# Stability and bonding in the ground and excited states of lithium fluoride $Li_nF$ clusters

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GdR Correl meeting, Marseilles

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# Outline

Hyperlithiated clusters

Insertion mechanism and bonding in $Li_2F/F^-$

Low-lying states of $Li_nF$ clusters

Concluding remarks

# Hyperlithiated clusters

- Hyperlithiated clusters $Li_3O$, $Li_4O$, $Li_5O$ first observed in the gas phase (1980's)
- "Are $CLi_6$, $NLi_5$, $OLi_4$ ...hypervalent?" (Schleyer, 1983)
  $\Rightarrow$ Hyperlithiated $ALi_n$ molecules : $A^-$ in a metallic $Li_n^+$ cage

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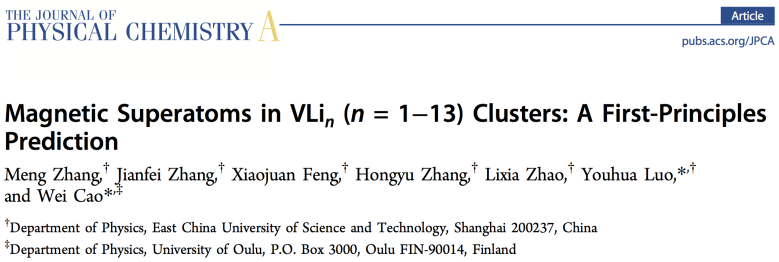
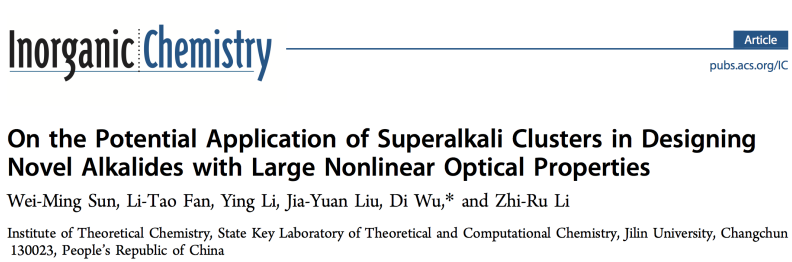
- "Are $CLi_6$, $NLi_5$, $OLi_4$ ...hypervalent?" (Schleyer, 1983)
  $\Rightarrow$ Hyperlithiated $ALi_n$ molecules : $A^-$ in a metallic $Li_n^+$ cage
- Hyperlithiated clusters are "superalkalis" (Boldyrev et al., 1982)
  $\Rightarrow$ very low I.Ps ($\simeq$ 4.0 eV) << I.P of Li atom (5.4 eV)
- Building blocks for novel materials with unique properties (magnetism, non-linear optics ...)


THE JOURNAL OF PHYSICAL CHEMISTRY A — Article — pubs.acs.org/JPCA

**Magnetic Superatoms in $VLi_n$ ($n$ = 1−13) Clusters: A First-Principles Prediction**

Meng Zhang,[†] Jianfei Zhang,[†] Xiaojuan Feng,[†] Hongyu Zhang,[†] Lixia Zhao,[†] Youhua Luo,*[,†] and Wei Cao*[,‡]

[†]Department of Physics, East China University of Science and Technology, Shanghai 200237, China
[‡]Department of Physics, University of Oulu, P.O. Box 3000, Oulu FIN-90014, Finland


Inorganic Chemistry — Article — pubs.acs.org/IC

**On the Potential Application of Superalkali Clusters in Designing Novel Alkalides with Large Nonlinear Optical Properties**

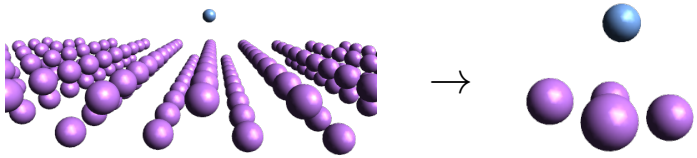
Wei-Ming Sun, Li-Tao Fan, Ying Li, Jia-Yuan Liu, Di Wu,* and Zhi-Ru Li

Institute of Theoretical Chemistry, State Key Laboratory of Theoretical and Computational Chemistry, Jilin University, Changchun 130023, People's Republic of China

# Lithium fluoride clusters

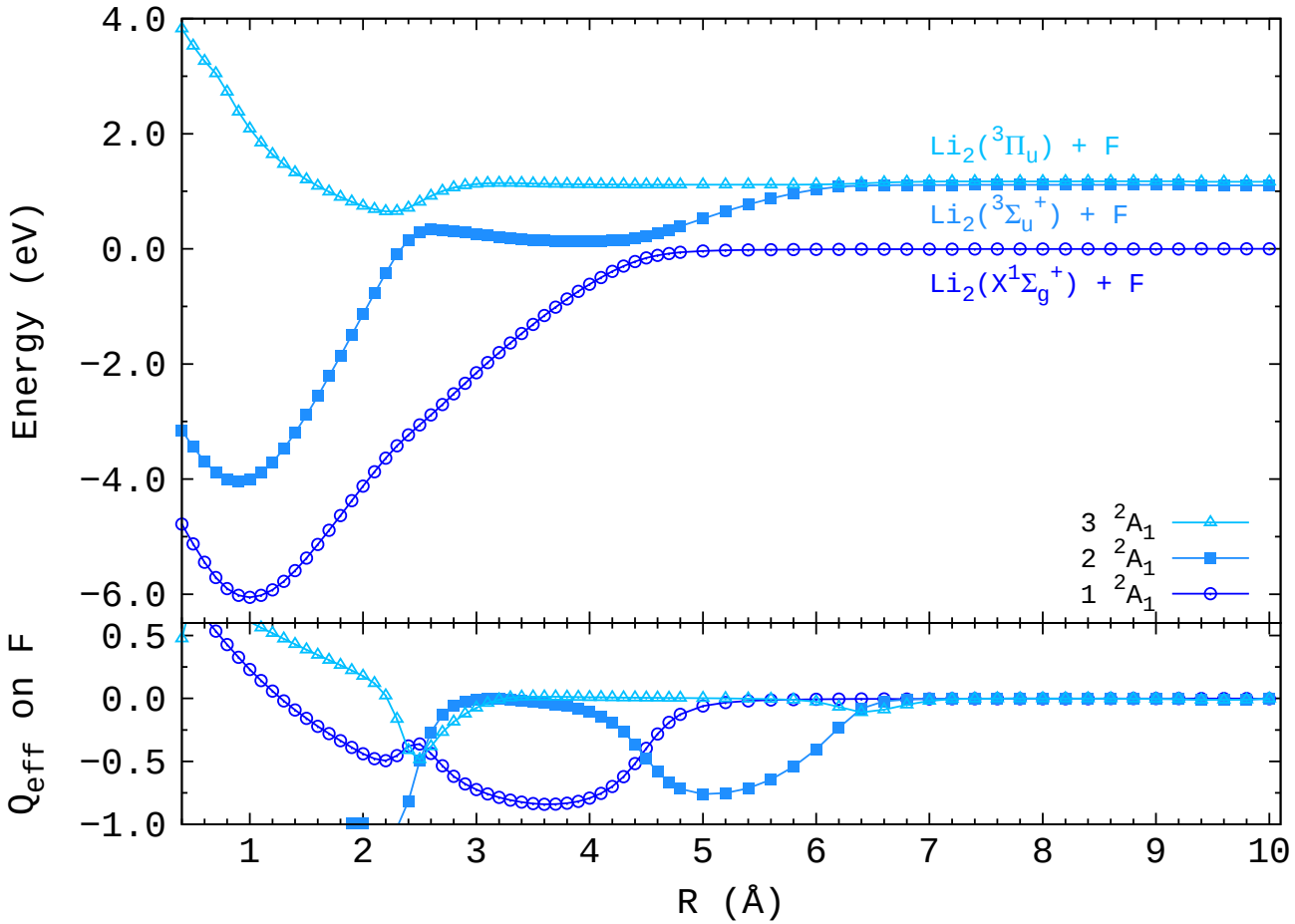
## Motivations

- Experimental evidence of $Li_nF$ clusters with $n = 2 - 6$ (2000's)
- Model for the study of adsorption on a metallic surface : role of excited states ?



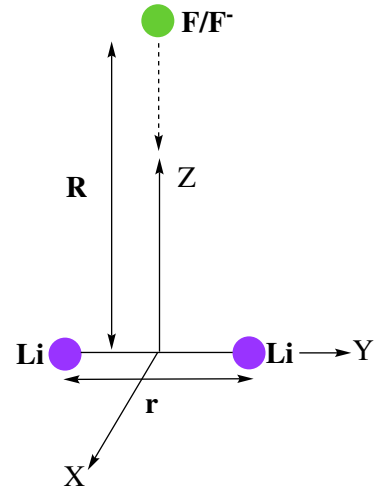
- Covalent and ionic interactions are expected along the reaction path $\Rightarrow$ multireference methods (CASSCF, MRCI-F12)
- $Li_2 + F \rightarrow Li_2F$ : possible candidate for ultracold temperature reactions (Lane et al., 2010). Insertion mechanism ?
- $Li_2 + F^- \rightarrow Li_2F^-$ ? no study so far

