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Introduction

The lithium chemistry has received a great attention in recent years due to the importance that LiH molecules and its ionic variants can have in the primordial universe [1,2]. The reaction $\text{LiH} + \text{H} \rightarrow \text{Li} + \text{H}_2$ is considered to contribute to LiH depletion, while the hydrogen-exchange reaction $\text{LiH} + \text{H} \rightarrow \text{LiH} + \text{H}$ leads to the retention of LiH in this process. In this work we report our recent studies on the long-range interactions between the reactants of those reactions. For the LiHH system, the main contribution for the long-range interactions is the dispersion interaction. To modeling the dispersion interaction, the parallel and perpendicular values of the polarizabilities, α , for the diatomics (H-H and Li-H) have been calculated and fitted using the follow equation (see figure).

$$F(R) = A + \left(\sum_{i=0}^3 B_i R^i \right) \exp\left(-\sum_{i=1}^3 C_i R^i\right) + (1 - \exp(-D_3 R^5)) E_3/R^3 + (1 - \exp(-D_6 R^8)) E_6/R^6$$

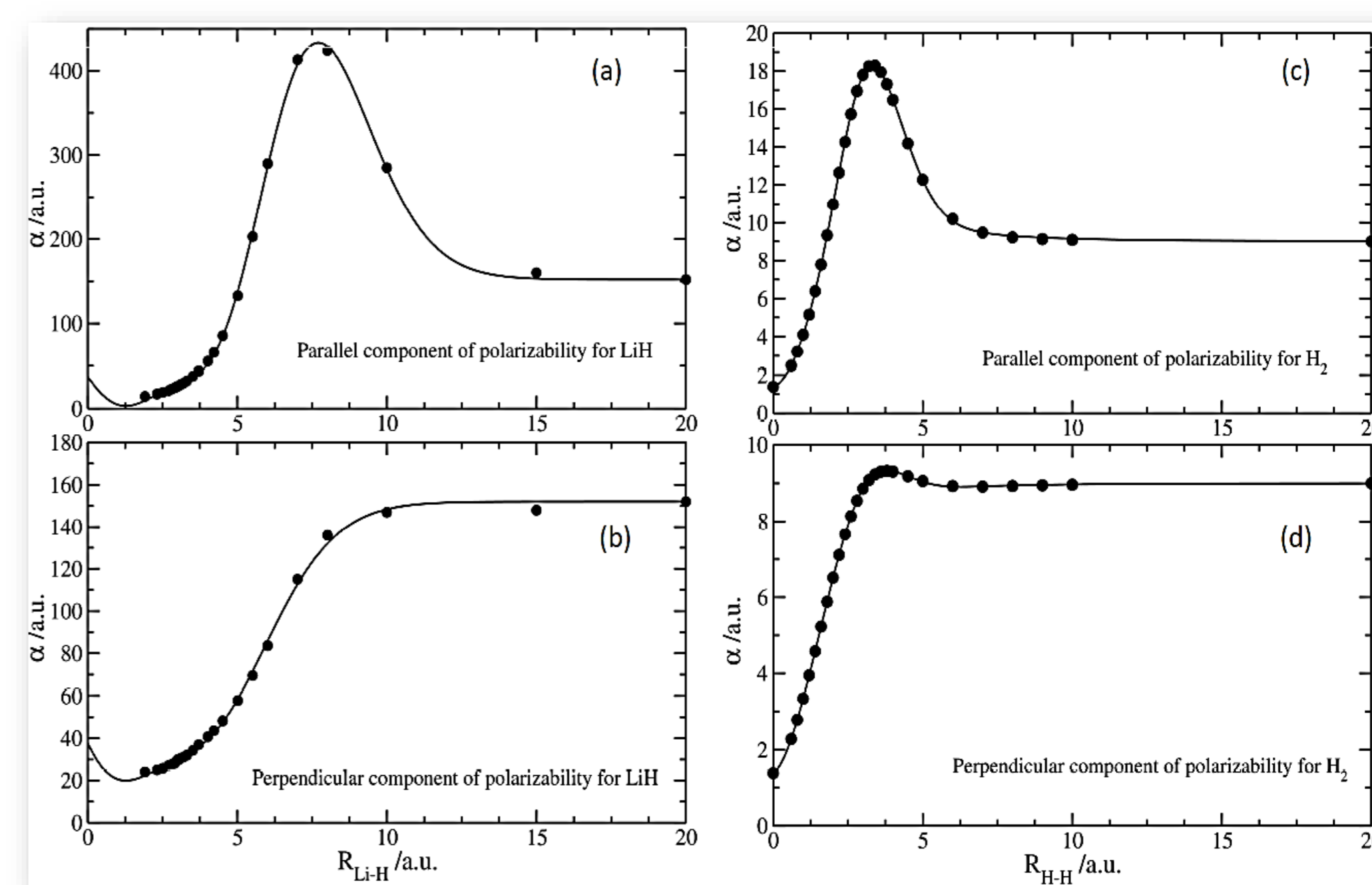


Figure: Parallel and perpendicular components of polarizabilities, α , for LiH ((a) and (b)) and H₂ ((c) and (d)). Solid lines are the functional form fit to the ab initio calculations (solid dots).

Dispersion interaction coefficients

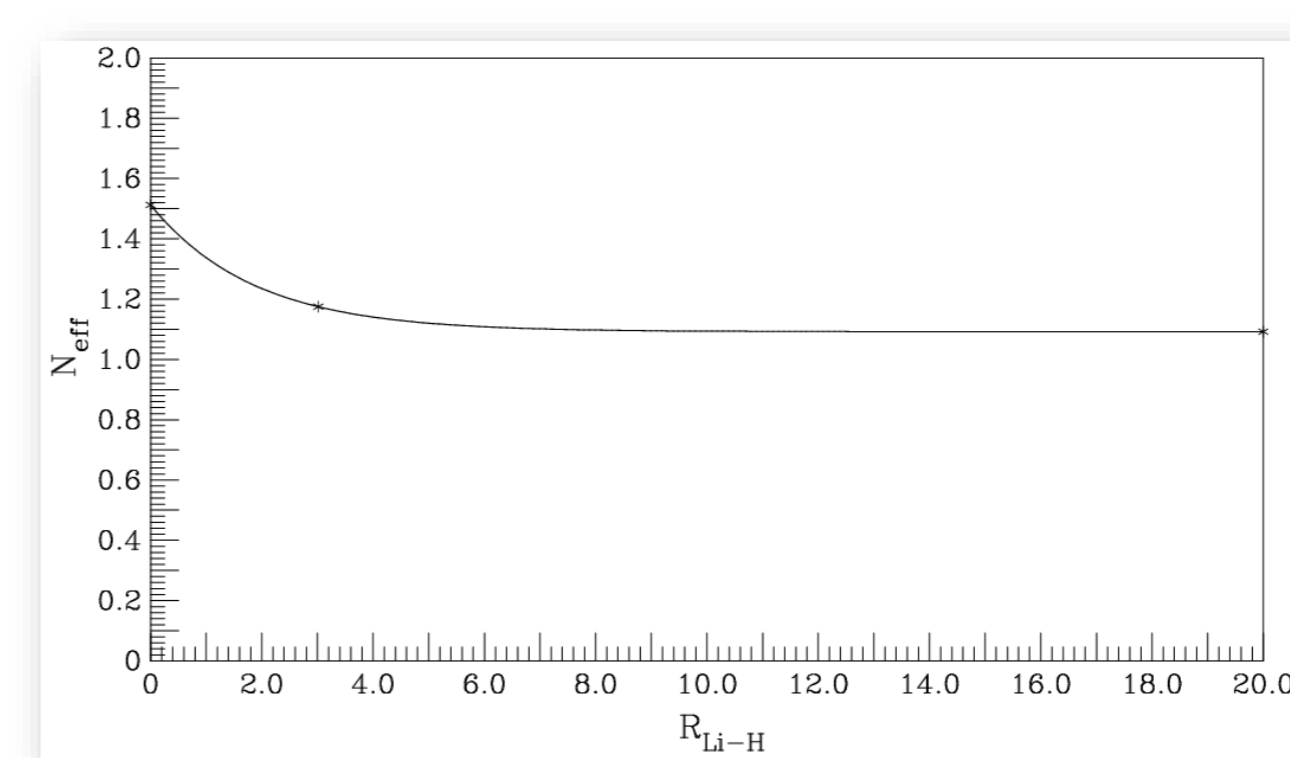
The dispersion interaction coefficients C_6 can then be computed as C_8 and C_{10} have been semiempirically estimated from C_6 using a universal correlation.

