Fit point-wise *ab initio* calculation potential energies to a multi-dimension Morse/Long-Range model

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Morse/Long-Range potential energy model

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The potential model is written as

$$V_{\mathrm{MLR}}(r) = \mathfrak{D}_{\mathrm{e}}\left\{1 - \frac{u_{\mathrm{LR}}(r)}{u_{\mathrm{LR}}(r_{\mathrm{e}})} e^{-\beta(r)\cdot y_p^{\mathrm{eq}}(r)}\right\}^2 + V_{\mathrm{min}} \tag{2}$$

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- Flexible: β's
- Everywhere differentiable to all orders
- Correct predicted long-range behaviour
- Physically meaningful parameters: $\mathfrak{D}_{\mathrm{e}}$, r_{e} and C_i

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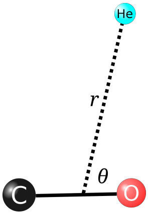
What about inter-“MOLECULAR” potential?

The simplest case

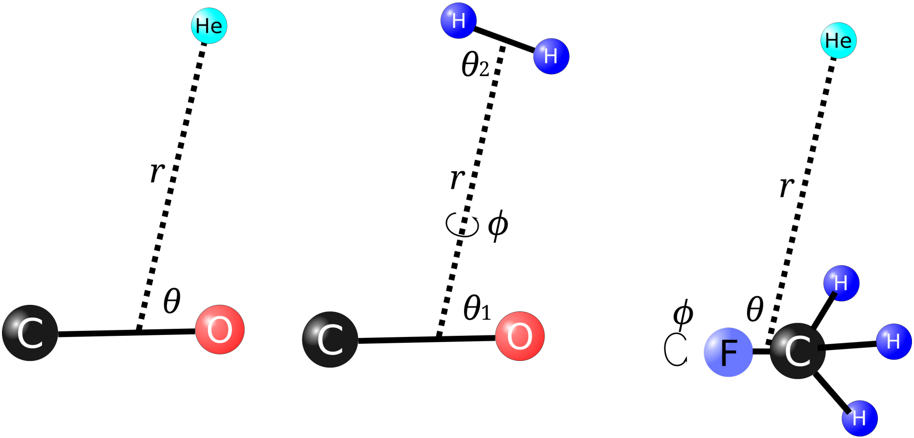


Treat all the parameters in MLR as function of θ!

- $\mathfrak{D}_\mathrm{e} \to \mathfrak{D}_\mathrm{e}(\theta)$
- $r_\mathrm{e} \to r_\mathrm{e}(\theta)$
- $C_i \to C_i(\theta)$
- $\beta_i \to \beta_i(\theta)$
- $\ldots$

What about inter-"MOLECULAR" potential?

Some more cases



- Must solve iteratively
- Initial guess is important

So how to fit the data?

Morse/Long-Range potential energy surface need accurate long-range coefficients as its parameter.

$$u_{\mathrm{LR}} = \sum_i \frac{C_i}{r^i} \tag{3}$$

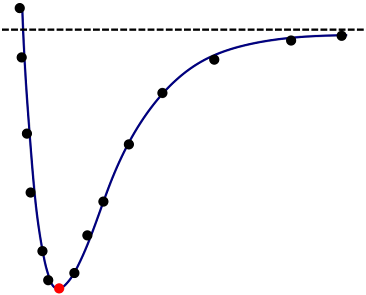
Long-range coefficients is fixed to theoretical/experimental in MLR.
We must find the very function to discribe the coefficients varying with the angles.
Using date in the long range (*e.g.*, $\geqslant 7$Å), fit them to the following formular.

$$u_{\mathrm{LR}} = \sum_i \frac{C_i(\boldsymbol{\theta})}{r^i} = \sum_i \frac{\sum_{l,m,l_j} C_i^{l,m,l_j} A_{l,m,l_j}}{r^i} \tag{4}$$

Apparently, it is a linear fitting.