# $Li_2$+F potential energy curves




CAS(7,8)/MRCI-F12, AVTZ

r=2.67Å




$$Q_{\text{eff}} = \frac{\mu_z}{R}$$

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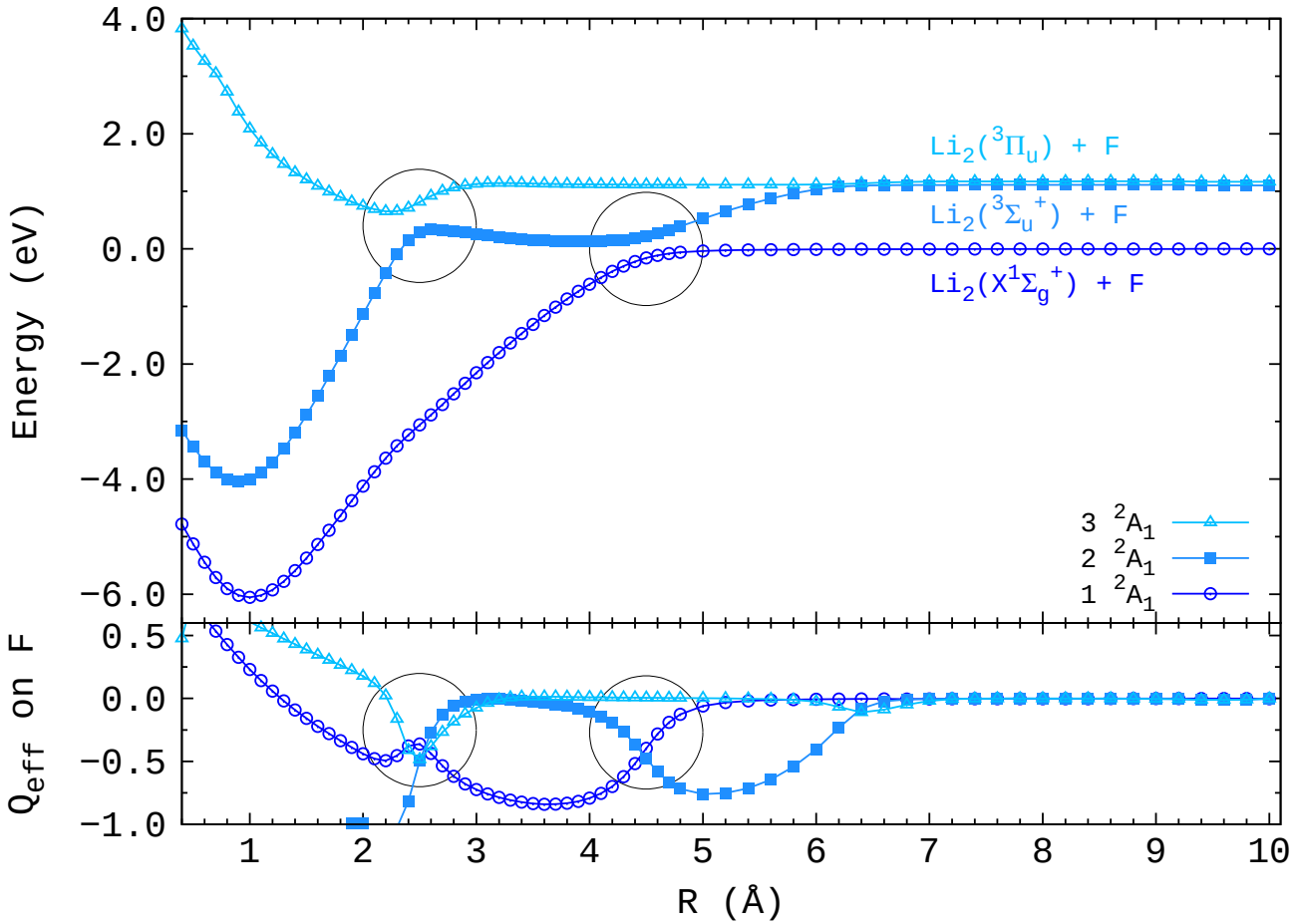


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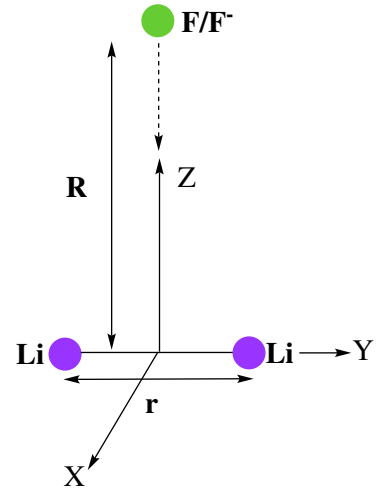


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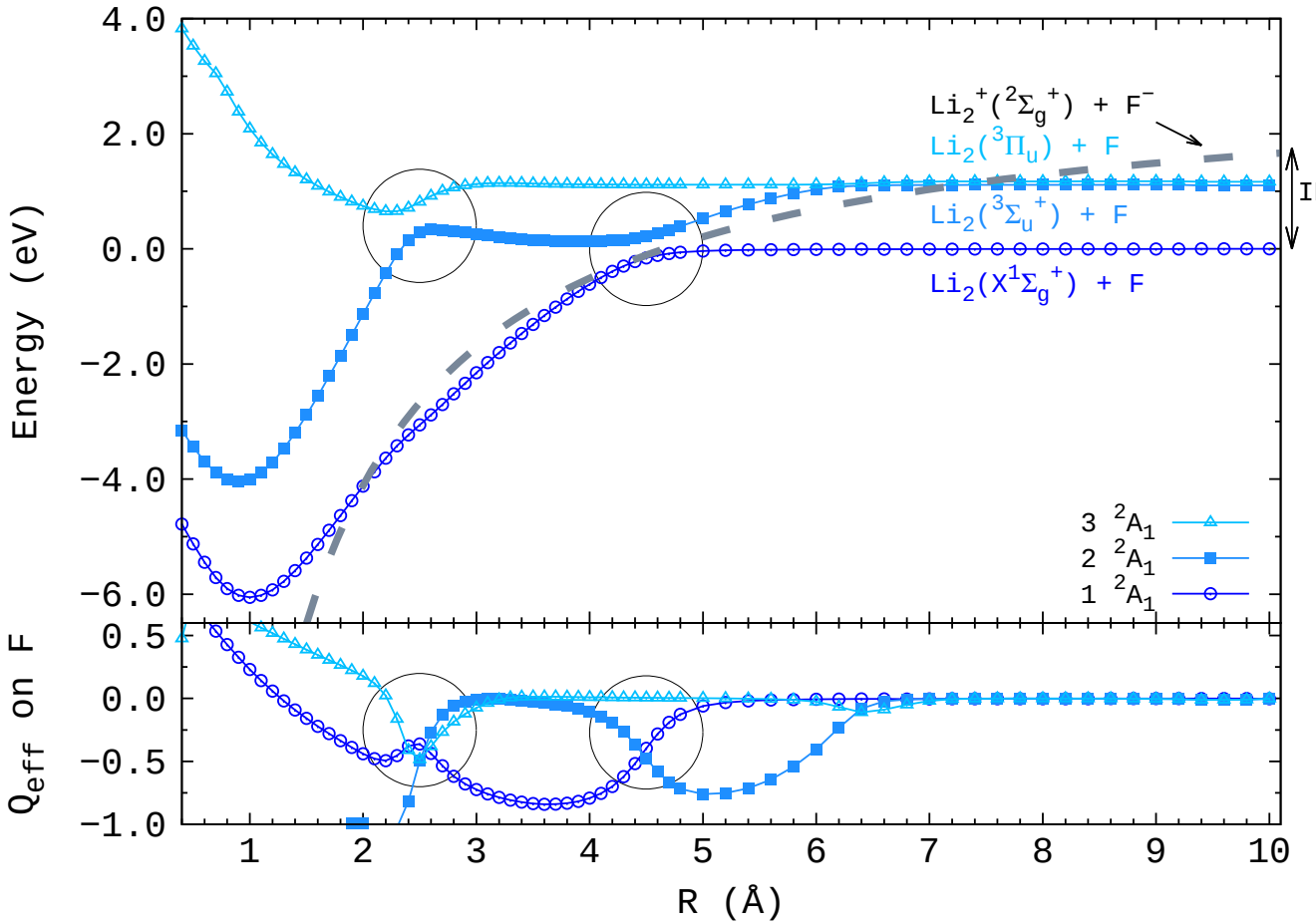


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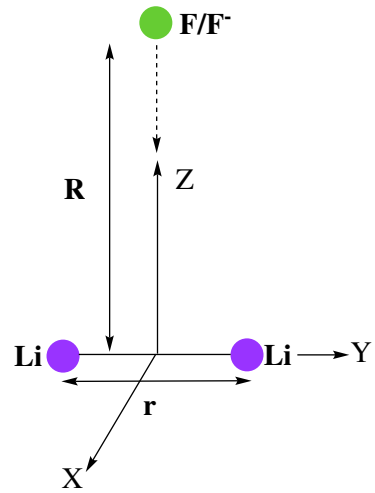