We found it convenient to use the follow expression for the variation of N_{eff} with the diatomic distance.

$$N_{eff}(R) = N_{\infty} + [a + b(R - R_e)] \exp[c(R - R_e)]$$

The parameters a , b and c have been defined in order to reproduce the united atom and far apart, N_{∞} , limits as well as an equilibrium value, if known.

$$C_6^{||,\perp}(AB-C)(R) = \frac{3}{2} \alpha_{AB}^{||,\perp}(0)(R) \alpha_C(0) \times \left[\left(\frac{\alpha_{AB}^{||,\perp}(0)(R)}{N_{eff}^{AB}(R)} \right)^{\frac{1}{2}} + \left(\frac{\alpha_C(0)}{N_{eff}^C} \right)^{\frac{1}{2}} \right]^{-1}$$

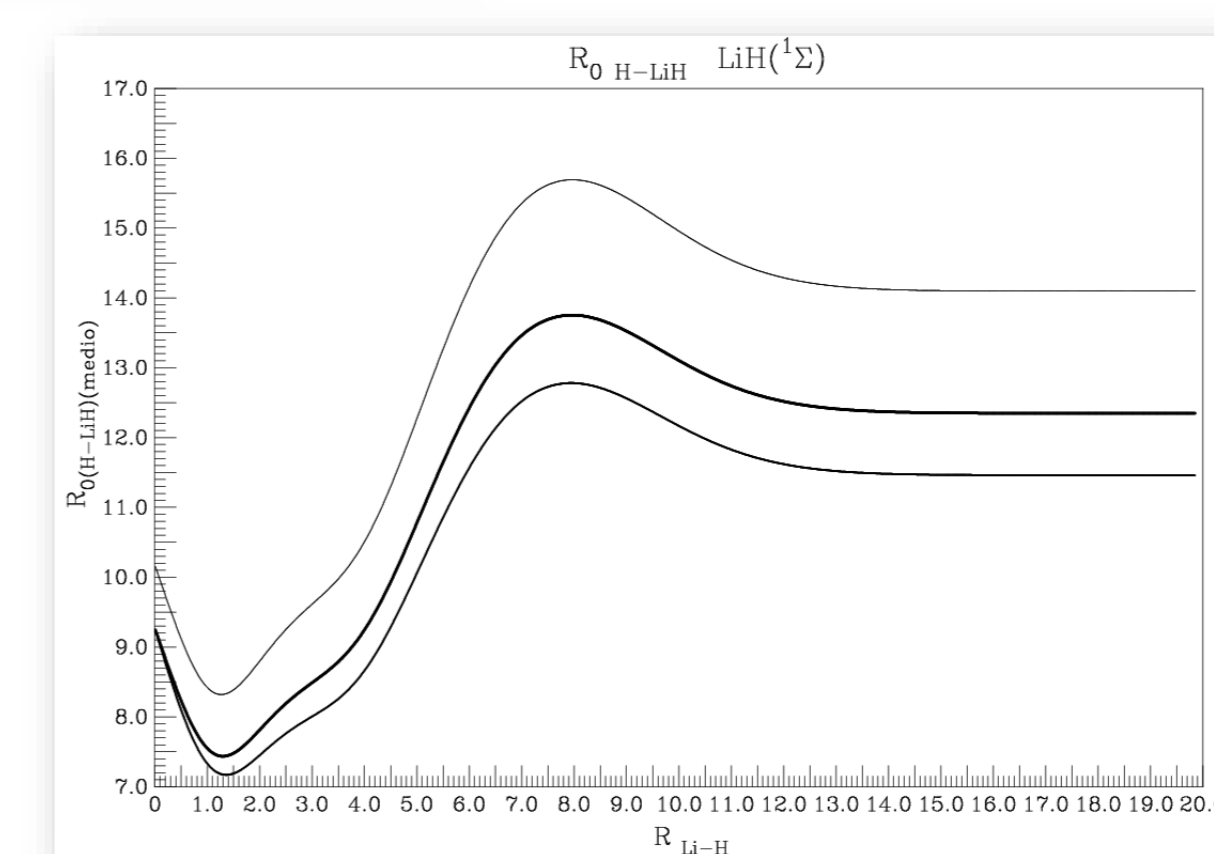


To better model the dispersion interaction we need the coefficients $C_n(AB-C)(R)$, $n = 8$ and 10 . When available we have used literature values, otherwise, we have semiempirically estimated those coefficients from C_6 using a universal correlation.

