LONG RANGE UNDULATION OF THE POTENTIAL ENERGY CURVES FOR DIATOMIC RYDBERG STATES.

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A large number of electronic states for the LiH, LiHe and LiNe molecules were calculated with an accurate ab initio configuration interaction method. The Rydberg states of Σ^+ symmetry systematically showed a number of undulations accompanying localized secondary potential wells. The number and the location of the barriers and local wells in the molecular potential energy curve appear to closely correlate with the shape of the atomic orbitals. The atomic density change is fully reflected in the potential energy at long distance indeed. This effect is shown to exist in the alkali dimers too. In the $F^1\Sigma_g^+$ state of Li_2, our calculated barrier height of 300 cm^{-1}, agrees well with the lowest observed[a] predissociated rovibational level, v=33, J=13, which lies 242.4 cm^{-1} over the assymptote. Our work gives for the first time a plausible explanation for the energy level of the shelf state which is in general higher that the corresponding assymptotes. We propose to modify the long-range potential theory of molecules to take the undulation effect of atomic orbitals into account.

[a] S. Antonova and K. Urbanski, private communication.