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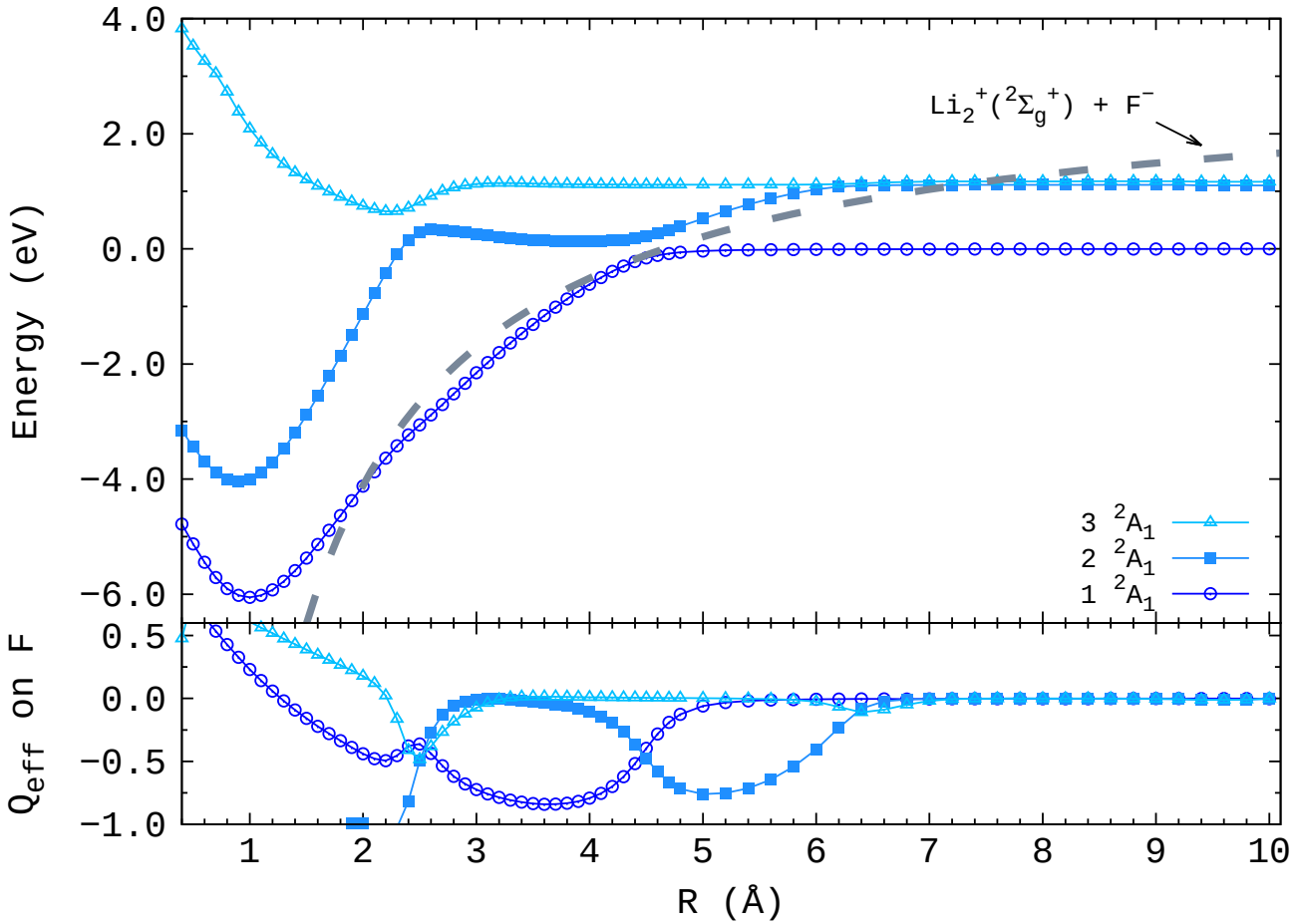


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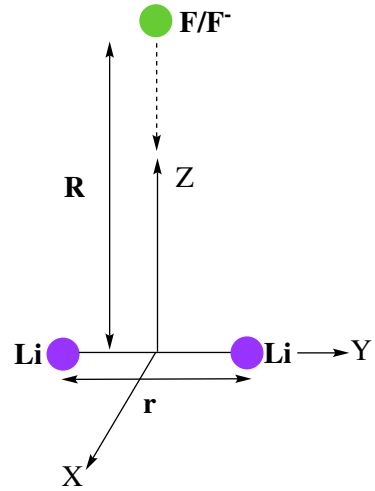


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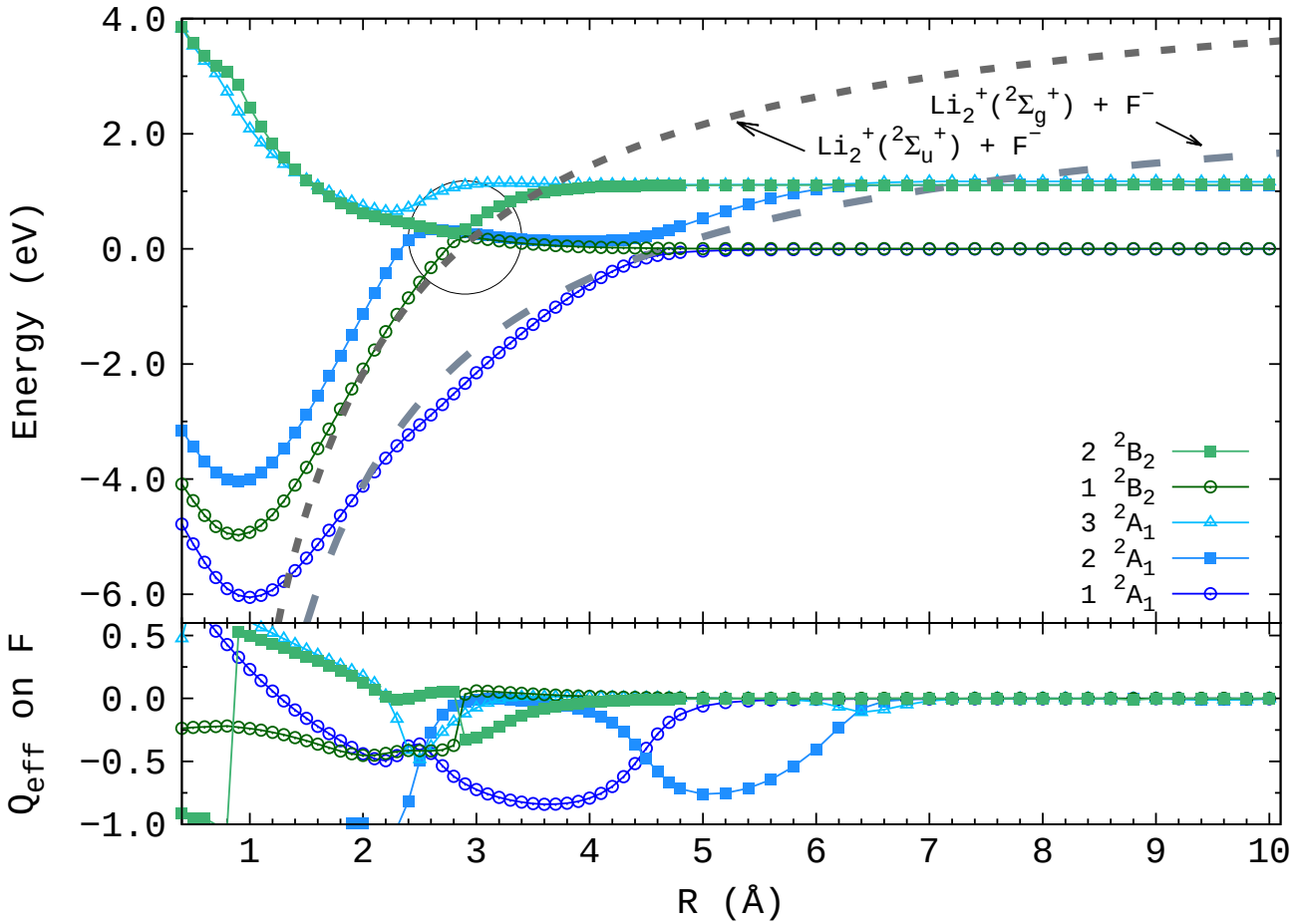


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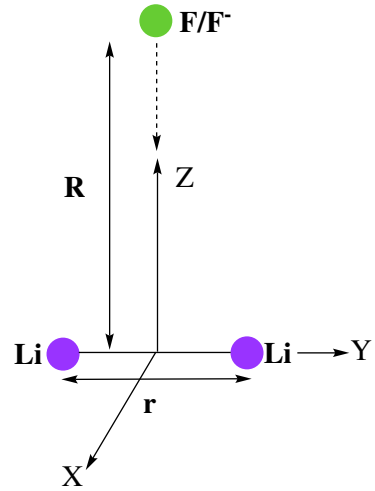


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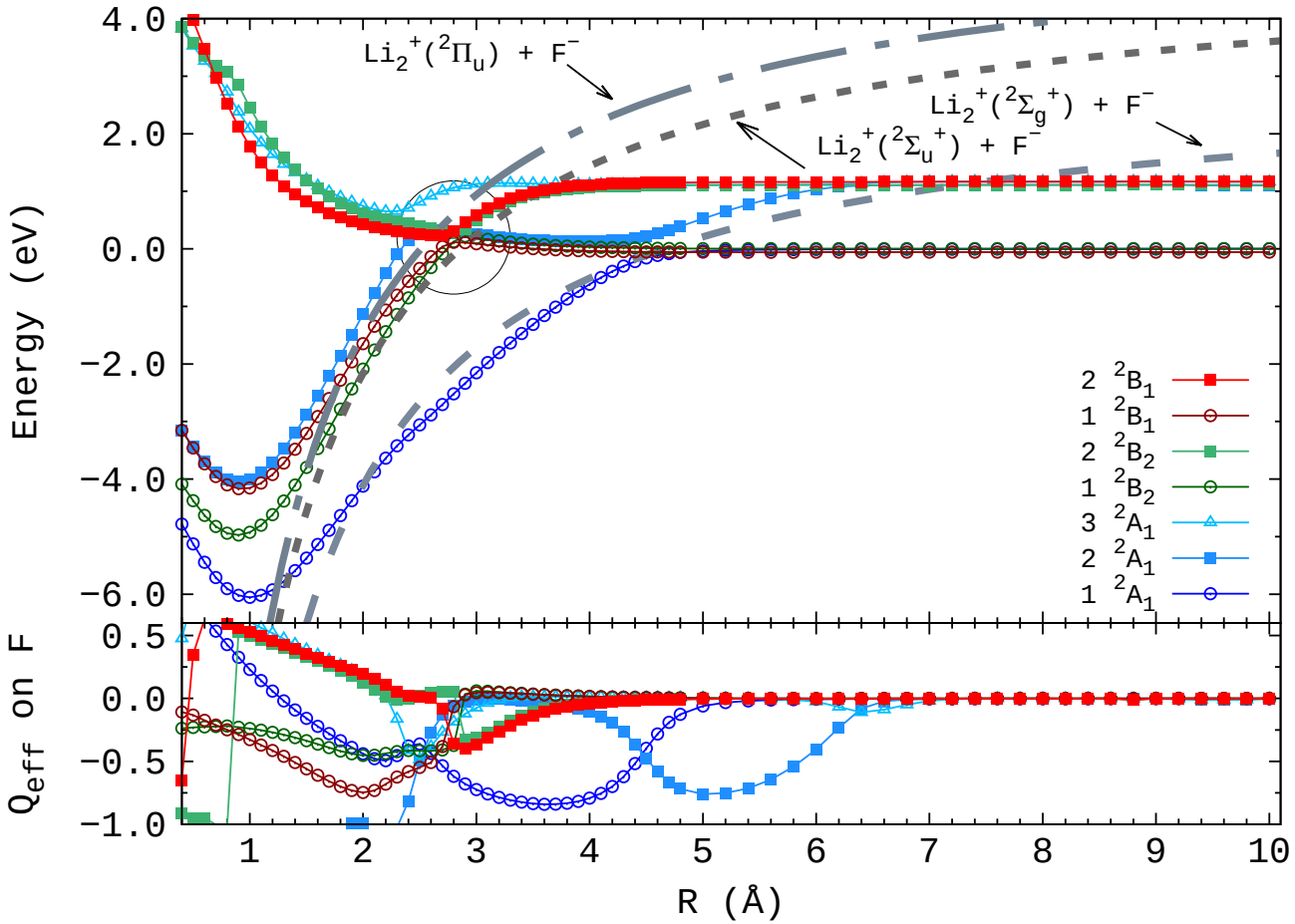


