



University of Caen Normandy

Density Functional Theory

## Project 2–Bond breaking in LiH

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# Chapter 1

## Theoretical study

### 1.1 Explain briefly the principle of the DFT method (in 10 lines maximum).

Density functional theory (DFT) is an approximation method applied in modern computational chemistry that describes the structural properties of matter in terms of electron density functional as a fundamental description of electrons rather than the electronic wavefunction.

This treatment simplifies investigation for the important properties like band structures, geometries and reaction mechanisms of many-body systems such as atoms, molecules and condensed matter. The electron density functional for a system of  $N$  electrons is written as a functional of the electron wavefunction as:

$$\rho(\vec{r}) = N \int \int \dots \int dr_2 dr_3 \dots dr_N |\Psi(\vec{r}, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N)|^2$$

The motivation for DFT is based on the important result due to Hohenberg and Kohn that the relation can be reversed i.e. for a ground-state  $\rho_0(r)$ , it is in principle possible to calculate the ground-state wavefunction  $\Psi_0(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N)$  of the electron. Specifically,  $\Psi_0(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N)$  is a unique functional of  $\rho_0(r)$ .

Mathematically, the theorems by Hohenberg and Kohn tell us that for a ground state the expectation value of any observable is a unique functional of the exact ground state density. So that for a ground state  $\Psi$ ,

$$E = \langle \Psi | H | \Psi \rangle = T + W + \int d^3r V_{\text{ext}}(\vec{r}) \rho(\vec{r})$$

The terms kinetic energy  $T[\rho]$  and electron-electron interaction  $W[\rho]$  are unique functionals of  $\rho$  and so is the ground state energy  $E[\rho]$ , as we see using  $F[\rho] = T[\rho] + W[\rho]$ ,

$$E[\rho] = F[\rho] + \int d^3r V_{\text{ext}}(\vec{r}) \rho(\vec{r})$$

### 1.2 Explain the principle of the Kohn-Sham approximation and write the corresponding Kohn-Sham energy.

The Kohn-Sham (KS) approximation replaces the original many-body interacting electron problem with a system of non-interacting electrons that reproduces the same ground-state

electron density. Specifically, Kohn-Sham equation is the non-interacting Schrodinger equation of a fictitious Kohn-Sham system of non-interacting particles that generate the same density as the original interacting system.

The energy functional of the Kohn-Sham formalism is given as,

$$E[\rho] = T_s[\rho] + \int d^3r V_{\text{ext}}(\vec{r})\rho(\vec{r}) + J[\rho] + E_{xc}[\rho]$$

Where  $J[\rho]$  is Hartree energy,  $E_{xc}$  is exchange correlation. This is compared with the energy functional with no interaction term,

$$E[\rho] = T[\rho] + \int d^3r V_{\text{eff}}(\vec{r})\rho(\vec{r}) = 0$$

### 1.3 From the above definition of the Kohn-Sham energy, demonstrate how to obtain the Kohn-Sham equations.

In order to obtain the Kohn-Sham equation, the energy functional  $E(\rho)$  is minimized by variational principle with the constraint that total electrons remain fixed,

$$\delta \left( E[\rho] - \mu \int d^3r \rho(\vec{r}) \right)$$

We will apply this variation to both energy expressions given above,

$$\frac{\delta E[\rho]}{\delta \rho(r)} = \mu = V_{\text{ext}} + \int d^3r' \frac{\rho(r')}{|r - r'|} + \frac{\delta T_s[\rho]}{\delta \rho(r)} + \frac{E_{xc}[\rho]}{\rho(r)}$$

Let us compare this expression with the same variation applied to non-interacting system,

$$\frac{\delta E[\rho]}{\delta \rho(r)} = \mu = \frac{\delta T_s[\rho]}{\delta \rho(r)} + \int d^3r V_{\text{eff}}(\vec{r})\rho(\vec{r})$$

Thus by comparison, we find that

$$V_{\text{eff}} = V_{\text{ext}} + \int d^3r' \frac{\rho(r')}{|r - r'|} + \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}$$

[Wills \(2010\)](#)

Where the last term is the exchange correlation potential  $V_{xc} = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}$ . So the new effective potential transforms the many-body problem into a single-particle formalism with the effective Hamiltonian being,

$$H_{\text{eff}} \psi_i(r) = \left[ -\frac{1}{2} \nabla^2 + V_{\text{eff}}(r) \right] \psi_i(r) = \epsilon_i \psi_i(r)$$

[Wills \(2010\)](#)

## 1.4 Have the Kohn-Sham orbitals and energies a physical meaning?

As per Koopman's theorem, the highest occupied orbital energy otherwise also known as HOMO energy in the Kohn-Sham formalism determines the ionization potential in exact DFT,

$$\epsilon_{\text{HOMO}} = -I$$

Apart from that, Kohn-Sham orbitals serve as an important computational tool in that they determine the exact ground-state electron density.

