

Kutzelnigg W, Staemmler V & Hoheisel C. Computed potential hypersurface (including electron correlation) of the system Li^+/H_2 . *Chem. Phys.* 1:27-44, 1973.
 [Institut für Physikalische Chemie und Elektrochemie, Abteilung für Theoretische Chemie, Universität Karlsruhe, Federal Republic of Germany]

The potential hypersurface of the system LiH_2^+ is computed for a large range of the internal coordinates by means of the independent electron pair approximation-pair natural orbital method in a moderately large Gaussian basis set. The H-H distance r was varied between 0.9 and 3.0 α_0 and the Li^+/H_2 distance R , between 1.0 and 15.0 α_0 , and three values (0° , 45° , and 90°) for the Jacobi angle ϑ were taken. The results are analyzed in detail. [The *SCI*® indicates that this paper has been cited in over 100 publications.]

Werner Kutzelnigg
 Lehrstuhl für Theoretische Chemie
 Ruhr-Universität Bochum
 D-4630 Bochum 1
 Federal Republic of Germany

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The story started when I first met J. Peter Toennies and we were discussing which system of a molecule colliding with an atom or another molecule might be best suited for a combined theoretical and experimental study. We decided that Li^+/H_2 was a good candidate.

On the theoretical side the work started in Göttingen in 1969 when Claus Hoheisel joined my research group for a few months as a postdoc. At that time the independent electron pair approximation-pair natural orbital (IEPA-PNO) method had been implemented with Gaussian lobe functions as a basis set.^{1,2} This method (reviewed in a general context in reference 3), which married the IEPA of O. Sinanoğlu and R.K. Nesbet with my approach towards the direct calculation of a natural orbital, has to a large extent been the work of Reinhart Ahlrichs.

IEPA-PNO was one of the first methods practically applicable to molecules to which went beyond Hartree-Fock and took care of a large part of electron correlation. It could be expected that Li^+/H_2 was a good "IEPA system" since the two electron pairs are well separated, and indeed IEPA-PNO could account fairly accurately for the correlation effects in this sys-

tem. This is one of the reasons more sophisticated calculations on LiH_2^+ were never published, although more refined methods³ like coupled electron pair approximation (CEPA) became available. It just turned out that the improvement over the old potential energy surface (PES) that is now possible is not so spectacular as to warrant redoing the PES. Our PES (as well as the older and somewhat complementary SCF-PES by W.A. Lester) has for various authors been the starting point for calculations of the dynamics of the collision between Li^+ and H_2 . The agreement with experiment turned out to be satisfactory and our PES helped to better understand the experimental results.⁴ This is one of the reasons this work is often quoted. The other reason is probably that it has been somewhat of a pioneering work, giving one of the first rather complete PES.

From 1970 to 1972, after I had moved to Karlsruhe, the calculations were completed by Volker Staemmler and me. I must admit that the calculation of a PES is a very tedious job and one does not want to do this very often, even if our experimental colleagues urge us to furnish more work of this kind. Staemmler has done a lot more PES, some of which became standard as well, like the ones on Li^+/N_2 or Li^+/CO .⁵ I must mention here another PES in which I was involved, namely, on HeH_2 .⁶ At first glance HeH_2 looks very similar to the isoelectronic LiH_2^+ , but on closer inspection it turns out to be much more difficult. The binding at the van der Waals minimum is extremely weak and therefore for acceptable results a very high accuracy is necessary. Even three-particle correlations had to be taken care of.

If asked whether this most-quoted paper of mine is also the one I like best, I would certainly answer that I am more fond of those papers in which I proposed methodologic innovations or where I tried to provide physical insight into chemical phenomena. If I were to come back to the calculation of a PES of a triatomic molecule in the near future, probably it would be in order to test a new method in which the interelectronic coordinates are explicitly involved.

[For a review of work in this field, see reference 7.]

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