LiH potential energy curves for ground and excited states with the free-complement-function local-Schrödinger-equation method

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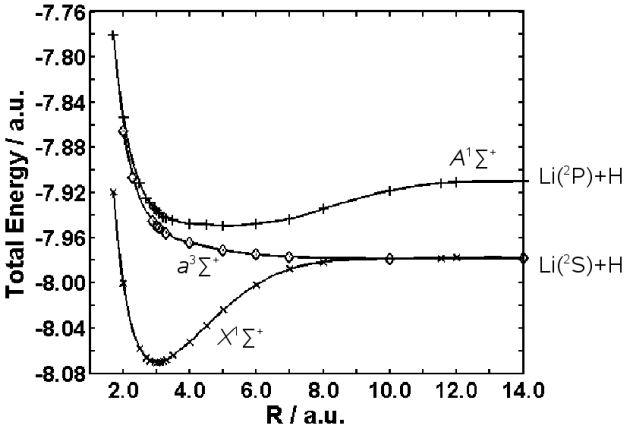
The potential energy curves of ground and several singlet and triplet excited Σ^+ states of LiH have been obtained as accurate solutions of the Schrödinger equation. This was achieved by using the free complement (FC)[1,2] local Schrödinger equation (LSE)[3] method. Starting from a simple initial wave function ψ_0 that contains the covalent and ionic terms constructed from the 1s and 2s atomic orbitals of Li and the 1s orbital of H, the potential energy curves of the X and $A^1\Sigma^+$ and the $a^3\Sigma^+$ states have been obtained among others (see Fig. 1). The curve for the $X^1\Sigma^+$ has already been published.[3]

They display some of the unique chemical properties of the LiH molecule. The electronic structures of the two singlet states, $X^1\Sigma^+$ and $A^1\Sigma^+$, change dramatically as a function of R. The minimum of the $A^1\Sigma^+$ is flatter due to the more strongly avoided crossing with the other states. Its shallow flat nature gives interesting vibrational and dynamics properties. The $a^3\Sigma^+$ state is weakly bond at an interatomic distance of around 11.5 a.u. due to van der Waals forces.

There are two straightforward ways to increase the accuracies for the higher excited states not shown here: increasing the order of the FC calculations and including higher excited states in the initial ψ_0. The latter is done by including 2p and 3s excited states. Such studies are now in progress.

Figure 1: Potential curves of the three lowest energy states of LiH.



References

[1] H. Nakatsuji, Phys. Rev. Lett. **93**, 030403 (2004).

[2] H. Nakatsuji, Phys. Rev. A **72**, 062110 (2005).

[3] H. Nakatsuji, H. Nakashima, Y. Kurokawa, and A. Ishikawa, Phys. Rev. Lett. **99**, 240402 (2007).