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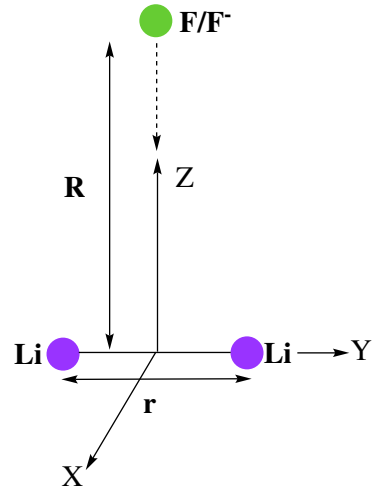


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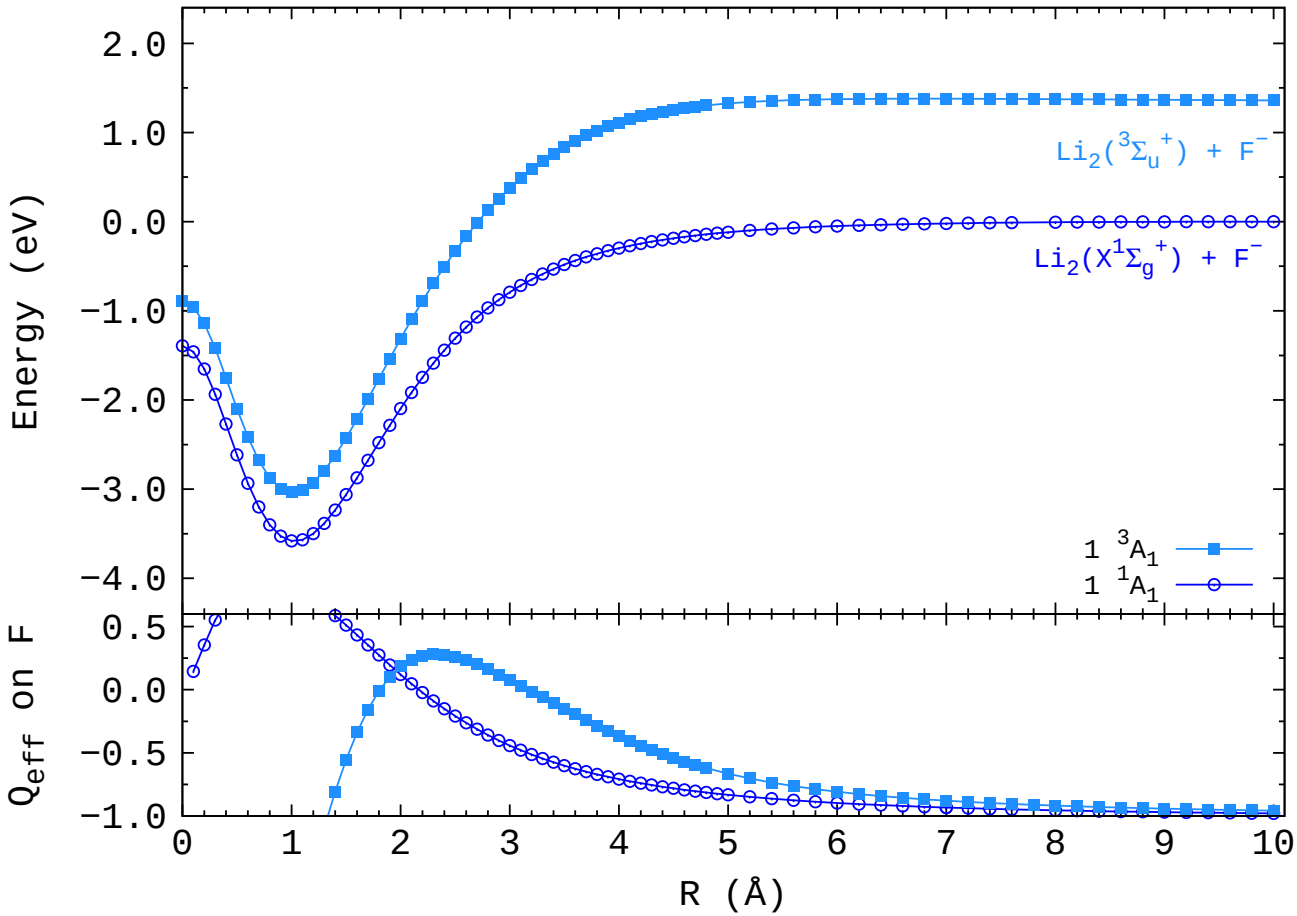
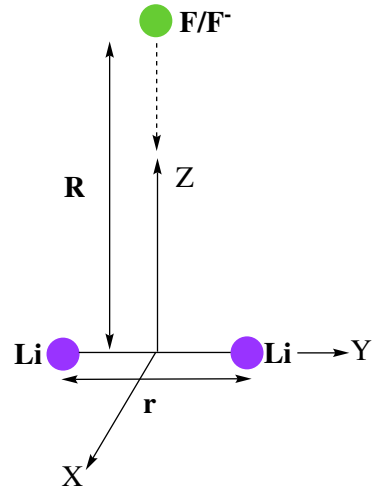
# $Li_2+F^-$ potential energy curves




CAS(8,9)/MRCI-F12, AVTZ

r=2.67Å

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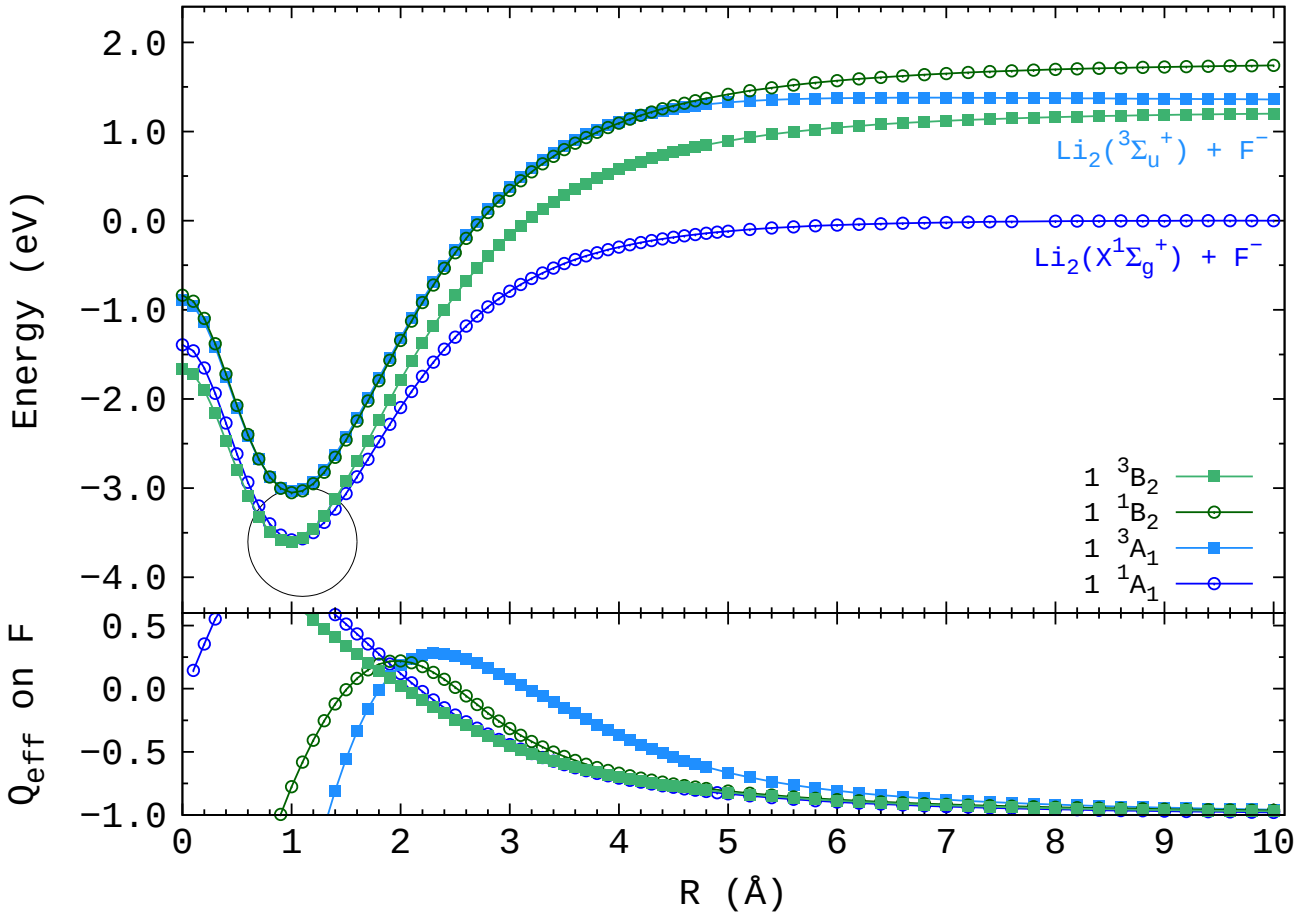


