An MLR potential energy function for polyatomic molecules

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We introduce an analytic potential energy function for polyatomic molecules which can be controlled to have the theoretically correct long-range and short-range behavior, and also has the favorable Morse-like properties near all local-minima.

The MLR (Morse/Long-range) function has been very successful for diatomic molecules (systems with one radial coordiate) [1–24]. Even for Van der Waals comlpexes, where the potential depends on one radial corrdinate and one or many anglular coordinates, it has been possible to build multi-dimensional MLR potential energy functions since for fixed values of all angular coordinates we can use the 1D-MLR to represent the energy dependence on the single radial coordinate [16, 25–29]. However the mathematics is much more complicated for systems with more than one radial coordinate and such systems are still commonly represented by splines (which are not analytic functons, do not extrapolate properly, and suffer from spurious oscillations between the points on which they are based). A very simple example of a system with two radial coordinates is CO_2. We will focus our discussion on building a potential for CO_2, and will generalize to systems with arbitrary numbers of radial and angular coordinates after.

One option we can take, is to just make every radially dependent variable in the 1D-MLR depend instead on two radial variables (r_1, r_2) (it is assumed that all C_m coefficients are DAMPED, because otherwise none of this would work):

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$$V\left(r_1,r_2\right)=\mathfrak{D}_e\left(1-\frac{u\left(r_1,r_2\right)}{u\left(r_{e,1},r_{e,2}\right)}e^{-\beta\left(r_1,r_2\right)y_p\left(r_1,r_2\right)}\right)^2 \tag{1}$$

$$\beta\left(r_1,r_2\right)=\beta_{1,\infty}y_{p,1}(r_1)+\left(1-y_{p,1}(r_1)\right)\sum_{i=0}^{N_{\beta,1}}\beta_i\left(y_{p,1}(r_1)\right)^i \tag{2}$$

$$+\beta_{2,\infty}y_{p,2}(r_2)+\left(1-y_{p,2}(r_2)\right)\sum_{i=0}^{N_{\beta,1}}\beta_i\left(y_{p,2}(r_2)\right)^i \tag{3}$$

$$\lim_{r_1\to\infty}\beta=\beta_{1,\infty}+\beta(r_2) \tag{4}$$

$$\lim_{r_2\to\infty}\beta=\beta_{2,\infty}+\beta(r_1) \tag{5}$$

$$\lim_{(r_1,r_2)\to\infty}\beta=\beta_{1,\infty}+\beta_{2,\infty} \tag{6}$$

$$=\beta_\infty \tag{7}$$

$$y_p=\frac{\left(y_{p,1+}y_{p,2}\right)}{N_{\text{radial coordinates}}} \tag{8}$$

$$\lim_{r_1\to\infty}y_p=\frac{1+y_{p,2}}{2} \tag{9}$$

$$\lim_{r_2\to\infty}y_p=\frac{1+y_{p,1}}{2} \tag{10}$$

$$\lim_{(r_1,r_2)\to\infty}y_p=1 \tag{11}$$

$$\lim_{(r_1,r_2)\to 0}y_p=-1 \tag{12}$$

$$\lim_{r_1\to\infty}\beta\left(r_1,r_2\right)y_p\left(r_1,r_2\right)=\beta_{1,\infty}(1+y_{p,2})/2+\beta\left(r_2\right)\left(1+y_{p,2}\right)/2 \tag{13}$$

$$\lim_{r_2\to\infty}\beta\left(r_1,r_2\right)y_p\left(r_1,r_2\right)=\beta_{2,\infty}(1+y_{p,1})/2+\beta\left(r_1\right)\left(1+y_{p,1}\right)/2 \tag{14}$$

$$\lim_{(r_1,r_2)\to\infty}\beta\left(r_1,r_2\right)y_p\left(r_1,r_2\right)=\beta_{1,\infty}+\beta_{2,\infty} \tag{15}$$

$$\lim_{r_1\to\infty}e^{-\beta(r_1,r_2)y_p(r_1,r_2)}=e^{-\beta_{1,\infty}(1+y_{p,2})/2}e^{-\beta(r_2)(1+y_{p,2})/2} \tag{16}$$

