhaps an even better way would be to avoid deletion of orbitals altogether by carefully selecting basis functions with less linear dependence among them.

## CONCLUSIONS

The procedure used in the present calculations appears to work well in predicting accurate values for dissociation energies, a property which is very sensitive to the correlation correction. For other properties, the correlation correction appears to be small and the results obtained are believed to be quite accurate. Since the procedure can be applied to larger and more complex systems at roughly the same level of the computational effort as that required for LiO, it will be worthwhile to investigate further the applicability of the procedure to more complex systems than the one studied in the present work.

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## FOOTNOTES

1. L. Brewer and G. M. Rosenblatt, *Advances in High Temperature Chemistry* 2, 1 (1969).
2. D. White, K. S. Seshadri, D. F. Dever, D. E. Mann, and M. J. Linevsky, *J. Chem. Phys.* 39, 2463 (1963).
3. W. Weltner, Jr., *Advances in High Temperature Chemistry* 2, 85 (1969).
4. C. Edmiston and M. Krauss, *J. Chem. Phys.* 45, 1833 (1966).
5. P. S. Bagus, T. L. Gilbert, and C. C. J. Roothaan, *J. Chem. Phys.* (to be published); A. D. McLean and M. Yoshimine, *Table of Linear Molecule Wave Functions, A Supplement to IBM J. Res. Develop.* 12, 206 (1968).
6. Because a fixed threshold was used to truncate the space, a different number of virtual orbitals could be obtained for different values of  $R$ . In fact, 28 virtual  $\sigma$  orbitals were obtained for  $R = 2.3$  to 3.1 a.u. and 29 for  $R = 3.2$  to 3.9 a.u. Although this does not give serious trouble, its effect on subsequent CI calculations did show up as a slight discontinuity in some computed properties.
7. A. W. Weiss, *Phys. Rev.* 162, 71 (1967).
8. J. Bauche and M. Klapisch, *J. Phys. B.* (to be published).
9. S. Green, *J. Chem. Phys.* 54, 827 (1971); *J. Chem. Phys.* 56, 739 (1972).
10. The value is taken from *Compendium of ab initio Calculations of Molecular Energies and Properties* (NBS Technical Note 438, 1967).
11. Atomic energy data are  $E_{\text{HF}}(\text{Li}, ^2\text{S}) = -7.4327$ ,  $E_{\text{HF}}(\text{O}, ^3\text{P}) = -74.8094$ ,  $E_{\text{c}}(\text{Li}, ^2\text{S}) = -.0453$ , and  $E_{\text{c}}(\text{O}, ^3\text{P}) = -.2539$ . The values of  $E_{\text{HF}}$  are taken from E. Clementi, *Table of Atomic Functions, a supplement to IBM J. Res. Develop.* 9, 2 (1965); the values of  $E_{\text{c}}$  are from E. Clementi, *J. Chem. Phys.* 38, 2248 (1963) and Ref. 12. All values

are in a.u.

12. R. K. Nesbet, Phys. Rev. 175, 1 (1968).
13. C. E. Moore, Atomic Energy Levels, Natl. Bur. Std. (U.S. GPO, Washington, D.C. 1949).
14. P. S. Eagus, Numerical Hartree-Fock results (private communication).
15. A. Snelson, J. Phys. Chem. 70, 3208 (1966).
16. L. Wharton and W. Klemperer, J. Chem. Phys. 38, 1203 (1963).
17. HF values are taken from Ref. 10 and observed values are from Ref. 16 for LiF and J. Drowart, G. Exteen and Verhaegen, Trans. Faraday Soc. 60, 1920 (1964) for BeO.

