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) [?]. 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 multidimensional 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 [? ? ? ? ? ?]. 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):

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

$$\beta(r_1,r_2) = \beta_{1,\infty}y_{p,1}(r_1) + (1-y_{p,1}(r_1))\sum_{i=} \tag{2}$$

$$+\beta_{2,\infty}y_{p,2}(r_2) + (1-y_{p,2}(r_2))\sum_{i=} \tag{3}$$

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

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

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

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

$$y_p = y_{p,1}y_{p,2} \tag{8}$$

$$= \left(\frac{r_1^p - r_{e,1}^p}{r_1^p + r_{e,1}^p}\right)\left(\frac{r_2^p - r_{e,2}^p}{r_2^p + r_{e,2}^p}\right) \tag{9}$$

$$\lim_{r_1\to\infty} y_p = y_{p,2} \tag{10}$$

$$\lim_{r_2\to\infty} y_p = y_{p,1} \tag{11}$$

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

$$\lim_{(r_1,r_2)\to 0} y_p = 1 \text{ [Problem \#1] !} \tag{13}$$

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

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

$$\lim_{(r_1,r_2)\to\infty}\beta(r_1,r_2)\,y_p(r_1,r_2) = \beta_{1,\infty} + \beta_{2,\infty} \tag{16}$$

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

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

$$\lim_{(r_1,r_2)\to\infty} e^{-\beta(r_1,r_2)y_p(r_1,r_2)} = e^{-\beta_{1,\infty}}e^{-\beta_{2,\infty}} \tag{19}$$

$$\lim_{r_1\to\infty} V(r_1,r_2) = \mathfrak{D}_e\left(1 - \frac{u(r_1,r_2)}{u(r_{e,1},r_{e,2})}e^{-\beta_{1,\infty}y_{p,2}}e^{-} \right. \tag{20}$$

$$\beta_{1,\infty} = \frac{\ln\left(\frac{\sqrt{2\mathfrak{D}_e}}{u(r_{e,1})}\right)}{y_{p,2}} \tag{21}$$

$$u(r_{e,1},r_{e,2}) = u(r_{e,1})\,u(r_{e,2}) \text{ [enforced]} \tag{22}$$

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The only issues with this formulation are the limit in Eq. 13 and potentially the fact that $u(r_1, r_2)$ has to be a product (Eq. 22), but maybe that's how the long range is supposed to look anyway.

Let's try an alternative formulation:

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

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

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

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

$$= \mathfrak{D}_e - u(r_1) + 2\mathfrak{D}_e \frac{u(r_2)}{u(r_{e,2})} e^{-\beta(r_2) y_p(r_2)} + \frac{u^2(r_1) + 2\mathfrak{D}_e u(r_1) \frac{u(r_2)}{u(r_{e,2})} e^{-\beta(r_2) y_p(r_2)} + 4\mathfrak{D}_e^2 \frac{u^2(r_2)}{u^2(r_{e,2})} e^{-2\beta(r_2) y_p(r_2)}}{4\mathfrak{D}_e} \tag{38}$$

$$= \mathfrak{D}_e - \frac{C_{6,1}(r_2)}{r_1^6} - \frac{C_{8,1}(r_2)}{r_1^8} + 2\mathfrak{D}_e \frac{u(r_2)}{u(r_{e,2})} e^{-\beta(r_2) y_p(r_2)} + \frac{C_{6,1}(r_2)^2 / 4\mathfrak{D}_e}{r_1^{12}} + \frac{C_{6,1}(r_2) C_{8,1}(r_2) / 4\mathfrak{D}_e}{r_1^{14}} + C_{8,} \tag{39}$$

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

$$\lim_{(r_1, r_2) \to \infty} V(r_1, r_2) = \mathfrak{D}_e \left(1 - \frac{u(r_1)}{2\mathfrak{D}_e} - \frac{u(r_2)}{2\mathfrak{D}_e}\right)^2 \tag{41}$$

$$= \mathfrak{D}_e \left(1 - \frac{u(r_1) + u(r_2)}{\mathfrak{D}_e} + \left(\frac{u(r_1) + u(r_2)}{2\mathfrak{D}_e}\right)^2\right) \tag{42}$$

$$= \mathfrak{D}_e - u(r_1) + u(r_2) + \frac{u^2(r_1) + u(r_1) u(r_2) + u^2(r_2)}{4\mathfrak{D}_e} \tag{43}$$

$$= \mathfrak{D}_e - \frac{C_{6,1}(r_2)}{r_1^6} - \frac{C_{8,1}(r_2)}{r_1^8} - \frac{C_{6,2}(r_1)}{r_2^6} - \frac{C_{8,2}(r_1)}{r_2^8} \tag{44}$$

$$+ \frac{C_{6,1}(r_2)^2 / 4\mathfrak{D}_e}{r_1^{12}} + \frac{C_{6,1}(r_2) C_{8,1}(r_2) / 4\mathfrak{D}_e}{r_1^{14}} + \frac{C_{8,1}(r_2)^2 / 4\mathfrak{D}_e}{r_1^{16}} \tag{45}$$

$$+ \frac{C_{6,2}(r_1)^2 / 4\mathfrak{D}_e}{r_2^{12}} + \frac{C_{6,2}(r_1) C_{8,2}(r_1) / 4\mathfrak{D}_e}{r_2^{14}} + \frac{C_{8,2}(r_1)^2 / 4\mathfrak{D}_e}{r_2^{16}} \tag{46}$$

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

A potential issue with the secnod 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.