$$\lim_{r_2\to\infty}e^{-\beta(r_1,r_2)y_p(r_1,r_2)}=e^{-\beta_{2,\infty}(1+y_{p,1})/2}e^{-\beta(r_1)(1+y_{p,1})/2} \tag{17}$$

$$\lim_{(r_1,r_2)\to\infty}e^{-\beta(r_1,r_2)y_p(r_1,r_2)}=e^{-\beta_{1,\infty}}e^{-\beta_{2,\infty}} \tag{18}$$

$$\lim_{r_1\to\infty}V\left(r_1,r_2\right)=\mathfrak{D}_e\left(1-\frac{u\left(r_1,r_2\right)}{u\left(r_{e,1},r_{e,2}\right)}e^{-\beta_{1,\infty}(1+y_{p,2})/2}e^{-\beta(r_2)(1+y_{p,2})/2}\right)^2 \tag{19}$$

$$\beta_{1,\infty}=\frac{2\ln\left(\frac{\sqrt{2\mathfrak{D}_e}}{u(r_{e,1})}\right)}{1+y_{p,2}} \tag{20}$$

$$u\left(r_{e,1},r_{e,2}\right)=u\left(r_{e,1}\right)u\left(r_{e,2}\right)\ \text{[enforced]} \tag{21}$$

$$\lim_{r_1\to\infty}V\left(r_1,r_2\right)=\mathfrak{D}_e\left(1-\frac{u\left(r_1,r_2\right)}{u\left(r_{e,1}\right)u\left(r_{e,2}\right)}\frac{u\left(r_{e,1}\right)}{\sqrt{2\mathfrak{D}_e}}e^{-\beta(r_2)(1+y_{p,2})/2}\right)^2 \tag{22}$$

$$=\mathfrak{D}_e\left(1-\frac{u\left(r_1,r_2\right)}{\sqrt{2\mathfrak{D}_e}u\left(r_{e,2}\right)}e^{-\beta(r_2)(1+y_{p,2})/2}\right)^2 \tag{23}$$

$$=\mathfrak{D}_e\left(1-\frac{u\left(r_1,r_2\right)}{\sqrt{2\mathfrak{D}_e}}f\left(r_2\right)\right)^2 \tag{24}$$

$$=\mathfrak{D}_e\left(1-\frac{\sqrt{2}u\left(r_1,r_2\right)}{\sqrt{\mathfrak{D}_e}}f\left(r_2\right)+\frac{u^2\left(r_1,r_2\right)}{2\mathfrak{D}_e}f^2\left(r_2\right)\right) \tag{25}$$

$$=\mathfrak{D}_e-u\left(r_1,r_2\right)\sqrt{2\mathfrak{D}_e}f\left(r_2\right)+\frac{u^2\left(r_1,r_2\right)f^2\left(r_2\right)}{2} \tag{26}$$

$$=\mathfrak{D}_e-\frac{C_{6,1}\left(r_2\right)\frac{\sqrt{2\mathfrak{D}_e}e^{-\beta(r_2)(1+y_{p,2})/2}}{u(r_{e,2})}}{r_1^6}-\frac{C_{8,1}\left(r_2\right)\frac{\sqrt{2\mathfrak{D}_e}e^{-\beta(r_2)(1+y_{p,2})/2}}{u(r_{e,2})}}{r_1^8} \tag{27}$$

$$+\frac{C_{6,1}\left(r_2\right)^2\frac{e^{-2\beta(r_2)(1+y_{p,2})/2}}{2u^2(r_{e,2})}}{r_1^{12}}+\frac{C_{6,1}\left(r_2\right)C_{8,1}\left(r_2\right)\frac{e^{-2\beta(r_2)(1+y_{p,2})/2}}{2u^2(r_{e,2})}}{r_1^{14}}+\frac{C_{8,1}\left(r_2\right)^2\frac{e^{-2\beta(r_2)(1+y_{p,2})/2}}{2u^2(r_{e,2})}}{r_1^{16}}$$

$$\lim_{(r_1,r_2)\to\infty} V\left(r_1, r_2\right) = \mathfrak{D}_e \left(1 - \frac{u\left(r_1, r_2\right)}{u\left(r_{e,1}, r_{e,2}\right)} e^{-\beta_{1,\infty}} e^{-\beta_{2,\infty}}\right)^2 \tag{29}$$