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Table 1. Slater-type functions used in SCF and CI calculations.

n $\ell$ m	Exponent	
	on Li	on O
1s $\sigma$	4.699, 2.478	12.418, 6.995
2s $\sigma$	1.500, .810, .643	3.900, 2.922, 1.818
3s $\sigma$	2.681, .500	8.681, 1.600
2p $\sigma$	3.900, 3.000, 2.111, 1.076, .736	8.450, 4.700, 3.744, 2.121, 1.318
3p $\sigma$	.600	1.300
3d $\sigma$	3.000, 2.000, 1.000	4.000, 3.000, 2.000
4f $\sigma$	4.000, 2.000	4.000, 2.000
2p $\pi$	3.900, 3.000, 2.111, 1.076, .736	8.450, 4.700, 3.744, 2.121, 1.318
3p $\pi$	.600	1.300
3d $\pi$	3.000, 2.000, 1.000	4.000, 3.000, 2.000
4f $\pi$	4.000, 2.000	4.000, 2.000
3d $\delta$	3.500, 2.500, 1.500	4.500, 3.500, 2.500
4f $\delta$	4.000, 2.000	4.000, 2.000
4f $\phi$	4.000, 2.000	4.500, 2.500

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Table II. Comparison of pair energies for the  $^2\Pi$  state of LiO computed with different size orbital sets<sup>a</sup> at  $R = 3.2$  a.u. Energies are in a.u.

Pair	Orbital Set		Difference	
	A	B	Magnitude	Percentage
3 $\sigma$ 3 $\sigma$	.01587	.01540	.00047	3.0
3 $\sigma$ 4 $\sigma$	.03655	.03580	.00075	2.0
4 $\sigma$ 4 $\sigma$	.02740	.02735	.00005	.2
3 $\sigma$ 1 $\pi$	.05723	.05570	.00153	2.7
4 $\sigma$ 1 $\pi$	.07401	.07362	.00039	.5
1 $\pi$ 1 $\pi$	.05453	.05411	.00042	.8
sum	.26559	.26199	.00360	1.4

<sup>a</sup>See the text for description of sets used and configurations included.

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Table III. Computed SCF and CI expectation values for the  $X^2$  and  $A^2$  states of  $LiO$ .

All quantities are given in a.u. unless explicitly specified.

State	2.		2 <sup>+</sup>	
	SCF	CI	SCF	CI
Internuclear distance R	3.20	3.20	3.00	3.00
Total energy E	-82.3115	-82.5342	-82.3008	-82.5236
Kinetic energy $\langle T \rangle$	82.2967	82.4999	82.2995	82.5179
Potential energy $\langle V \rangle$	-164.6082	-165.0341	-164.6004	-165.0415
Virial coefficient $\langle T \rangle / \langle V \rangle$	-2.0002	-2.0004	-2.0000	-2.0001
$\langle 1/r_{Li} \rangle$	8.2477	8.2487	8.3888	8.3902
$\langle 1/r_O \rangle$	23.3975	23.3898	23.4420	23.4363
$\langle \sum_{i,j < l} 1/r_{ij} \rangle$	39.8157	39.3302	40.1022	39.6198
$\langle Z_{Li} \rangle$	28.3040	28.2589	26.3962	26.3433
Dipole moment $\mu$ (Debye) ( $Li^+O^-$ )	6.872	6.758	6.090	5.955
$\langle \rho \rangle$	8.4421	8.5265	8.8565	8.9349
$\langle r_{Li} \rangle$	31.2585	31.2866	29.6294	29.6564
$\langle r_O \rangle$	16.3530	16.4630	15.9807	16.0926
$\langle Z_{Li}^2 \rangle$	95.6060	95.5425	83.0025	82.9119
$\langle \rho^2 \rangle$	11.4507	11.8318	12.6056	12.9988
$\langle r_{Li}^2 \rangle$	107.0567	107.3743	95.6081	95.9107
Quadrupole mom. $\Theta$ ( $10^{-26}$ esu $cm^2$ ) <sup>a</sup>	5.471	5.544	7.120	7.210
$\langle Z_{Li}/r_{Li}^3 \rangle$	0.7831	0.7789	0.8891	0.8855
$\langle Z_O/r_O^3 \rangle$	-0.2949	-0.2914	-0.3344	-0.3338
Force on Li $\vec{F}_{Li}$	0.006	-0.007	0.001	-0.010
Force on O $\vec{F}_O$	-0.016	0.013	-0.009	-0.004
Net force on nuclei $\vec{F}_{Li} + \vec{F}_O$	-0.010	0.006	-0.008	-0.014
$\langle (3Z_{Li}^2 - r_{Li}^2)/2r_{Li}^5 \rangle$	0.2695	0.2674	0.3006	0.2985
$\langle (3Z_O^2 - r_O^2)/2r_O^5 \rangle$	0.8544	0.8589	-1.2661	-1.2886
$q_{Li} = -(2V/z^2)_{Li}$	-0.051	-0.047	-0.009	-0.004
$q_O = -(2V/z^2)_O$	-1.526	-1.535	2.754	2.799

<sup>a</sup>  $\Theta$  is computed with respect to the center of mass for  ${}^7Li{}^{16}O$ .