Additionally, the total energy is related to the orbital energies by the equation,

$$E = \sum_{i=0}^N \epsilon_i - \frac{1}{2} \int d^3r d^3r' \frac{\rho(r)\rho(r')}{|r-r'|} - \int d^3r V_{xc}[\rho]\rho(r) + E_{xc}[\rho]$$

## 1.5 Explain the differences between the three following exchange and correlation functionals: LDA, PBE and B3LYP.

In DFT, the major part of the electron-electron interaction term  $W$  consists of the Hartree energy  $J = \int \int \frac{\rho(r)\rho(r')}{|r-r'|} d^3r d^3r'$  but not exactly. This term alone does not cater for the quantum mechanical effects due to the Pauli exclusion principle such as exchange and correlation. LDA (Local Density Approximation), PBE (Perdew-Burke-Ernzerhof), and B3LYP (Becke, 3-parameter, Lee-Yang-Parr) are different exchange-correlation functionals to approximately calculate the  $V_{xc}[\rho]$  term.

- **Local Density Approximation (LDA)** simply assumes dependence on just the local electron density so that the form of the functional is  $E_{xc}[\rho] = \int \epsilon_{xc}(\rho)\rho(r)d^3r$ .
- **Perdew-Burke-Ernzerhof (PBE)** improves upon LDA by additionally accounting for the dependence on the gradient of density so that the functional is given as  $E_{xc} = \int f_{xc}(\rho, \nabla\rho)\rho(r)d^3r$ . The dependence on  $\nabla\rho$  is adapted through Generalized Gradient Approximation (GGA) functional.
- **Becke, 3-parameter, Lee-Yang-Parr (B3LYP)** generalizes the form of GGA to take a contribution from exact exchange energy from Hartree-Fock theory and additionally incorporates Becke's 3-parameter mixing of exchange terms and Lee-Yang-Parr correlation functional based on GGA.

## 1.6 Discuss the differences and the similarities between the HF and DFT theories.

Hartree-Fock (HF) method computes the ground state wavefunctions of electrons in a self-consistent manner, while the Density Functional Theory (DFT) is based on electron density as fundamental descriptions of electronic structure and also solves the non-interacting

Schrodinger equation self-consistently in cycles. Hartree-Fock theory can exactly account for the quantum mechanical effects including Pauli exclusion principle while DFT requires approximations for the correlation functionals such as those mentioned in the previous part. Hartree-Fock theory solves Schrodinger equation by applying variational principle while DFT is additionally based on Hohenburg-Kohn theorems.

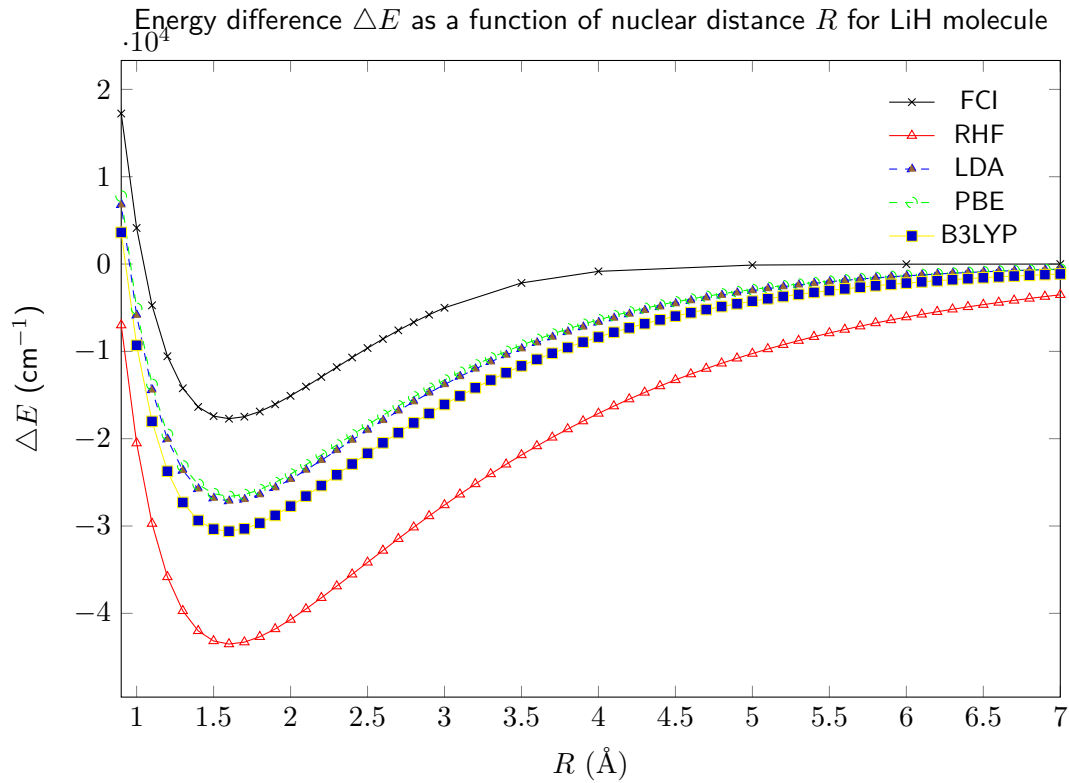
## Chapter 2

# Study of bond-breaking reaction in LiH molecule

### 2.1 Presentation of the results

#### 2.1.1 Plot the energy difference (expressed in $\text{cm}^{-1}$ ) in function of the nuclear distance $R$ (expressed in $\text{\AA}$ ) of the molecule. On the same graph, add your results obtained at the RHF and DFT levels (LDA, PBE and B3LYP).