$$= \mathfrak{D}_e \left(1 - \frac{u\left(r_1, r_2\right)}{u\left(r_{e,1}\right) u\left(r_{e,2}\right)} \frac{u\left(r_{e,1}\right)}{\sqrt{2\mathfrak{D}_e}} \frac{u\left(r_{e,2}\right)}{\sqrt{2\mathfrak{D}_e}}\right)^2 \tag{30}$$

$$= \mathfrak{D}_e \left(1 - \frac{u\left(r_1, r_2\right)}{2\mathfrak{D}_e}\right)^2 \tag{31}$$

$$= \mathfrak{D}_e \left(1 - \frac{u\left(r_1, r_2\right)}{\mathfrak{D}_e} + \frac{u^2\left(r_1, r_2\right)}{4\mathfrak{D}_e^2}\right) \tag{32}$$

$$= \mathfrak{D}_e - u\left(r_1, r_2\right) + \frac{u^2\left(r_1, r_2\right)}{4\mathfrak{D}_e^2} \tag{33}$$

Eq. 33 looks almost exactly the same as in the 1D MLR case, which is promising, but:

1. Eq. 27 might not have the desired form,

2. Eq. 21 means that $u(r_1, r_2)$ is enforced to be $u(r_1)u(r_2)$ when at the global equilibrium – it should be damped so much that this is numerically irrelevant at the global equilibrium, but it is sub-ideal that the units are energy squared.

LET'S TRY AN ALTERNATIVE FORMULATION:

$$V\left(r_1,r_2\right)=\mathfrak{D}_e\left(1-\frac{u\left(r_1\right)}{u\left(r_{e,1}\right)}e^{-\beta(r_1)y_p(r_1)}-\frac{u\left(r_2\right)}{u\left(r_{e,2}\right)}e^{-\beta(r_2)y_p(r_2)}\right)^2 \tag{34}$$

$$\lim_{r_1\to\infty}V\left(r_1,r_2\right)=\mathfrak{D}_e\left(1-\frac{u\left(r_1\right)}{2\mathfrak{D}_e}-f\left(r_2\right)\right)^2 \tag{35}$$

$$=\mathfrak{D}_e\left(1-\frac{u\left(r_1\right)+2\mathfrak{D}_ef\left(r_2\right)}{\mathfrak{D}_e}+\left(\frac{u\left(r_1\right)+2\mathfrak{D}_ef\left(r_2\right)}{2\mathfrak{D}_e}\right)^2\right) \tag{36}$$

$$=\mathfrak{D}_e-u\left(r_1\right)+2\mathfrak{D}_ef\left(r_2\right)+\frac{u^2\left(r_1\right)+2\mathfrak{D}_eu\left(r_1\right)f\left(r_2\right)+4\mathfrak{D}_e^2f^2\left(r_2\right)}{4\mathfrak{D}_e} \tag{37}$$

$$=\mathfrak{D}_e-u\left(r_1\right)+2\mathfrak{D}_e\frac{u\left(r_2\right)}{u\left(r_{e,2}\right)}e^{-\beta(r_2)y_p(r_2)} \tag{38}$$

$$+\frac{u^2\left(r_1\right)+2\mathfrak{D}_eu\left(r_1\right)\frac{u(r_2)}{u(r_{e,2})}e^{-\beta(r_2)y_p(r_2)}+4\mathfrak{D}_e^2\frac{u^2(r_2)}{u^2(r_{e,2})}e^{-2\beta(r_2)y_p(r_2)}}{4\mathfrak{D}_e} \tag{39}$$

$$=\mathfrak{D}_e-\frac{C_{6,1}\left(r_2\right)}{r_1^6}-\frac{C_{8,1}\left(r_2\right)}{r_1^8}+2\mathfrak{D}_e\frac{u\left(r_2\right)}{u\left(r_{e,2}\right)}e^{-\beta(r_2)y_p(r_2)} \tag{40}$$

$$+\frac{C_{6,1}\left(r_2\right)^2/4\mathfrak{D}_e}{r_1^{12}}+\frac{C_{6,1}\left(r_2\right)C_{8,1}\left(r_2\right)/4\mathfrak{D}_e}{r_1^{14}}+\frac{C_{8,1}\left(r_2\right)^2/4\mathfrak{D}_e}{r_1^{16}} \tag{41}$$

