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An intersection of the two lowest doublet potential energy surfaces of LiNaK has been established by ab-initio calculations.

An interesting controversy in recent years has been on whether potential-energy surfaces of polyatomic molecules cross in regions of space where the two wavefunctions belong to the same symmetry species [1–6]. Such crossings are forbidden for diatomic potential energy curves but, as was first pointed out by Teller [1], and later amplified by Herzberg and Longuet-Higgins [2], crossings are allowed in $(N-2)$-dimensional space for a polyatomic with N internal coordinates. This conclusion has recently been challenged [3,4] but, in turn, the basis for this challenge has been refuted [5].

The existence of a crossing point can be established by the following theorem [2,5,6]. If S is a surface in nuclear configuration space bounded by a closed loop L and if the electronic wavefunction changes sign when transported adiabatically once around L then there must be at least one point on S at which the wavefunction is a discontinuous function of the internal coordinates. Longuet-Higgins [5] showed that for the lowest energy doublet state of three ^2S atoms there was such a change in sign provided that a loop could be found around which certain hamiltonian matrix elements had an assumed parametric form. It was argued that such a loop was qualitatively justified. Stone [6] has likewise shown by qualitative arguments the existence of an intersection for the surface of a d^1 transition metal with six non-equivalent ligands. Our objective in this paper is to establish by ab-initio calculations the existence of a loop satisfying the sign reversal criterion for the system LiNaK.

The system was examined using a minimal STO-3G expansion of the molecular orbital with no p orbitals in the valence shell. Although this basis will not, of course, give accurate wavefunctions, there has been no suggestion that approximate potential energy surfaces should have different characteristics to the true Born–Oppenheimer surface provided that there are no hidden symmetries within the approximation.

Paths in the potential energy surface for a triatomic molecule are conveniently expressed in the coordinates (S_1, ρ, θ) where

$$\begin{bmatrix} S_1 \\ S_2 \\ S_3 \end{bmatrix} = \begin{bmatrix} 3^{-1/2} & 3^{-1/2} & 3^{-1/2} \\ 0 & 2^{-1/2} & -2^{-1/2} \\ (\frac{2}{3})^{1/2} & -6^{-1/2} & -6^{-1/2} \end{bmatrix} \begin{bmatrix} R_1 - R_1^0 \\ R_2 - R_2^0 \\ R_3 - R_3^0 \end{bmatrix} \tag{1}$$

and

$$\rho = (S_2^2 + S_3^2)^{1/2}, \quad \tan\theta = S_2/S_3. \tag{2}$$

R_i are the three internuclear distances and R_i^0 are reference bond lengths. We took these to be all equal to the arithmetic mean of the equilibrium bond lengths of the three homonuclear diatomic molecules, thus

$$R_i^0 = \tfrac{1}{3}(R_{\mathrm{Li}_2}^{\mathrm{e}} + R_{\mathrm{Na}_2}^{\mathrm{e}} + R_{\mathrm{K}_2}^{\mathrm{e}}) = 3.2\ \text{Å}. \tag{3}$$

Calculations were all made along a path for which $S_1 = 0$, that is, the perimeter of the triangle is fixed and equal to the sum of the three homonuclear diatomic

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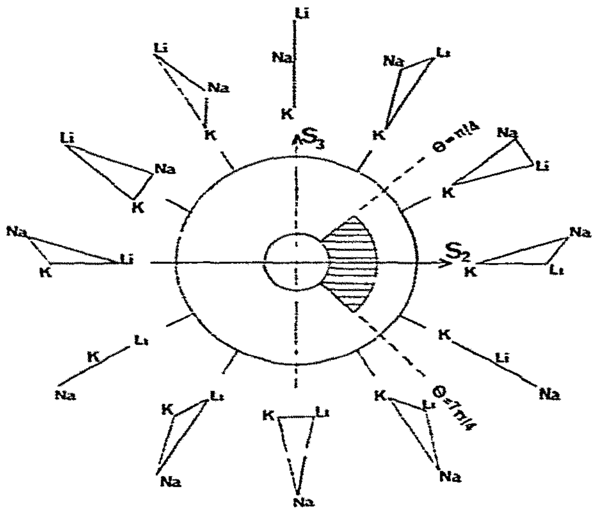