Table IV. Molecular properties for the  $2^2\Pi$  state of LiO computed with the CI (1632 configurations) wavefunction. All quantities are given in a.u.

R	E	T	V	V/T	$\Delta E^a$		
2.3000	-82.413809	83.275053	-165.68862	-1.989658	-0.216364		
2.5500	-82.485487	82.937640	-165.423127	-1.994548	-0.218078		
2.7000	-82.508988	82.788665	-165.297653	-1.996622	-0.219081		
2.8000	-82.519337	82.708196	-165.227533	-1.997717	-0.219836		
2.9000	-82.526421	82.641448	-165.167869	-1.998608	-0.220588		
3.0000	-82.530932	82.586080	-165.117012	-1.999332	-0.221335		
3.1000	-82.533394	82.539728	-165.073123	-1.999923	-0.222047		
3.2000	-82.534181	82.499906	-165.034088	-2.000415	-0.222663		
3.3000	-82.533558	82.459132	-164.992690	-2.000903	-0.223096		
3.4000	-82.532009	82.427752	-164.959761	-2.001265	-0.223558		
3.5000	-82.529692	82.400559	-164.930251	-2.001567	-0.223986		
3.6000	-82.526787	82.376912	-164.903699	-2.001819	-0.224384		
3.7500	-82.521625	82.346681	-164.868306	-2.002124	-0.224932		
3.9000	-82.515815	82.321931	-164.837746	-2.002355	-0.225427		
R	$\mu^b$	$\alpha^c$	$\mathcal{F}_{Li}$	$\mathcal{F}_O$	$\mathcal{F}_{Li+O}$	$q_{Li}$	$q_O$
2.3000	1.953	1.795	-0.408	0.390	-0.018	-0.013	-2.447
2.5500	2.148	2.430	-0.207	0.175	-0.032	-0.037	-2.162
2.7000	2.265	2.809	-0.132	0.095	-0.037	-0.044	-1.996
2.8000	2.343	3.063	-0.095	0.060	-0.035	-0.047	-1.891
2.9000	2.421	3.321	-0.065	0.038	-0.027	-0.048	-1.793
3.0000	2.500	3.583	-0.041	0.026	-0.016	-0.048	-1.702
3.1000	2.579	3.850	-0.022	0.019	-0.003	-0.048	-1.616
3.2000	2.659	4.122	-0.007	0.013	0.006	-0.047	-1.535
3.3000	2.738	4.401	0.005	-0.011	-0.006	-0.046	-1.466
3.4000	2.819	4.685	0.014	-0.018	-0.004	-0.044	-1.395
3.5000	2.899	4.975	0.022	-0.024	-0.003	-0.042	-1.329
3.6000	2.981	5.272	0.028	-0.029	-0.001	-0.040	-1.267
3.7500	3.103	5.728	0.034	-0.035	-0.000	-0.038	-1.184
3.9000	3.227	6.200	0.039	-0.038	0.000	-0.035	-1.110

<sup>a</sup> $\Delta E$  is difference between the CI and HF energies.

<sup>b</sup>polarity is  $Li^+O^-$ .

<sup>c</sup> $\alpha$  is computed with respect to the center of mass for  ${}^7Li{}^{16}O$ .



Table V. Molecular properties for the  $2^+_{\Sigma}$  state of LiO computed with the CI (1458 configurations) wavefunction. All quantities are given in a.u.