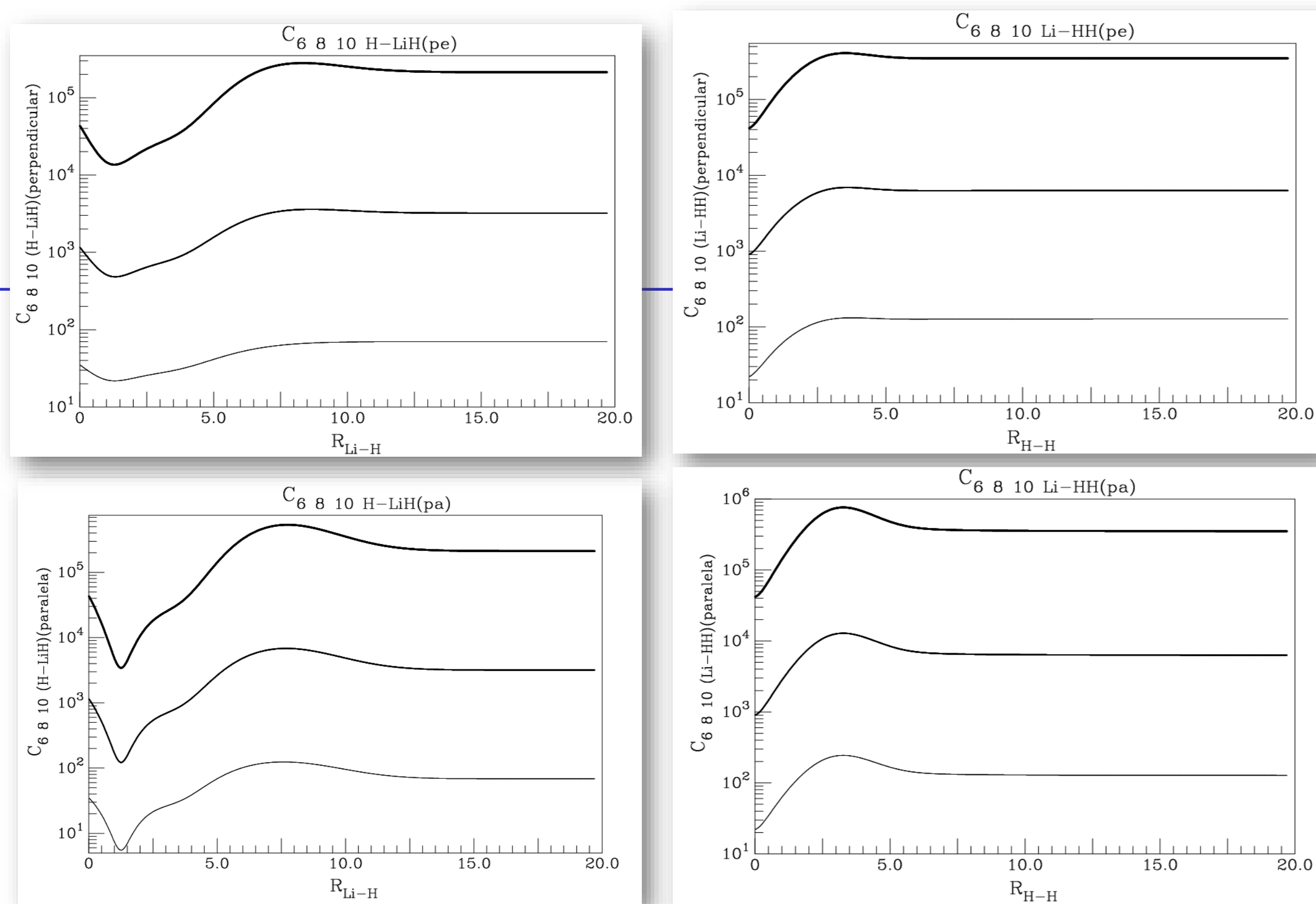
$$C_n^{||,\perp}(AB-C)(R) = C_6^{||,\perp}(AB-C)(R) k_n R_0^{[a(n-6)/2]}(AB-C)(R)$$

In lack of accurate values for the Le Roy's parameter, $R_0(AB-C)(R)$, we have estimated it using the follow equation, where we use the mean polarizability of the diatomic as a measure of the diatomic volume and the atomic radius is taken from the literature.