$$+\frac{C_{6,1}\left(r_2\right)\frac{u(r_2)}{u(r_{e,2})}e^{-\beta(r_2)y_p(r_2)}}{2r_1^6}+\frac{C_{8,1}\left(r_2\right)\frac{u(r_2)}{u(r_{e,2})}e^{-\beta(r_2)y_p(r_2)}}{2r_1^8}+\mathfrak{D}_e\frac{u^2\left(r_2\right)}{u^2\left(r_{e,2}\right)}e^{-2\beta(r_2)y_p(r_2)} \tag{42}$$

$$\lim_{(r_1,r_2)\to\infty}V\left(r_1,r_2\right)=\mathfrak{D}_e\left(1-\frac{u\left(r_1\right)}{2\mathfrak{D}_e}-\frac{u\left(r_2\right)}{2\mathfrak{D}_e}\right)^2 \tag{43}$$

$$=\mathfrak{D}_e\left(1-\frac{u\left(r_1\right)+u\left(r_2\right)}{\mathfrak{D}_e}+\left(\frac{u\left(r_1\right)+u\left(r_2\right)}{2\mathfrak{D}_e}\right)^2\right) \tag{44}$$

$$=\mathfrak{D}_e-u\left(r_1\right)-u\left(r_2\right)+\frac{u^2\left(r_1\right)+2u\left(r_1\right)u\left(r_2\right)+u^2\left(r_2\right)}{4\mathfrak{D}_e} \tag{45}$$

$$=\mathfrak{D}_e-\frac{C_{6,1}\left(r_2\right)}{r_1^6}-\frac{C_{8,1}\left(r_2\right)}{r_1^8}-\frac{C_{6,2}\left(r_1\right)}{r_2^6}-\frac{C_{8,2}\left(r_1\right)}{r_2^8} \tag{46}$$

$$+\frac{C_{6,1}\left(r_2\right)^2/4\mathfrak{D}_e}{r_1^{12}}+\frac{C_{6,1}\left(r_2\right)C_{8,1}\left(r_2\right)/2\mathfrak{D}_e}{r_1^{14}}+\frac{C_{8,1}\left(r_2\right)^2/4\mathfrak{D}_e}{r_1^{16}} \tag{47}$$

$$+\frac{C_{6,2}\left(r_1\right)^2/4\mathfrak{D}_e}{r_2^{12}}+\frac{C_{6,2}\left(r_1\right)C_{8,2}\left(r_1\right)/2\mathfrak{D}_e}{r_2^{14}}+\frac{C_{8,2}\left(r_1\right)^2/4\mathfrak{D}_e}{r_2^{16}} \tag{48}$$

$$+\frac{C_{6,1}\left(r_2\right)C_{6,2}\left(r_1\right)/2\mathfrak{D}_e}{r_1^6r_2^6}+\frac{C_{6,1}\left(r_2\right)C_{8,2}\left(r_1\right)/2\mathfrak{D}_e}{r_1^6r_2^8}+\frac{C_{8,1}\left(r_2\right)C_{6,2}\left(r_1\right)/2\mathfrak{D}_e}{r_1^8r_2^6}+\frac{C_{8,1}\left(r_2\right)C_{8,2}\left(r_1\right)/2\mathfrak{D}_e}{r_1^8r_2^8} \tag{49}$$

A potential issue with the second formulation is that for large r, there are a lot more r^6 terms that need to be cancelled out, but this should be possible to do, similar to the way we did it for C_6^{adj}, but now C_6^{adj} is a function of r_2 or r_1:

$$C_{6,1}(r_2)\to C_{6,1}(r_2)-\frac{C_{6,1}\left(r_2\right)C_{6,2}\left(r_1\right)}{4\mathfrak{D}_er_2^6} \tag{50}$$

$$C_{6,1}^{\mathrm{adj}}(r_2)=C_{6,1}(r_2)\left(1-\frac{C_{6,2}\left(r_1\right)}{4\mathfrak{D}_er_2^6}\right). \tag{51}$$