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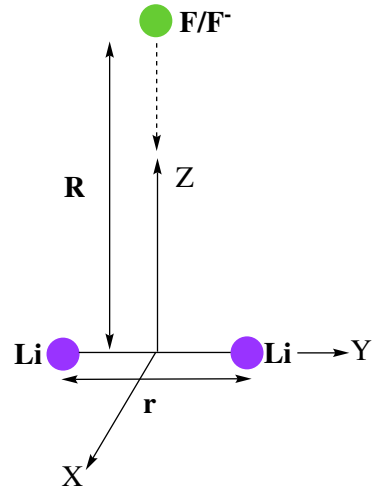


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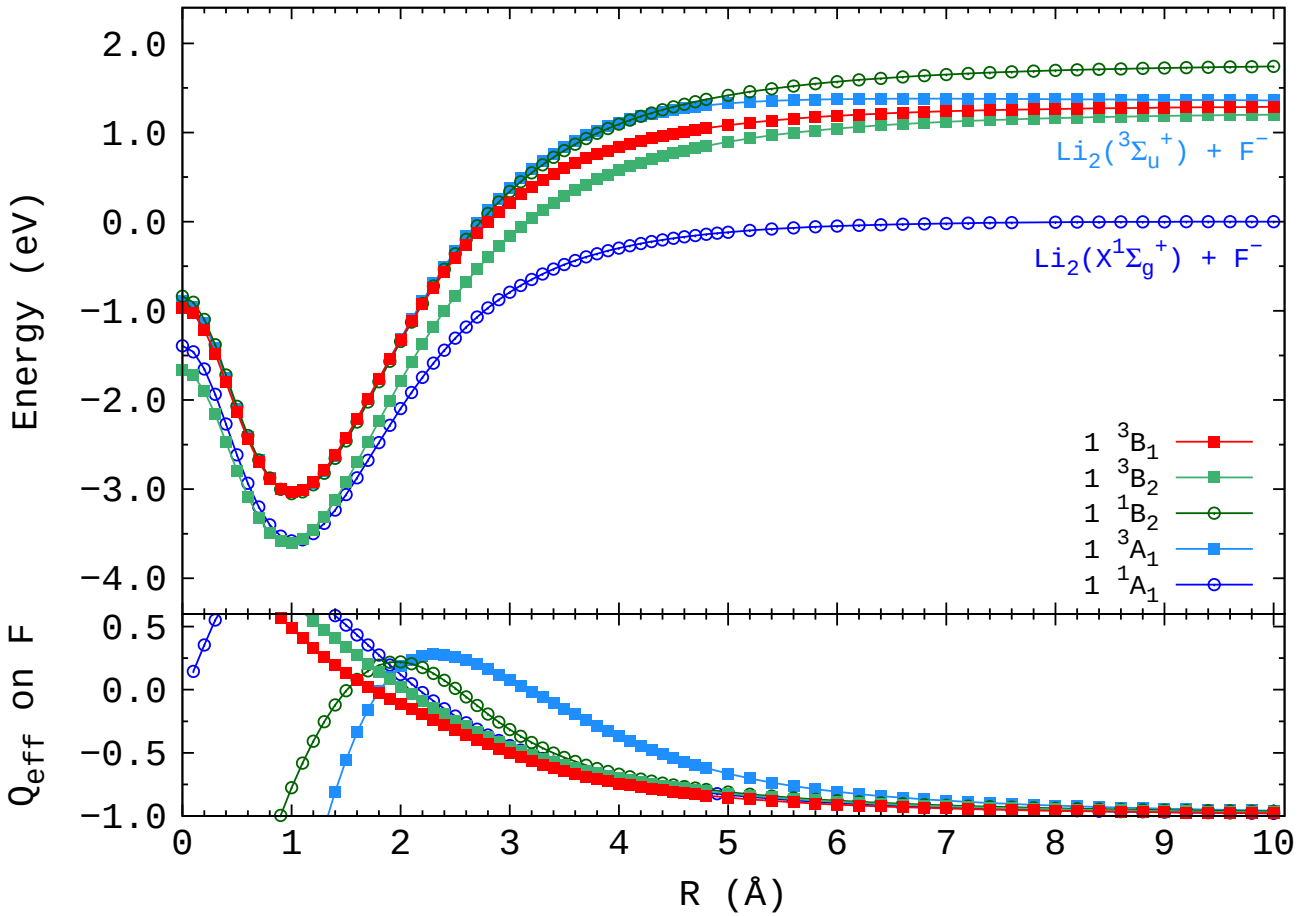


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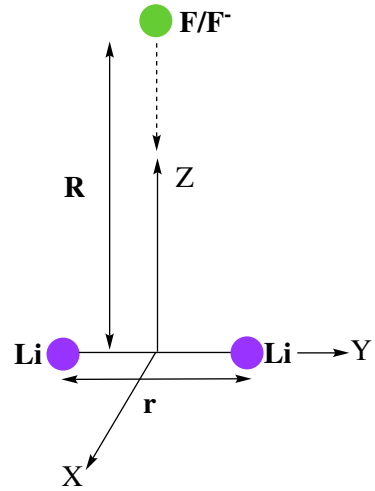
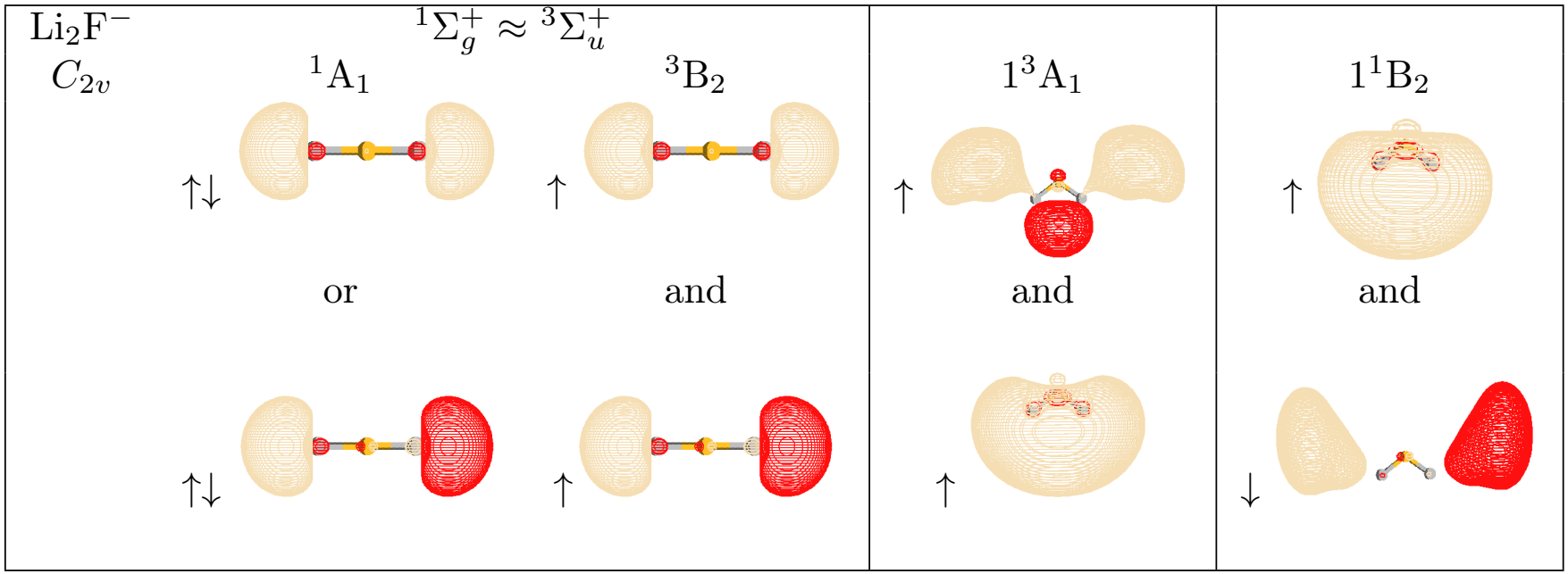



$$Q_{\text{eff}} = \frac{\mu_z}{R}$$

# Bond analysis of the low-lying states of $Li_2F^-$

- ✔ The ground state is linear, the excited states are bent
- ✔ The triplet states are mono-configurational, the singlets are multi-configurational