Fig. 1. Coordinates defining the paths along which calculations have been made. The circles have radii $\rho = 1/2\sqrt{6}$ and $4.8/\sqrt{6}$ and the intermediate arc a radius $3/\sqrt{6}$. The origin corresponds to an equilateral triangle of perimeter 9.6 A.

distances. We are thus seeking a point of discontinuity in the wavefunction and not the line of such points that can exist in the complete three-dimensional surface.

Wavefunctions were first obtained for the restricted Hartree–Fock approximation along the circular path shown in fig. 1. The wavefunction is a single determinant with a set of doubly filled orbitals representing inner shells, one doubly occupied valence orbital and one singly occupied orbital; there is also one virtual valence orbital. The latter three are all of A′ symmetry in the C_s group.

It is clear from fig. 2 that the RHF wavefunction changes sign on passing once around the loop. This wavefunction is not a variational lower bound for the Born–Oppenheimer hamiltonian within the adopted basis set because it does not allow for full correlation of the electrons. We can, however, obtain such a bound by configuration interaction within the RHF orbitals to give a wavefunction.

$$\Psi = \Psi_{\mathrm{RHF}} + \sum_i \lambda_i \Psi_i, \tag{4}$$

where Ψ_i are other configurations. As the individual RHF orbitals vary smoothly around the loop so must the Ψ_i. Providing that configuration interaction is small ($\lambda_i \approx 0$) it is reasonable to assume that λ_i is continuous and hence, if Ψ_{RHF} changes sign so must $\Sigma_i \lambda_i \Psi_i$ and hence Ψ.

The variation of wavefunction was next examined along the diagonals $S_2 = 0$ and $S_3 = 0$ of the circular path already described. For the $S_2 = 0$ diagonal the wavefunction was continuous and we established that the non-analytic point was in the sector $-\frac{1}{2}\pi < \theta < \frac{1}{2}\pi$. For the $S_3 = 0$ diagonal, however, the RHF procedure was difficult to converge for $\rho \approx 1.0$ and this

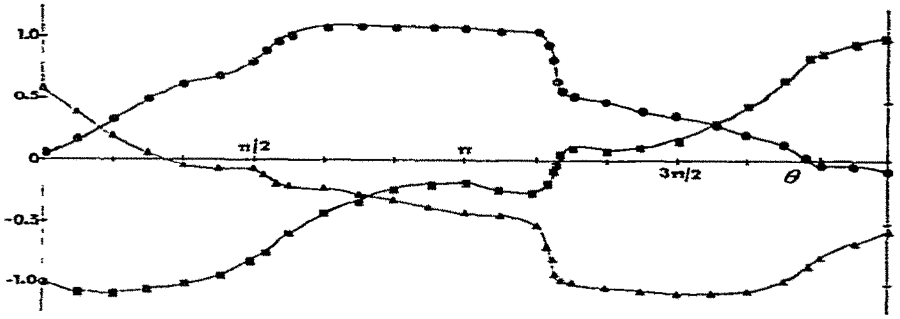

Fig. 2. Variation in the coefficients of the valence basis functions in the singly occupied RHF molecular orbital along the outer circular path shown in fig. 1. The actual points calculated have been shown with the symbols Li(2s) = ●, Na(3s) = ▲, K(4s) = ■.