R	E	T	V	V/T	$\Delta E^a$
2.3000	-82.450184	83.063373	-165.513556	-1.992618	-0.218024
2.5500	-82.499226	82.795974	-165.295200	-1.996416	-0.220069
2.7000	-82.513735	82.679693	-165.193428	-1.997993	-0.221109
2.8000	-82.519296	82.616619	-165.135915	-1.998822	-0.221716
2.9000	-82.522392	82.563196	-165.085588	-1.999506	-0.222252
3.0000	-82.523566	82.517886	-165.041452	-2.000069	-0.222718
3.1000	-82.523251	82.479297	-165.002547	-2.000533	-0.223117
3.2000	-82.521787	82.446623	-164.968410	-2.000912	-0.223457
3.3000	-82.519235	82.414534	-164.933768	-2.001270	-0.223527
3.4000	-82.516258	82.391020	-164.907278	-2.001520	-0.223788
3.5000	-82.512818	82.370941	-164.883759	-2.001722	-0.224037
3.6000	-82.509045	82.353651	-164.862696	-2.001887	-0.224269
3.7500	-82.502969	82.332450	-165.835419	-2.002071	-0.224596
3.9000	-82.496591	82.315764	-164.812355	-2.002197	-0.224874

R	$\mu^b$	$\odot^c$	$\mathcal{F}_{Li}$	$\mathcal{F}_O$	$\mathcal{F}_{Li+O}$	$q_{Li}$	$q_O$
2.3000	1.685	3.593	-0.289	0.286	-0.003	0.092	2.451
2.5500	1.910	4.206	-0.135	0.127	-0.008	0.036	2.581
2.7000	2.051	4.581	-0.078	0.067	-0.011	0.017	2.658
2.8000	2.147	4.837	-0.049	0.037	-0.012	0.008	2.708
2.9000	2.245	5.096	-0.027	0.014	-0.013	0.001	2.755
3.0000	2.343	5.361	-0.010	-0.004	-0.014	-0.004	2.799
3.1000	2.443	5.630	0.003	-0.019	-0.015	-0.008	2.841
3.2000	2.544	5.905	0.014	-0.030	-0.016	-0.011	2.879
3.3000	2.645	6.187	0.022	-0.037	-0.014	-0.013	2.912
3.4000	2.747	6.473	0.029	-0.044	-0.016	-0.014	2.944
3.5000	2.850	6.765	0.033	-0.051	-0.017	-0.015	2.973
3.6000	2.953	7.064	0.037	-0.056	-0.019	-0.016	2.999
3.7500	3.109	7.523	0.040	-0.061	-0.021	-0.016	3.033
3.9000	3.267	7.997	0.043	-0.065	-0.022	-0.016	3.063

<sup>a</sup> $\Delta E$  is difference between the CI and HF energies.

<sup>b</sup> $\mu$  polarity is  $Li^+O^-$ .

<sup>c</sup> $\odot$  is computed with respect to the center of mass for  ${}^7Li{}^{16}O$ .

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Table VI. Computed dissociation energies and term energies for LiO.

Calculation	HF		CI	
	$2_{\Pi}$	$2_{\Sigma}^{+}$	$2_{\Pi}$	$2_{\Sigma}^{+}$
$E(R_e)$ (a.u.)	-82.3115	-82.3008	-82.5342	-82.5239
$E(R=50)$ (a.u.)	-82.2427	-82.1756	-82.4104	-82.3434
$D_e^a$ (eV)	1.87	3.41	3.37	4.90
$T_e(2_{\Pi}-2_{\Sigma}^{+})$ ( $\text{cm}^{-1}$ )	2342		2330	

<sup>a</sup>The observed value for  $D_e(X^2_{\Pi})$  is  $3.39 \pm 0.26$  eV taken from Ref. 1.

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Table VII. Computed spectroscopic constants for LiO. Units for the spectroscopic constants are  $\text{cm}^{-1}$ .

Isotope	State	Calc.	$\omega_e$	$\omega_e x_e$	$v(1-0)$	$B_e$	$\alpha_e$	$R_e (\text{\AA})$
${}^7\text{Li}^{16}\text{O}$	$X^2\Pi$	CI	851.5	12.5	825.2	1.202	0.0151	1.695
		HF	854.4	7.1	840.4	1.235	0.0175	1.673
	$A^2\Sigma^+$	CI	866.7	6.7	853.4	1.349	0.0199	1.599
		HF	881.5	8.3	865.0	1.376	0.0213	1.585
${}^6\text{Li}^{16}\text{O}$	$X^2\Pi$	CI	899.4	14.2	870.1	1.341	0.0178	
		HF	902.4	7.9	886.8	1.378	0.0206	
	$A^2\Sigma^+$	CI	915.5	7.5	900.5	1.505	0.0234	
		HF	931.0	9.3	912.8	1.535	0.0252	