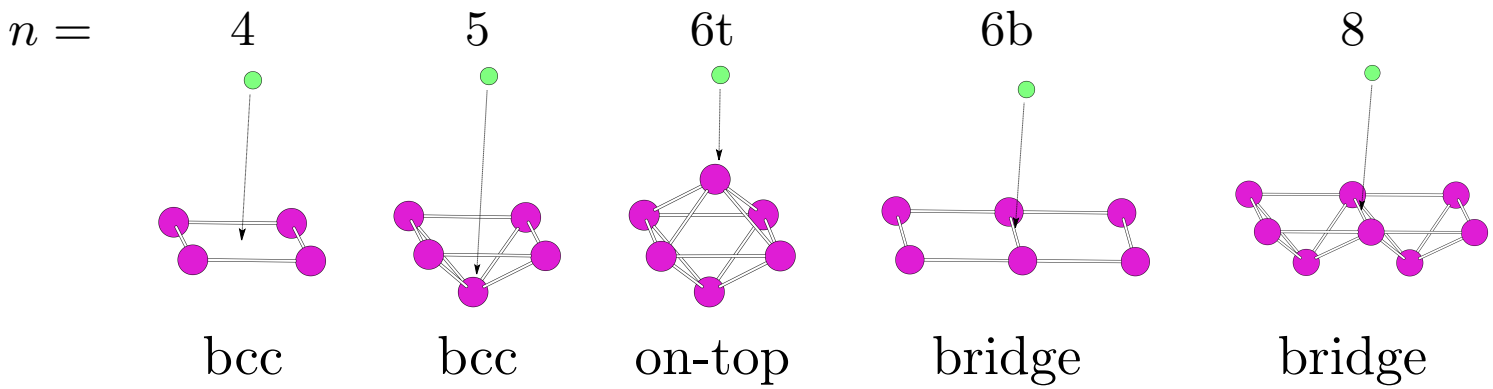

$\Rightarrow$ 3c/4e$^-$ $\hat{\sigma}$ type "long bonding" [a] as in Li−Be−Li : L- -A----L' $\longleftrightarrow$ L Ä L'

a. C. Landis & F. Weinhold, Inorg. Chem. 52, **2013**, 5154

# Low-lying states of $Li_nF$ clusters

## Choice of clusters and method

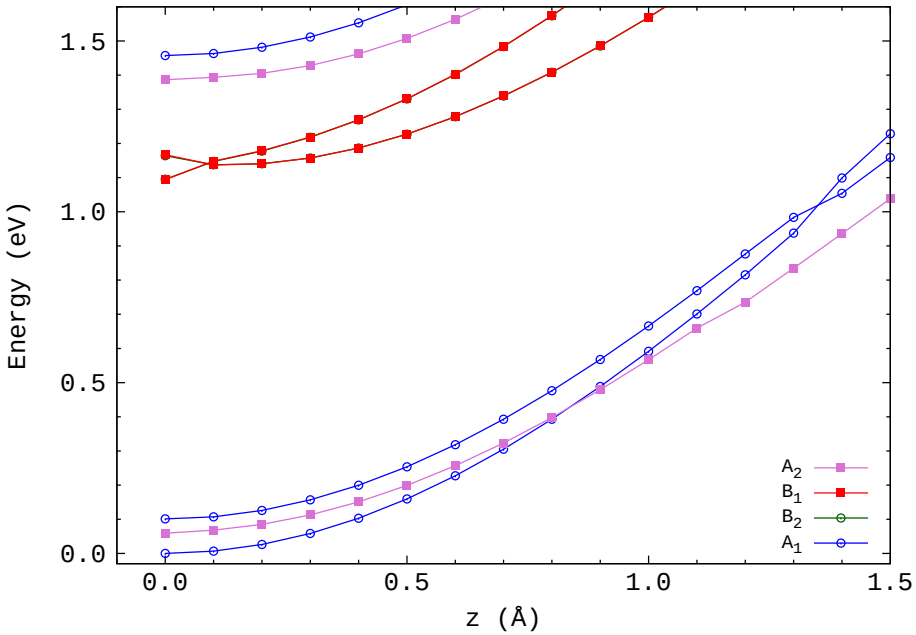
- The $Li_n$ clusters correspond to a (100) plane of the bcc crystal (r=3.51Å )
- The $Li_nF/F^-$ clusters have a $C_{2v}$ symmetry
- Method : CAS(n+5,11)/MRCI, AVTZ − ECP for $n = 8$
- Bridge and on-top adsorption sites