Unfortunately this appears to be much harder than for the case of C_6^{adj} coming from C_3. Here is it is coming from C_6 itself, and not arising from a $u(r)^2$ term, but a term linear in $u(r)$. Essentially we have:

$$-u\left(r_1\right)-u\left(r_2\right)+u\left(r_1\right)^2+u\left(r_1\right)u\left(r_2\right)+u\left(r_2\right)^2, \tag{52}$$

and while the squared terms are usually much smaller than the first two terms, the $u(r_1)u(r_2)$ term NEEDS to be removed some how because we have:

$$\frac{C_{6,1}\left(r_2\right)}{r_1^6}+\frac{C_{6,1}\left(r_2\right)C_{6,2}\left(r_1\right)}{r_1^6 r_2^6} \tag{53}$$

and no matter what we subtract from $C_{6,1}\left(r_2\right)$ in $u(r)$ will show up again in the $u(r_1)u(r_2)$ term.

WE THEREFORE TURN TO A POTENTIAL WHICH DOESN'T HAVE A QUADRATIC LONG-RANGE TERM (THE DELR)

We first try the second way (using a summation) because that turned out to be a lot easier to think about:

$$V\left(r_1,r_2\right)=\left(A_1e^{-2\beta_1(r_1)(r_1-r_{1,e})}-B_1e^{-\beta_1(r_1)(r_1-r_{1,e})}+A_2e^{-2\beta_2(r_2)(r_2-r_{2,e})}-B_2e^{-\beta_2(r_2)(r_2-r_{2,e})}+\mathfrak{D}_e\right)-u\left(r_1,r_2\right) \tag{54}$$

$$A_i=\mathfrak{D}_{e,i}-u\left(r_{i,e}\right)-\left(\frac{\partial u\left(r_{e,1},r_{e,2}\right)}{\partial r_{e,i}}\right)/\beta_{i,0} \tag{55}$$

$$B_i=2\mathfrak{D}_{e,i}-2u\left(r_{i,e}\right)-\left(\frac{\partial u\left(r_{e,1},r_{e,2}\right)}{\partial r_{e,i}}\right)/\beta_{i,0} \tag{56}$$

$$V\left(r_1,r_2\right)\big|_{u(r_1,r_2)=0}=\left(\mathfrak{D}_{e,1}e^{-2\beta_1(r_1)(r_1-r_{1,e})}-2\mathfrak{D}_{e,1}e^{-\beta_1(r_1)(r_1-r_{1,e})}+\mathfrak{D}_{e,2}e^{-2\beta_2(r_2)(r_2-r_{2,e})}-2\mathfrak{D}_{e,2}e^{-\beta_2(r_2)(r_2-r_{2,e})}\right) \tag{57}$$

$$=\mathfrak{D}_{e,1}\left(1-e^{-\beta_1(r_1)(r_1-r_{1,e})}\right)^2+\mathfrak{D}_{e,2}\left(1-e^{-\beta_2(r_2)(r_2-r_{2,e})}\right)^2, \tag{58}$$

where $\mathfrak{D}_{e,i}$ is the $\mathfrak{D}_e$ for the 1D potential along the $\left\{r_j=r_{j,e}\right\}_{j\neq i}$ slice. An immediate problem is that for a symmetric potetial, $\mathfrak{D}_e$ should be $\mathfrak{D}_e=\mathfrak{D}_{e,1}=\mathfrak{D}_{e,2}$ but instead we have $\mathfrak{D}_e=\mathfrak{D}_{e,1}+\mathfrak{D}_{e,2}$.

We can therefore try the first way (making each function of r a function of two r's):

$$V\left(r_1,r_2\right)=\left(Ae^{-2\beta(r_1,r_2)((r_1-r_{1,e})+(r_2-r_{2,e}))}-Be^{-\beta(r_1,r_2)((r_1-r_{1,e})+(r_2-r_{2,e}))}\right)-u\left(r_1,r_2\right) \tag{59}$$

$$A=\mathfrak{D}_e-u\left(r_{e,1},r_{e,2}\right)-\left(\frac{\partial u\left(r_{e,1},r_{e,2}\right)}{\partial r_{e,1}}+\frac{\partial u\left(r_{e,1},r_{e,2}\right)}{\partial r_{e,2}}\right)/\beta_0 \tag{60}$$