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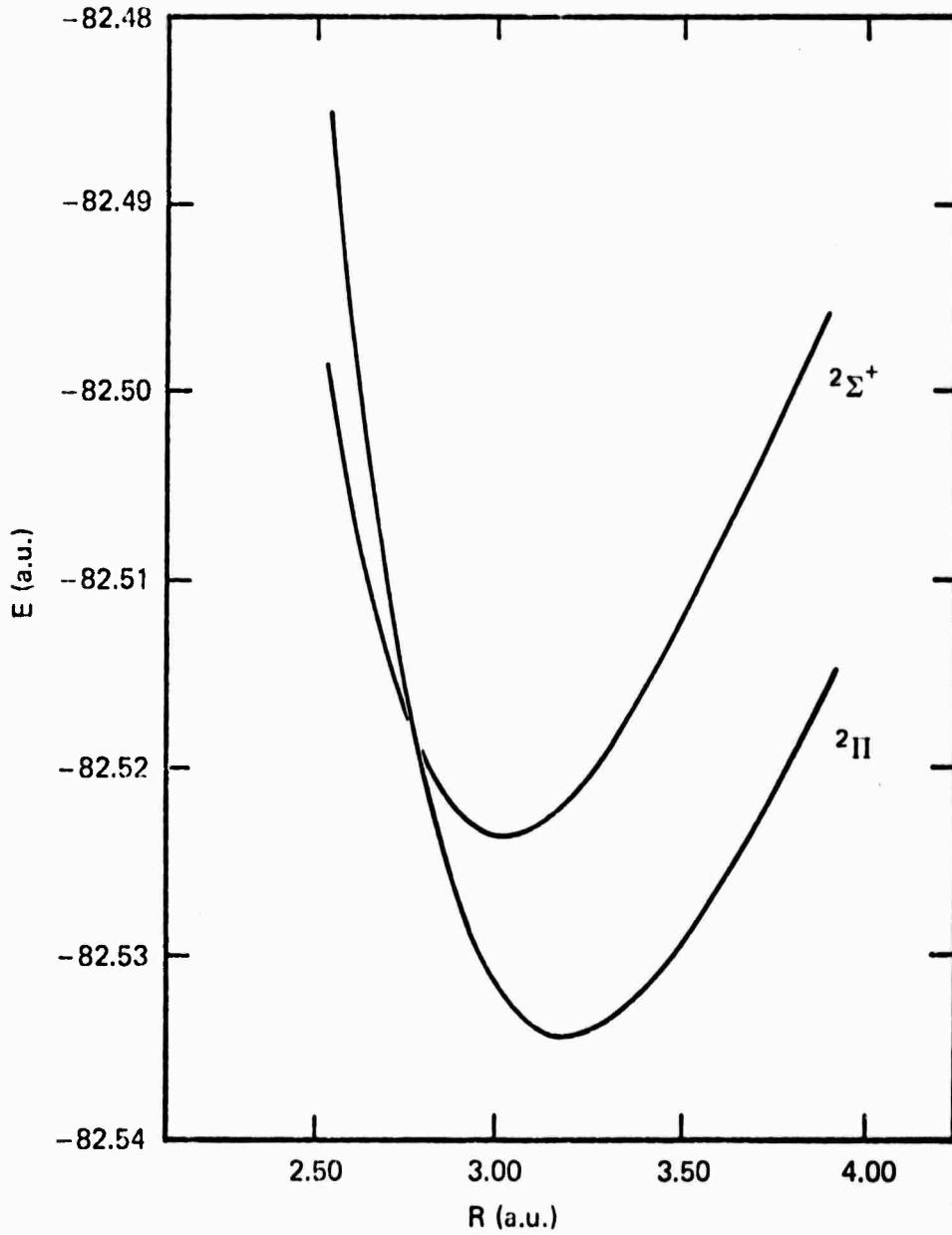


Figure 1. Potential energy curves for the  $X^2\Pi$  and  $A^2\Sigma^+$  states of LiO obtained from CI wavefunctions