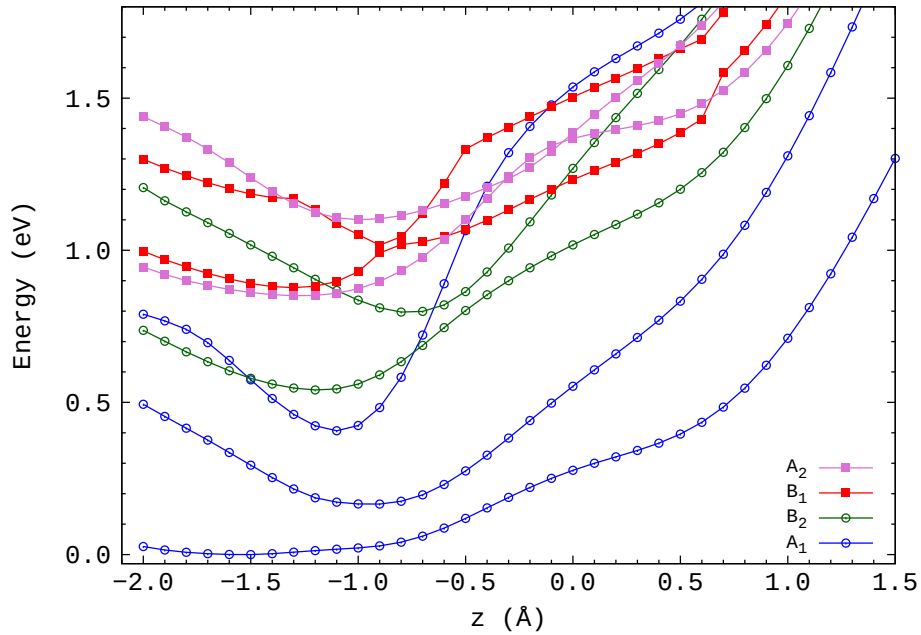
# Low-lying states of $Li_nF$ clusters

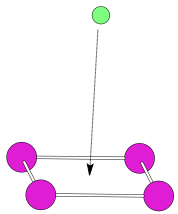
## $Li_nF^-$ potential energy curves

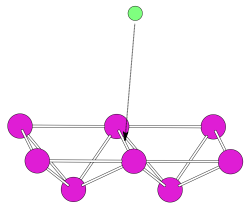
$Li_4F^-$




$Li_8F^-$

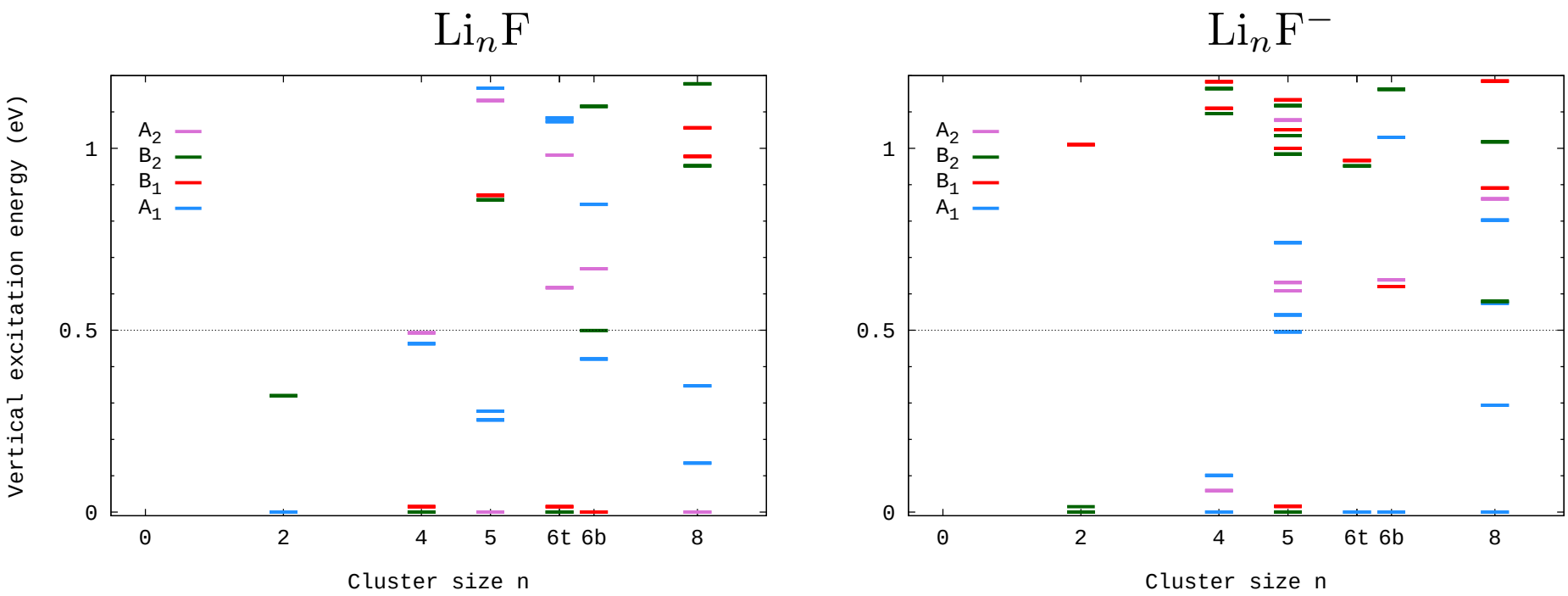


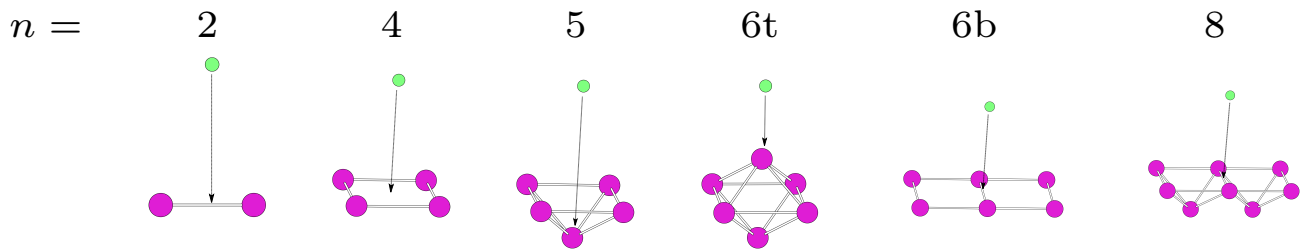





# Low-lying states of $Li_nF$ clusters

## Vertical excitation energies

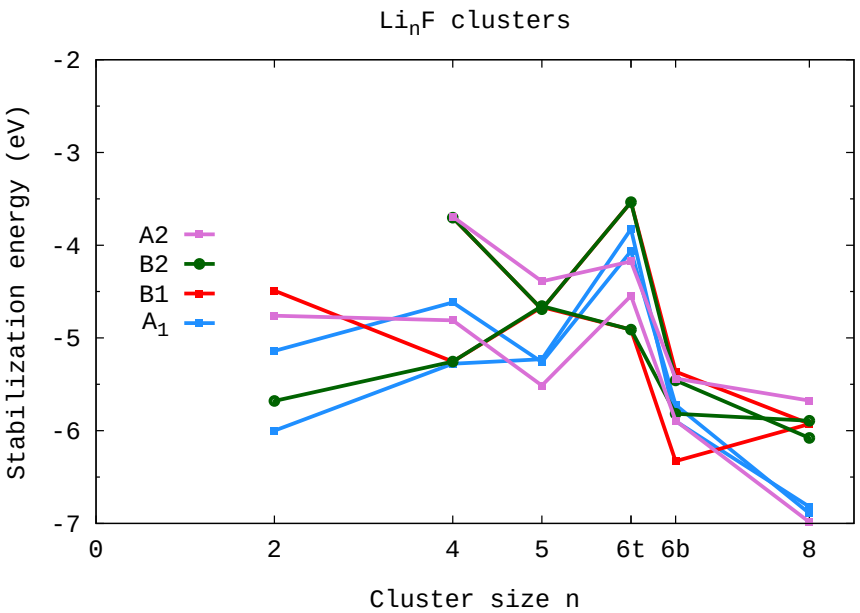


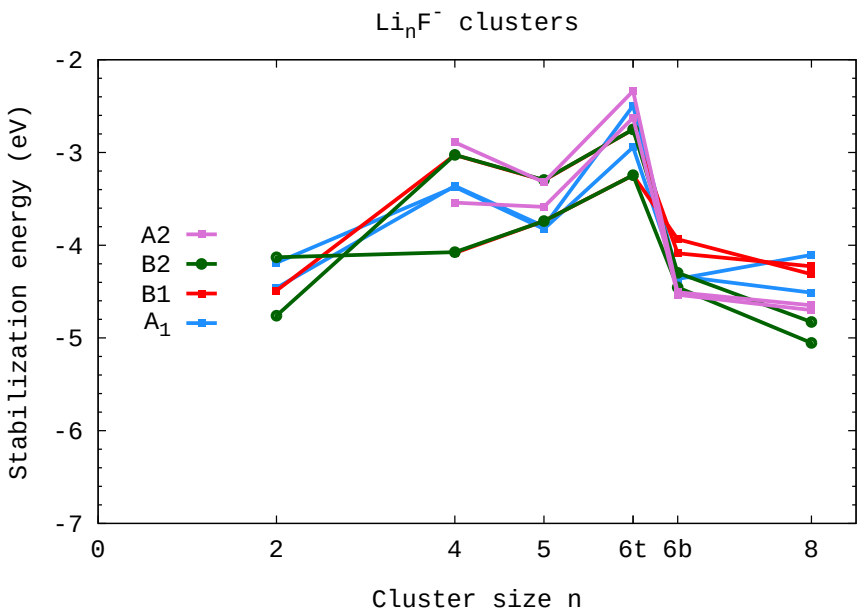



# Low-lying states of $Li_nF$ clusters

## Stabilization energies

- $Li_nF$ clusters are more stabilized than $Li_nF^-$ clusters
- Bridge positions are favoured
- The second layer is stabilizing



# Concluding remarks

- ✔ Lithium fluoride clusters display charge-transfer properties, covalent/ionic interactions
- ✔ Correlated *ab initio* methods are needed to properly describe their dissociation
- ✔ Ground and excited states of $Li_2F$ and $Li_2F^-$ display unusual electronic structures

- ✔ Existence of low-lying states ($< 0.5$ eV above the GS) in $Li_nF$ clusters
- ✔ Strong stabilization of the $Li_nF$ clusters

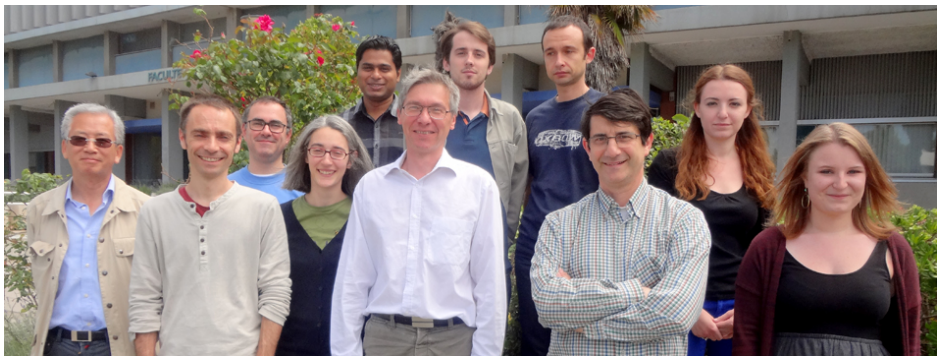
# Future work

- Bonding and dipole moment analysis of $Li_nF$ clusters
- The computation of the excited states on bigger $Li_nF$ ($n > 10$) clusters is ongoing
- Computation of first ionization (neutral) and detachment (anionic) energies $\rightarrow$ superalkalis
- Valence-Bond description of the excited states of the small complexes $\rightarrow$ projection method developped in our group (J. Racine & S. Humbel)

# Aknowledgments

ctom*

- Somnath Bhowmick (PhD)
- Julien Racine (PhD)
- Paola Nava
- Yannick Carissan
- Jean-Marc Mattalia
- Gwang-Hi Jeung
- Stéphane Humbel



Aix*Marseille université

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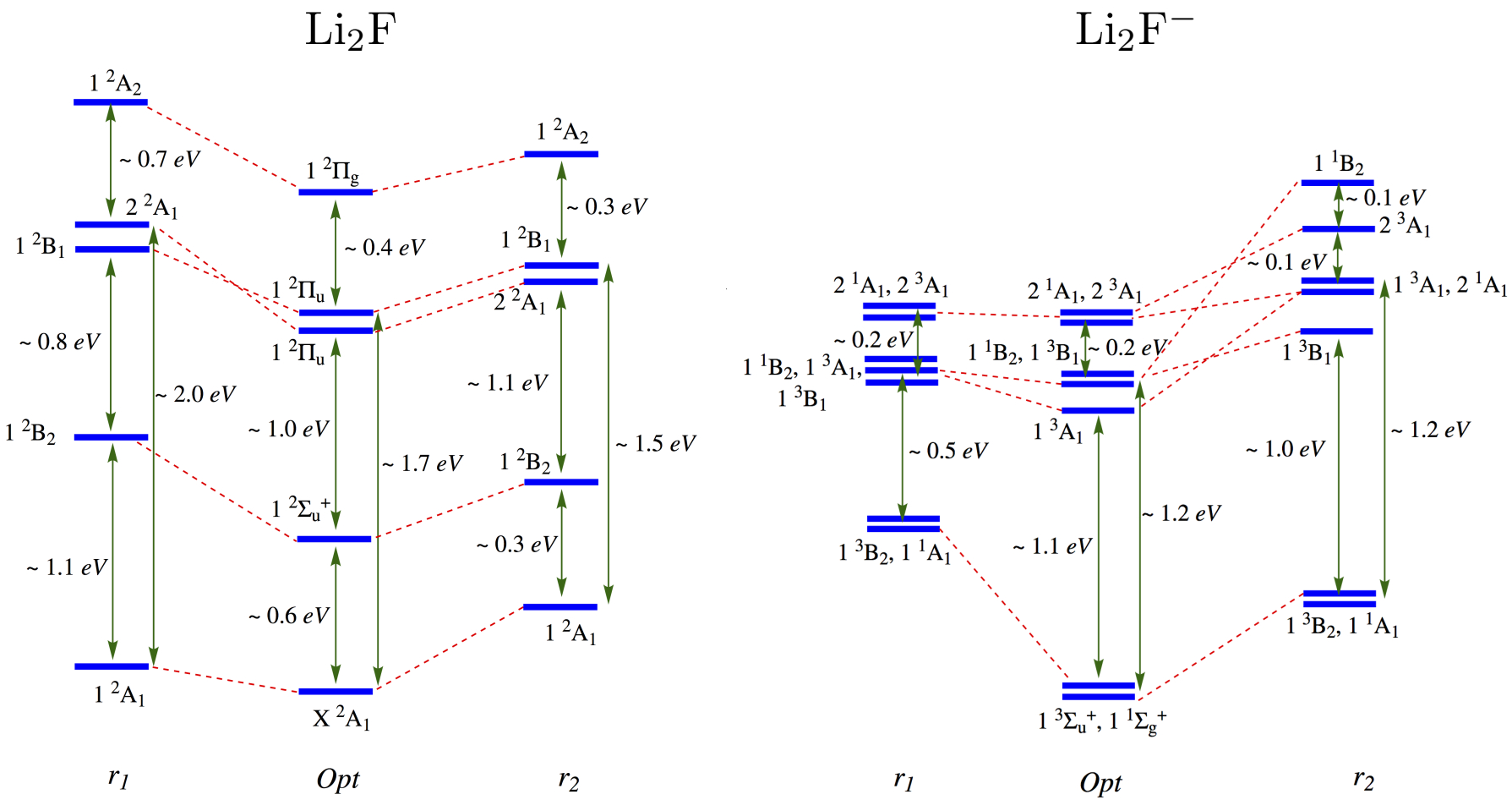
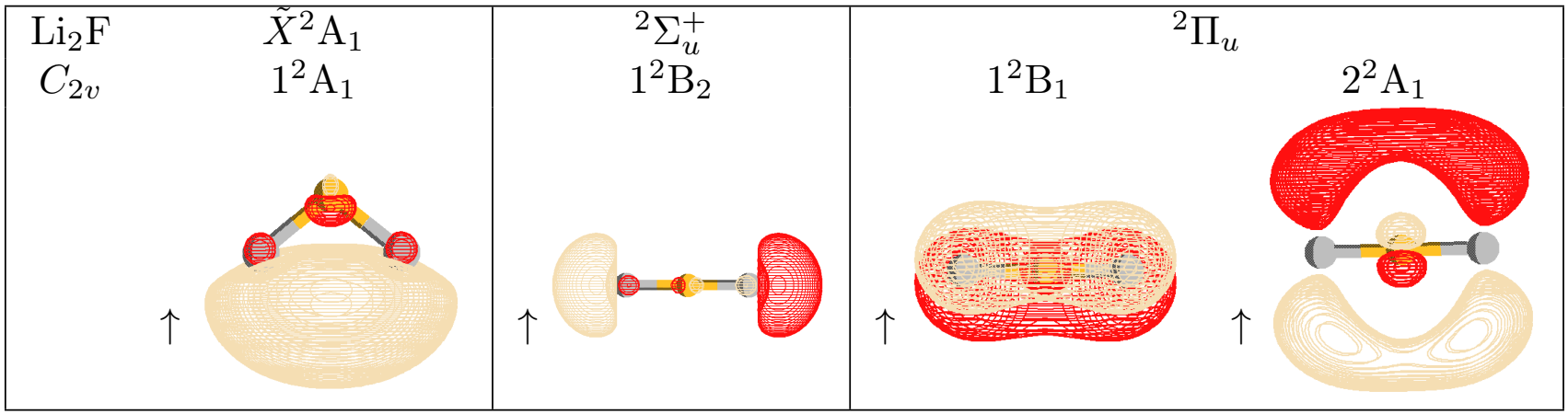
# Optimized states of $Li_2F$ and $Li_2F^-$