$$B=2\mathfrak{D}_e-2u\left(r_{e,1},r_{e,2}\right)-\left(\frac{\partial u\left(r_{e,1},r_{e,2}\right)}{\partial r_{e,1}}+\frac{\partial u\left(r_{e,1},r_{e,2}\right)}{\partial r_{e,2}}\right)/\beta_0 \tag{61}$$

$$V\left(r_1,r_2\right)\big|_{u(r_1,r_2)=0}=\left(\mathfrak{D}_ee^{-2\beta(r_1,r_2)((r_1-r_{1,e})+(r_2-r_{2,e}))}-2\mathfrak{D}_ee^{-\beta(r_1,r_2)((r_1-r_{1,e})+(r_2-r_{2,e}))}\right) \tag{62}$$

$$=\mathfrak{D}_e\left(1-e^{-\beta(r_1,r_2)((r_1-r_{1,e})+(r_2-r_{2,e}))}\right)^2. \tag{63}$$

A better way might be the following:

$$V\left(r_1,r_2\right) = \left(Ae^{-2\beta_1(r_1)(r_1-r_{1,e})-2\beta_2(r_2)(r_2-r_{2,e})} - Be^{-\beta_1(r_1)(r_1-r_{1,e})-\beta_2(r_2)(r_2-r_{2,e})}\right) - u\left(r_1,r_2\right) \tag{64}$$

$$= \left(Ae^{-2\beta_1(r_1)(r_1-r_{1,e})}e^{-2\beta_2(r_2)(r_2-r_{2,e})} - Be^{-\beta_1(r_1)(r_1-r_{1,e})}e^{-\beta_2(r_2)(r_2-r_{2,e})}\right) - u\left(r_1,r_2\right) \tag{65}$$

$$A = \mathfrak{D}_e - u\left(r_{e,1},r_{e,2}\right) - \frac{\partial u\left(r_{e,1},r_{e,2}\right)}{\partial r_{e,1}}/\beta_{1,0} - \frac{\partial u\left(r_{e,1},r_{e,2}\right)}{\partial r_{e,2}}/\beta_{2,0} \tag{66}$$

$$B = 2\mathfrak{D}_e - 2u\left(r_{e,1},r_{e,2}\right) - \frac{\partial u\left(r_{e,1},r_{e,2}\right)}{\partial r_{e,1}}/\beta_{1,0} - \frac{\partial u\left(r_{e,1},r_{e,2}\right)}{\partial r_{e,2}}/\beta_{2,0} \tag{67}$$

$$V\left(r_1,r_2\right)\big|_{u(r_1,r_2)=0} = \left(\mathfrak{D}_e e^{-2\beta_1(r_1)(r_1-r_{1,e})}e^{-2\beta_2(r_2)(r_2-r_{2,e})} - 2\mathfrak{D}_e e^{-\beta_1(r_1)(r_1-r_{1,e})}e^{-\beta_2(r_2)(r_2-r_{2,e})}\right) \tag{68}$$

$$= \mathfrak{D}_e\left(1 - e^{-\beta_1(r_1)(r_1-r_{1,e})}e^{-\beta_2(r_2)(r_2-r_{2,e})}\right)^2 \tag{69}$$

Of all candidates, Eq. 69 seems to be the best choice.

2D MORSE POTENTIAL

$$V\left(r_1,r_2\right) = \mathfrak{D}_e\left(1 - e^{-\beta_1(r_1-r_{1,e})}\right)^2\left(1 - e^{-\beta_2(r_2-r_{2,e})}\right)^2 \tag{70}$$

$$V\left(r_1,r_2\right) = \mathfrak{D}_e\left(1 - e^{-\beta_1(r_1-r_{1,e})}e^{-\beta_2(r_2-r_{2,e})}\right)^2 \tag{71}$$

The first one only becomes a Morse potential for r_2 when $r_1 \to \infty$, so the second one is better.

2D HARMONIC OSCILLATOR

$$V\left(r_1,r_2\right) = \frac{1}{2}\left(k_1\left(r_1 - r_{1,e}\right)^2 + k_2\left(r_2 - r_{2,e}\right)^2\right) \tag{72}$$

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