# An Embedded Fragment Approach to Large Molecular Clusters in Strong Magnetic Fields

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## Introduction

- Recent advances have enabled fast and efficient electronic structure calculations on molecular systems within arbitrary magnetic fields[1].
- This introduces additional complexities however, further adding to the computational cost.
- One way to overcome this is to use an **Embedded Fragment Method** (EFM)[2][3].

## Theory

- We can divide a molecular cluster into individual fragments, then combine the energies of these fragments using the Many-Body Expansion,

$$E = \sum_i E_i + \sum_{j>i} E_{ij} - E_i - E_j \quad \ldots$$

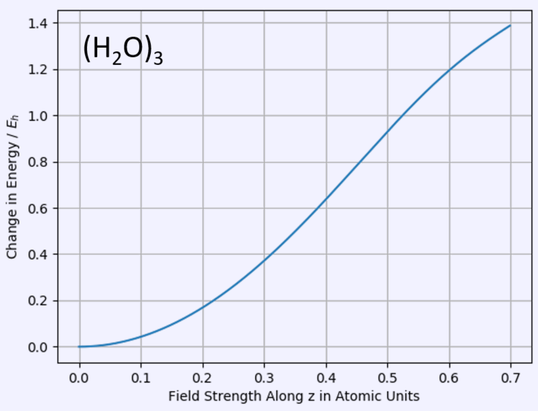
- The energies of the fragments are determined within an **embedded electrostatic field** defined by dipole-dipole interactions within the cluster,

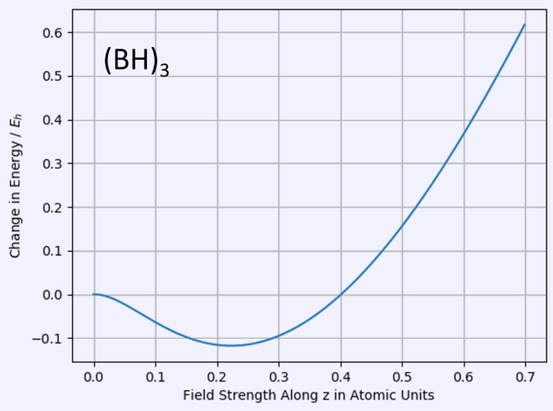
$$H'_i = H_i + \sum_n \sum_{j \neq i} V_j(\mathbf{r}_n) \qquad \text{and} \qquad H'_{ij} = H_{ij} + \sum_n \sum_{k \neq i,j} V_k(\mathbf{r}_n)$$

$$\text{where} \qquad V_j(\mathbf{r}_n) = \frac{e_j}{|\mathbf{r}_n - \mathbf{R}_j - \left(\frac{\mathbf{d}}{2}\right)|} - \frac{e_j}{|\mathbf{r}_n - \mathbf{R}_j + \left(\frac{\mathbf{d}}{2}\right)|}$$

## Introducing a Magnetic Field

- Using EFM coupled with the **London atomic orbital approach** , provides us with a tool to study large molecular clusters within arbitrary strength magnetic fields.
- It can successfully reproduce the expected diamagnetic and paramagnetic trends in water and BH molecular clusters respectively.