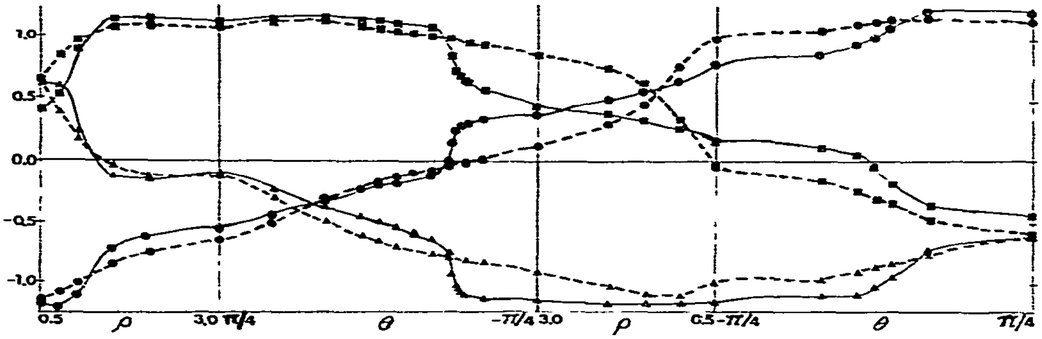

Fig. 3. Variation in the coefficients of the valence basis functions for the RHF (full line) and SE RHF (dashed line) singly occupied orbital. The path followed is the perimeter of the shaded region shown in fig. 1. Symbols as in fig. 2.

suggested that the crossing point lies near this line. A wedge-shaped path bounded by the radial paths $\theta = \frac{1}{4}\pi$ and $\theta = \frac{7}{4}\pi$ and the circular paths $\rho = 0.5$ and $\rho = 3.0$ was then studied and as can be seen from fig. 3 the RHF coefficients are smoothly varying but change sign on going around this path.

The RHF hamiltonian allows for Coulomb repulsion and exchange between the electrons and is therefore a function of its eigenvector and the orbital population. For incompletely filled shells the hamiltonian does not necessarily have the symmetry of the Born–Oppenheimer hamiltonian. For example, a standard RHF calculation on H_3 in D_{3h} configurations will not give degenerate E' orbitals because only one of these orbitals will be occupied and this does not give an RHF hamiltonian with D_{3h} symmetry. One can correct this by a symmetry equivalencing (SE) procedure which effectively puts equal fractional populations of electrons into symmetry equivalent orbitals [7]. Moreover, if this procedure is adopted when there is no symmetry requirement (e.g. for H_3 in C_s symmetries) then the convergence of open shell calculations is improved and the eigenfunctions merge smoothly into those appropriate to the high symmetry structures.

SE RHF calculations on LiNaK were made for an electron configuration which has equal (notionally half-electron) occupation of the two highest molecular orbitals. The resulting orbitals are very little different from those obtained by the standard RHF procedure for the path shown in fig. 2 and this is because the path is far away from the surface crossing point. Close to the crossing point the orbitals do show significant differences as can be seen from fig. 3 which shows SE RHF and RHF coefficients for the same path. A brief examination of the wavefunctions within this bounded area shows that degeneracy of the two equivalent orbitals occurs approximately at the point $\rho = 1.20\, a_0, \theta = 0°$.

We have finally to show that the coefficients of the CI expansion are analytic around the closed loop. CI calculations, using all configurations that can be generated from the three valence orbitals, have been carried out around the closed loop defined in fig. 3. The variation in the coefficient of the SE RHF component is shown in fig 4 and, within the interval chosen, appears to be continuous. If one coefficient is continuous then all are. Moreover, we can argue on perturbation grounds that the inclusion of configurations in which the inner shell electrons are promoted would not change this conclusion.

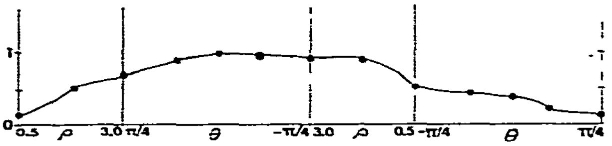

Fig. 4. Coefficient of the SE RHF root function in the CI expansion for the path referred to in fig. 3. The points calculated were indicated thus •.

It might be argued that no finite set of computations can disprove the existence of additional sign changes in the intervals between computed points. We can appeal only to the experienced eye. Are the intervals shown in figs. 2, 3 and 4 sufficiently convincing? To us they are and we can only suggest that those who doubt fill in a few more points.

All calculations reported in this paper were carried out on the ATMOL/3 and SPLICE system of programs documented by the Atlas Computing Division, Rutherford Laboratory.

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