How to fit the data?
Step 2. 1-D fitting

The 1-D fitting itself is a non-linear fitting.
Thanks to `betaFIT`[2], this procedure can be down easy.
To use `betaFIT`, one can fit point-wise data, just with initial guesses of $\mathfrak{D}_\mathrm{e}$, r_e and C_i.
It is not strange that you happened to miss the lowest point. Never mind, `betaFIT` will take care of it for you.



[2]http://scienide2.uwaterloo.ca/ rleroy/betaFIT/

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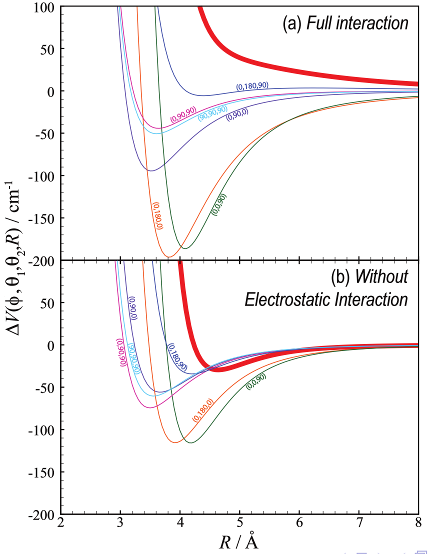

How to fit the data?

Step 3. Polynomial expensions of $\mathfrak{D}_\mathrm{e}$ and r_e

$$\mathfrak{D}_\mathrm{e}(\boldsymbol{\theta}) = \sum_{l,m,l_j} \mathfrak{D}_\mathrm{e}^{l,m,l_j} A_{l,m,l_j}(\boldsymbol{\theta}) \tag{5}$$

$$r_\mathrm{e}(\boldsymbol{\theta}) = \sum_{l,m,l_j} r_\mathrm{e}^{l,m,l_j} A_{l,m,l_j}(\boldsymbol{\theta}) \tag{6}$$

$$\beta_i(\boldsymbol{\theta}) = \sum_{l,m,l_j} \beta_i^{l,m,l_j} A_{l,m,l_j}(\boldsymbol{\theta}) \tag{7}$$

Again, it is a linear fitting.

How to fit the data?

Step 4. Global fitting

Now we have got all the reasonable initial guess of each parameter.

- Keep the long-range parameters fixed.
- Add more parameters to reduce the fitting Root Mean Square Difference (RMSD).
- Fix some lower-order parameters to zero to add higher-order parameters.

This time, it is a non-linear fitting and may cost a lot of time.

What about short range?

In old version of MLR, the long-range extrapolational behaviour is just perfect.

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Short range?
No, at very short distance,

$$V_{\mathrm{MLR}} \propto r^{-2m_{\mathrm{last}}}. \tag{8}$$

Starting from the 'damping' behaviour, by introducing 'MLR-flavoured damping function', the improvement of short-range for 1D MLR had been well discussed.[3]

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What about short range?

Here, we just use the same idea. Using MLR-flavoured Tang-Toennies type damping function,

$$D_m^{\mathrm{TT}(s)}(r) = 1 - \exp[-b^{\mathrm{tt}}(s)(\rho r)] \sum_{k=0}^{m-1+s} \frac{[b^{\mathrm{tt}}(s)(\rho r)]^k}{k!} \tag{9}$$

we have

$$u_{\mathrm{LR}}(r) = \sum_{i=1}^{\mathrm{last}} \frac{D_m(r) C_{m_i}}{r^{m_i}} \tag{10}$$

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- From definition

$$\rho_{AB} = \frac{2\rho_A\rho_B}{\rho_A + \rho_B} \tag{11}$$

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- Numerically, it is a correction to long-range coefficients and aims to reduce the number of β's.

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$$\mathrm{UNC} = \begin{cases} 0.1 + \frac{\varDelta V - V_{\text{switch}}}{C} & , \varDelta V \geqslant V_{\text{switch}}; \\ 0.1 & , \varDelta V < V_{\text{switch}}. \end{cases} \tag{13}$$

Acknowledgements

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The end.
Thank you for your attention.