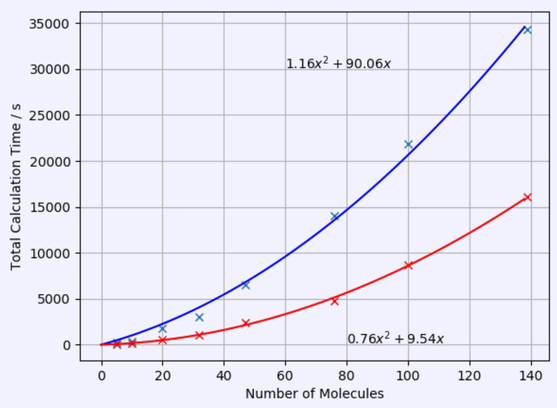

## Energies at Zero Field

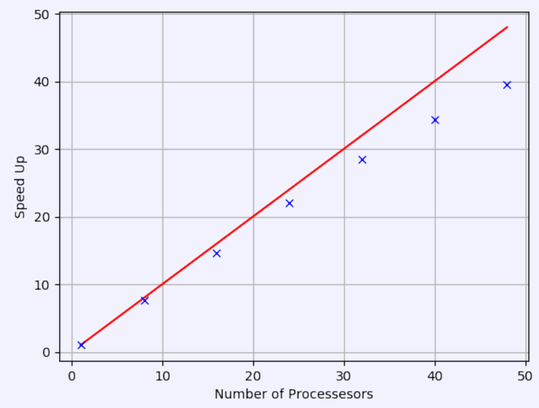
- This method has consistently proven to be accurate and reliable for **any level of theory** at 0 field.

| | Conventional / $E_h$ | EFM / $E_h$ | Error / $mE_h$ |
|---|---|---|---|
| HF | -228.14413 | -228.14435 | 0.22 |
| BLYP | -229.29501 | -229.29590 | 0.89 |
| PBE | -229.09795 | -229.09823 | 0.28 |
| MP2 | -228.81240 | -228.81299 | 0.59 |
| CCSD | -228.83423 | -228.83481 | 0.58 |
| CCSD(T) | -228.85071 | -228.85136 | 0.65 |

## Computational Cost Scaling

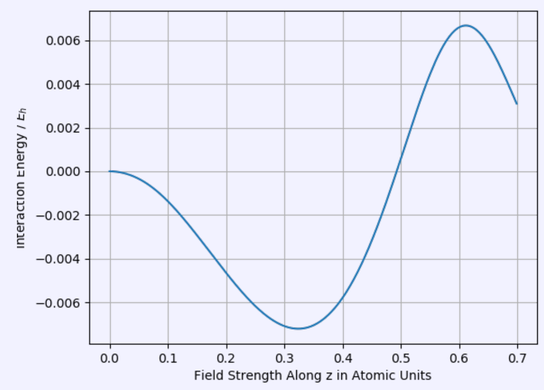
- Truncating the Many-Body expansion at the $2^{nd}$ term, *binary interaction approximation*, results in the **cost scaling as $N^2$** whilst retaining a high level of accuracy.
- The scaling pre-factor can be drastically reduced by introducing density fitting (RI) resulting in **calculations on large molecular clusters being highly accessible** .
- It can additionally be implemented in an **embarrassingly parallel** manner, taking advantage of modern day high performance computing facilities.

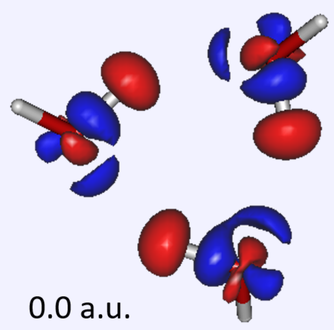


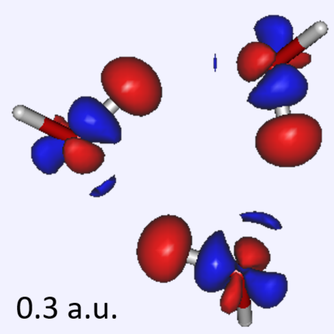




## Investigating The Effect of an External Field on Hydrogen Bonding

- This embedded fragment approach can be used to **study the weak intermolecular interactions** holding molecular clusters together, such as hydrogen bonding within water clusters.
- This can be demonstrated by plotting the **energy difference between the total cluster and its isolated constituents**. This is shown for a cyclic water trimer.
- The the **electron density difference** between the cluster and its isolated fragments at different field strengths reveals how the interactions change.
- We can **compare these experimental results**, which show that even relatively low magnetic fields can have a noticeable affect on properties such as melting points and surface tension of very large molecular systems[4][5].
- Using this comparison provides a method for determining the molecular origin of the effects we observe from experimental studies.




## References

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