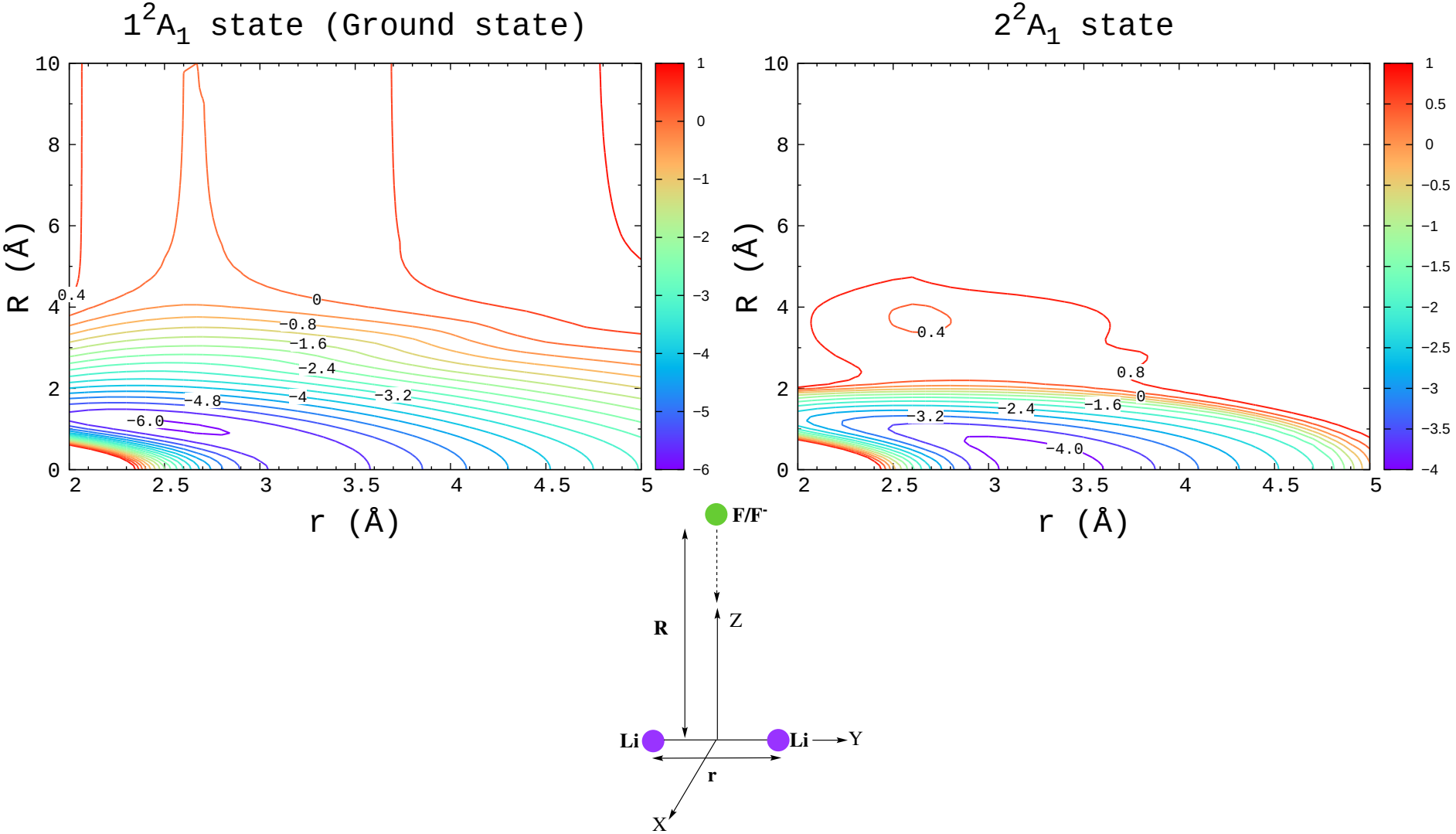

$r_1 = 2.67$ Å (free $Li_2$) $\quad r_2 = 3.51$ Å (crystal)

# Bond analysis of the low-lying states of $Li_2F$

- ✔ The low-lying states are mono-configurational
- ✔ The ground state is bent, the excited states are linear



# $Li_2F$ potential energy surfaces



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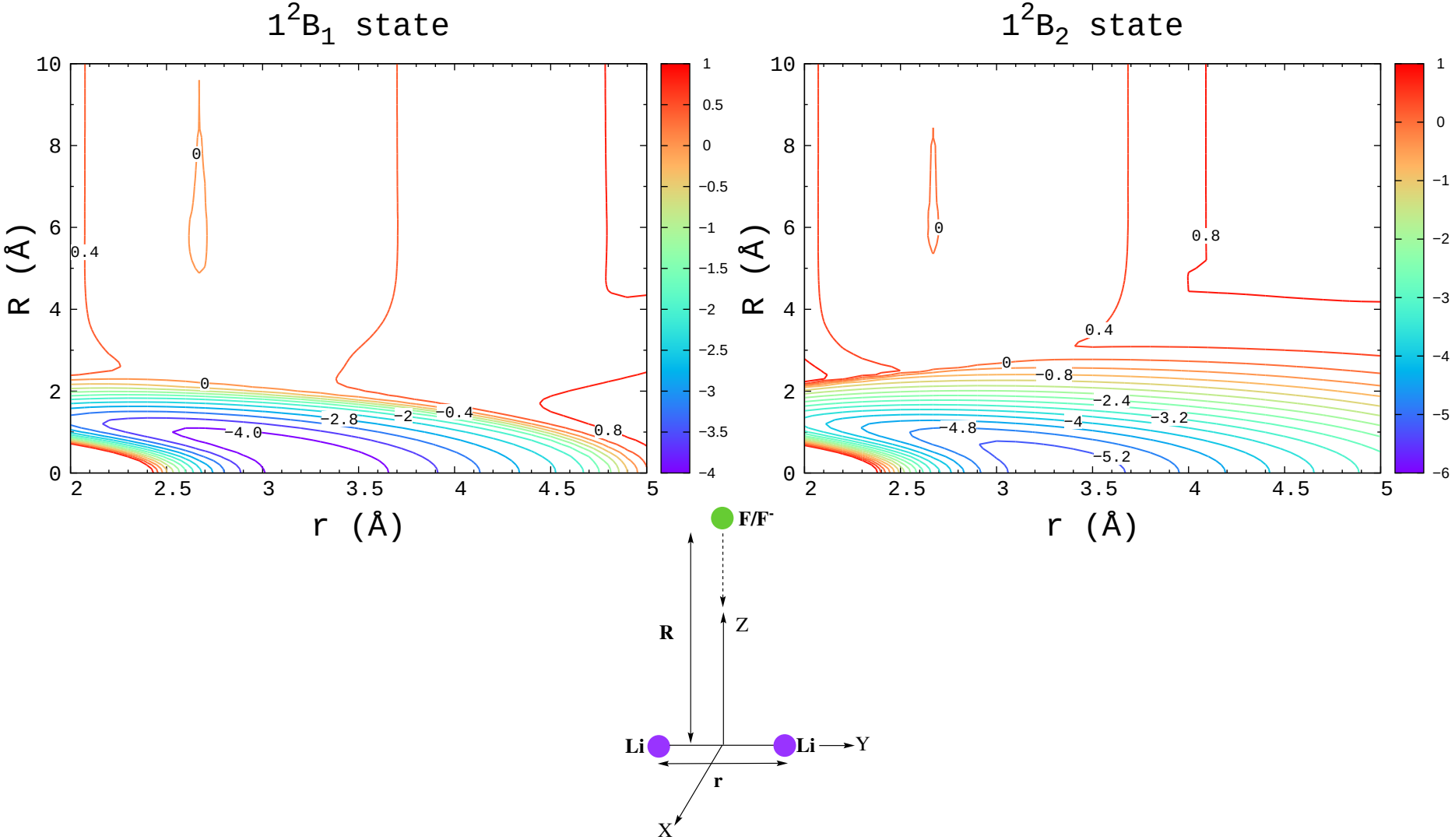

# $Li_2F^-$ potential energy surfaces