Figure 2.1: Energy difference plotted as a function of nuclear separation for LiH molecule obtained at different FCI, RHF and DFT levels (LDA, PBE, B3LYP)



## 2.2 Analysis of the numerical results

### 2.2.1 For each atom, give the def2-svp basis and say if it is larger than the STO-3G

Basis definitions of def2-svp for Li and H atoms were found to be:

Group 1 Type H : 4s1p contracted to 2s1p pattern

Group 2 Type Li : 7s3p contracted to 3s2p pattern

Basis definitions of STO-3G for Li and H atoms were found to be:

Group 1 Type H : 3s contracted to 1s pattern

Group 2 Type Li : 6s3p contracted to 2s1p pattern

The def2-svp basis are larger than STO-3G as they represent valence orbitals in multiple basis functions.

### 2.2.2 For each calculation give the equilibrium distance of LiH and the corresponding potential depth

Table 2.1

	FCI	RHF	LDA	PBE	B3LYP
$R_{eq}$ (Å)	1.6	1.6	1.6	1.6	1.6
$D_e$ cm <sup>-1</sup>	-17709.3	-43516.0	-27140.6	-26606.2	-30600.2

### 2.2.3 For each calculation specify the two fragments obtained when the molecule dissociates and analyze the shape and relative position of the curves and compare them to the FCI one. (distinguish the cases where R is lower / higher than the equilibrium distance).

When analyzing the dissociation of LiH, the predicted fragments depend on the computational method. FCI, the reference standard, indicates that LiH dissociates into ionic fragments, Li<sup>+</sup> and H<sup>-</sup>. B3LYP also supports ionic dissociation, closely matching FCI with minor differences in bond length and energy. PBE predicts slightly weaker interactions but still suggests ionic dissociation. LDA struggles to capture Coulombic interactions accurately and may favor neutral dissociation into Li and H atoms. RHF, due to its limitations in electron correlation, predicts neutral fragments (Li and H) instead of ionic ones.

## 2.3 Discussion

### 2.3.1 Why is the potential depth calculated at the RHF level always higher than the experimental value or/and other ab initio calculations?

RHF does not include the correlation energy so this missing contribution in the predicted value tends to converge it to a value higher than the experimental value and the predictions by other approaches. Furthermore, RHF includes exchange interactions exactly for electrons with the same spin leading to an overestimated energy.



**2.3.2 Is there a difference between the RHF and UHF potential depths? Develop your answer.**

RHF produces shallow potentials as it fills each calculated spatial orbital twice with opposite spins while UHF can produce deeper potential depths as it allows for spin-contamination especially for systems with unpaired electrons. UHF allows electrons with  $\alpha$ - and  $\beta$ - spins to occupy different spatial orbitals leading to broken spin-symmetry, a feature absent in RHF. This results in an overestimation of energy in RHF whereas the independent treatment of  $\alpha$ - and  $\beta$ - spins allows UHF to capture some effects of electron correlation producing a deeper potential.

**2.3.3 Among all the calculations RHF, DFT-LDA, DFT-PBE and DFT-B3LYP, which one is the most suitable for studying the bond breaking in LiH molecule? Develop your answer.**

For studying bond breaking in the LiH molecule, DFT with the B3LYP functional is the best choice among RHF, DFT-LDA, DFT-PBE, and DFT-B3LYP. B3LYP combines Hartree-Fock exchange effects with density functional methods through  $E_{xc}[\rho]$  functional, making it good at capturing both electron interactions and correlation. RHF is not suitable because it misses important correlation effects already mentioned above, and LDA shows a tendency to overestimate bonding. While PBE is better than LDA, it still struggles with describing bond dissociation accurately. B3LYP offers the best mix of accuracy and efficiency for this type of calculation.

## Chapter 3

# Conclusion

The dissociation of LiH was analyzed using RHF, LDA, PBE, B3LYP, and FCI. FCI predicts ionic dissociation into  $\text{Li}^+$  and  $\text{H}^-$ , with accurate bond distances and dissociation energy. B3LYP closely matches FCI, with a slightly shorter bond distance and deeper potential well, also predicting ionic dissociation. PBE aligns well with FCI but predicts a slightly longer bond distance, supporting ionic fragmentation. LDA overestimates the bond distance and dissociation energy, favoring neutral dissociation into Li and H. RHF shows the weakest interactions, predicting neutral dissociation due to its neglect of electron correlation. B3LYP and PBE improve over simpler methods by incorporating exchange-correlation functionals, while LDA and RHF are not so reliable due to overly simplified treatment of electron correlation and spin effects.

# References

Wills, J. M. (2010), *Full-Potential Electronic Structure Method*, Springer, Strasbourg.