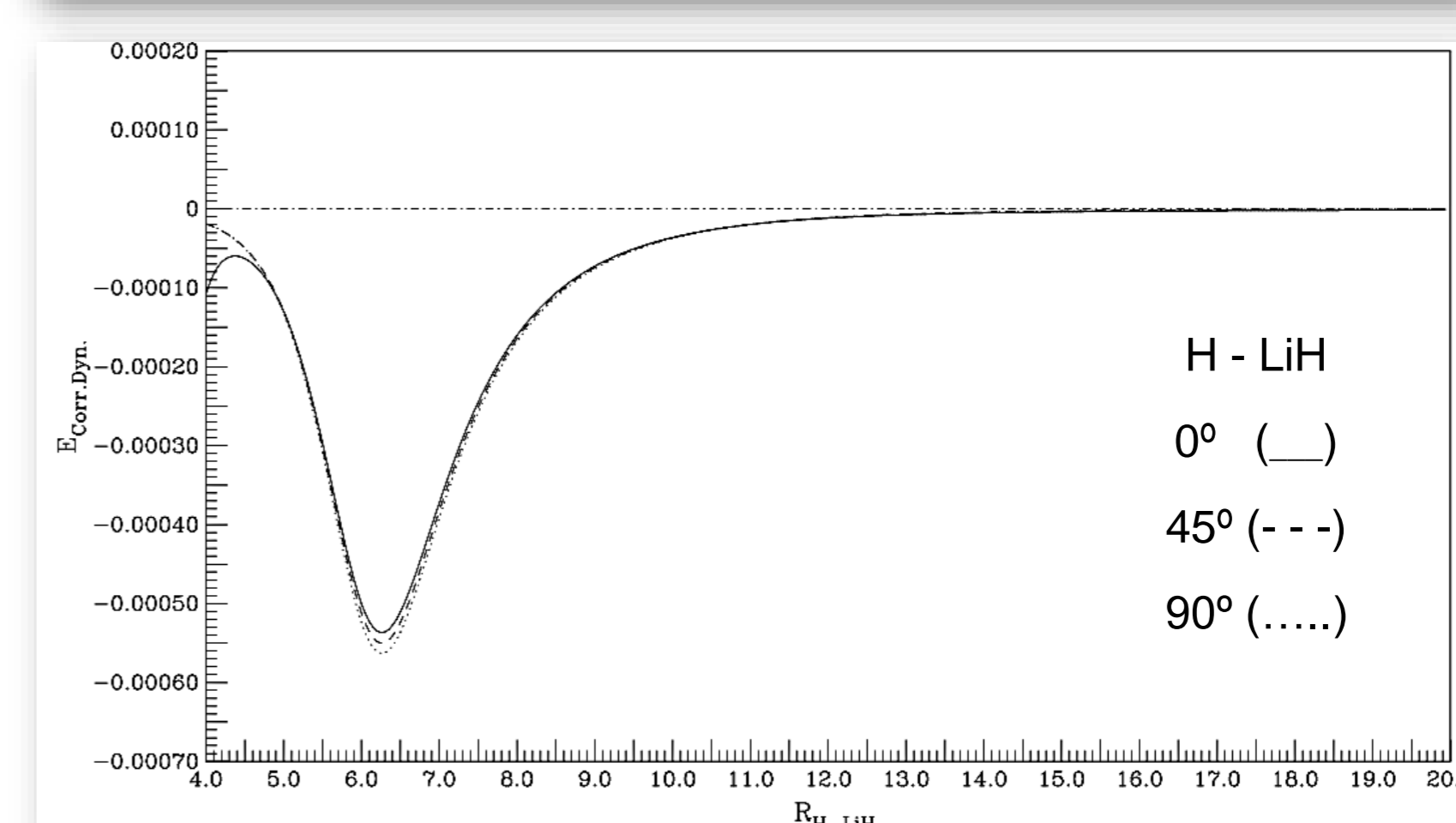
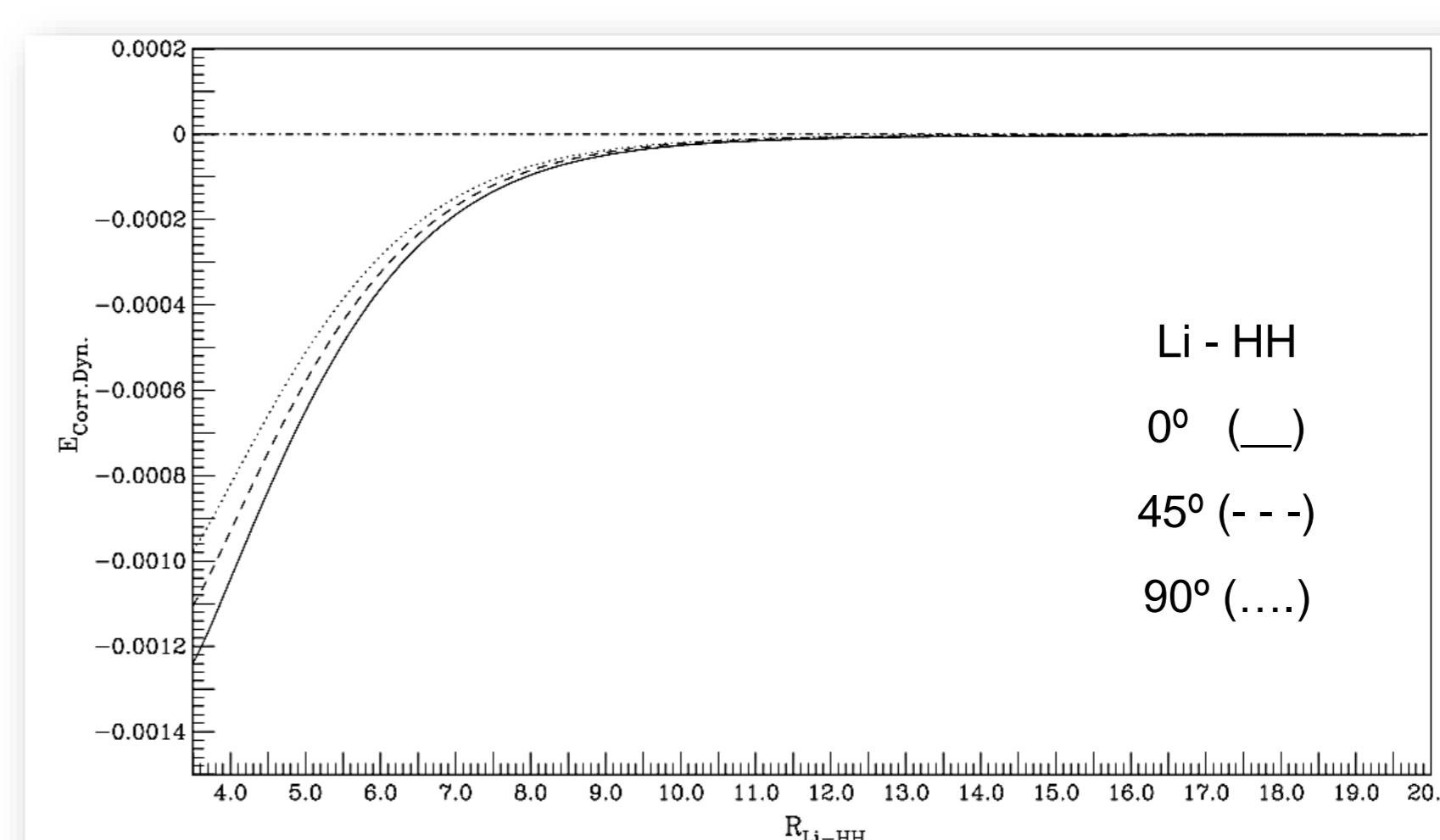
$$R_0(AB-C)(R) = 2 \left[\langle \bar{\alpha}_{AB}(0)(R) \rangle^{\frac{1}{3}} + \langle r_C^2 \rangle^{\frac{1}{2}} \right] f_{corr}^n(R)$$



The total dispersion interaction will be computed as a function of C_n and inter-atomic distances [3].



$$C_n(R_i, \theta_i) = \frac{1}{3} (2C_n^{\perp}(R) + C_n^{\parallel}(R)) + \frac{1}{3} (C_n^{\parallel}(R) - C_n^{\perp}(R)) \times (3 \cos^2 \theta_i - 1)$$



The dynamical correlation energy has been computed using the follow equation.

$$V_{dc} = \sum_{i=1}^3 S(R_i, r_i) \sum_{n=6}^{10} C_n^i(R_i, \theta_i) \chi_n(r_i) r_i^{-n} + \sum_{i=1}^3 \left[\prod_{j \neq i} (1 - S(R_j, r_j)^2) \right] \sum_{n=6}^{10} C_n^i \chi_n(R_i) R_i^{-n}$$

The dynamical correlation energy is shown for the interaction Li-HH and H-LiH, at different approaching angles between atom and diatomic molecule 0°, 45° and 90°.

References:

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3. João Brandão and Carolina M.A. Rio, *Chem. Phys. Lett.* **2003**, 372, 866.