

**Accurate New Potential Energy Function(s)  
From Spectroscopic and Virial Coefficient Data  
for the Ten Rare Gas Pairs formed  
from Ne, Ar, Kr and Xe**

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# Intermolecular Potentials for Rare-Gas Pairs

- Under serious study for  $\sim 50$  years
  - Early work used scattering cross-sections or bulk property data (virial, viscosity, diffusion & thermal diffusion coefficients). However:
    - resulting estimates of well depths and equilibrium distances depended on what property was being fitted and were heavily model-dependent.
- Also:  $\mathfrak{D}_e$  and  $r_e$  values obtained sensitive to form of model potential.*
- used model analytic potential functions which failed to incorporate theoretically known inverse-power long-range behaviour

$$V_{\text{LR}} \simeq \mathfrak{D} - \frac{C_6}{r^6} - \frac{C_8}{r^8} - \frac{C_{10}}{r^{10}} - \dots$$

- High resolution spectroscopic data not available until relatively recently
- Later semi-empirical work (most notably by Ronald A. Aziz and co-workers)
  - potential functions did incorporate appropriate long-range behaviour
  - simultaneously considered a range of bulk properties

*However :*

..... *however*:

- Those analyses were based on manual trial-and-error ‘fits’!
- The ‘HFD-B’ potential function used has significant shortcomings:

$$V_{\text{HFD}}(r) = A e^{-\alpha r - \beta r^2} - F(r) \left\{ \frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} \right\}$$

$$F(r) = \begin{cases} e^{-[d(r_e/r)-1]^2} & r/r_e < d \\ 1 & r/r_e \geq d \end{cases}$$

- \* second and higher derivatives of  $F(r)$  (and hence of the potential!) are discontinuous at  $r/r_e = d$

[  $F(r)$  was introduced to prevent  $1/r^n$  singularities as  $r \rightarrow 0$  from causing short-range potential function turnover.]

- \* parameters  $A$ ,  $\alpha$  and  $\beta$  allow limited degree of flexibility
- \* key physical properties  $\mathfrak{D}_e$  and  $r_e$  not defining parameters
- \* Gives poor agreement with modern MW and high-resolution UV data!

## Objective:

*Determine a new set of empirical analytic potentials for the rare-gas pairs:*

- using an objective, quantitative ‘direct-potential-fit’ procedure that fully exploits all available spectroscopic data
- based on an improved potential function form which takes account of ‘damping function’ behaviour and whose derivatives are smooth everywhere

$$V_{\text{MLR}}(r) = \mathfrak{D}_e \left\{ 1 - \frac{u_{\text{LR}}(r)}{u_{\text{LR}}(r_e)} e^{-\beta(r) \cdot y_p(r)} \right\}^2$$
$$\xrightarrow{r \gg r_e} \mathfrak{D}_e - \left( \frac{2\mathfrak{D}_e e^{-\beta_\infty}}{u_{\text{LR}}(r_e)} \right) u_{\text{LR}}(r) \simeq \mathfrak{D}_e - u_{\text{LR}}(r)$$

in which 
$$u_{\text{LR}}(r) = \sum_m D_m(r) \frac{C_m}{r^m} = D_6(r) \frac{C_6}{r^6} + D_8(r) \frac{C_8}{r^8} + D_{10}(r) \frac{C_{10}}{r^{10}}$$

*{incorporates both theoretically known  $C_m$ ’s and damping functions  $D_m(r)$ }*

where 
$$\beta(r) = \beta_{\text{MLR}}(r) = \beta_\infty y_p(r) + [1 - y_p(r)] \sum_{i=0}^N \beta_i y_p(r)^i$$

with 
$$\beta_\infty \equiv \beta(r=\infty) = \ln\{2\mathfrak{D}_e/u_{\text{LR}}(r_e)\} \quad \text{and} \quad y_p(r) = \frac{r^p - r_e^p}{r^p + r_e^p}$$

## *‘Direct Potential Fits’*

*{For 3-D Van der Waals molecules since 1974, and for diatomics since  $\sim 1990$ }*

- ***For spectroscopy:*** simulate level energies as eigenvalues of some parametrized analytic potential energy function  $V(r; \{p_j\})$

$$\nu_{\text{obs}}(v', J'; v'', J'') = E(v' J') - E(v'', J'')$$

Partial derivatives of observables w.r.t. parameters  $p_j$  that are required for fitting are generated readily using the Hellmann-Feynman theorem:

$$\frac{\partial E(v, J)}{\partial p_j} = \left\langle \psi_{v,J} \left| \frac{\partial V(r; \{p_j\})}{\partial p_j} \right| \psi_{v,J} \right\rangle$$

Compare predicted transition energies with experiment, and optimize potential parameters via an iterative least-squares fit.

### *Features*

- final result is a global analytic potential energy function
- such a ‘global’ potential allows realistic predictions in ‘extrapolation’ region outside the data range, and of non-spectroscopic properties
- yields full quantum mechanical accuracy

- *For virial coefficients:*  $\frac{PV}{nRT} = 1 + B(T) \left(\frac{n}{V}\right) + \dots$

$$B(T) = B_{\text{cl}}(T) + \left(\frac{\hbar^2}{2m k_{\text{B}}T}\right) B_{\text{qm},1}(T) + \left(\frac{\hbar^2}{2m k_{\text{B}}T}\right)^2 B_{\text{qm},2}(T) + \dots$$

where

$$B_{\text{cl}}(T) = -2\pi \tilde{N}_A \int_0^\infty \left[ e^{-V(r)/k_{\text{B}}T} - 1 \right] r^2 dr$$

$$B_{\text{qm},1}(T) = 2\pi \tilde{N}_A \int_0^\infty [V'(r)/k_{\text{B}}T]^2 e^{-V(r)/k_{\text{B}}T} r^2 dr$$

$$B_{\text{qm},2}(T) = \dots\dots$$

Partial derivatives of  $B(T)$  w.r.t. parameters  $p_j$  required for fitting are generated readily by differentiating the above expressions:

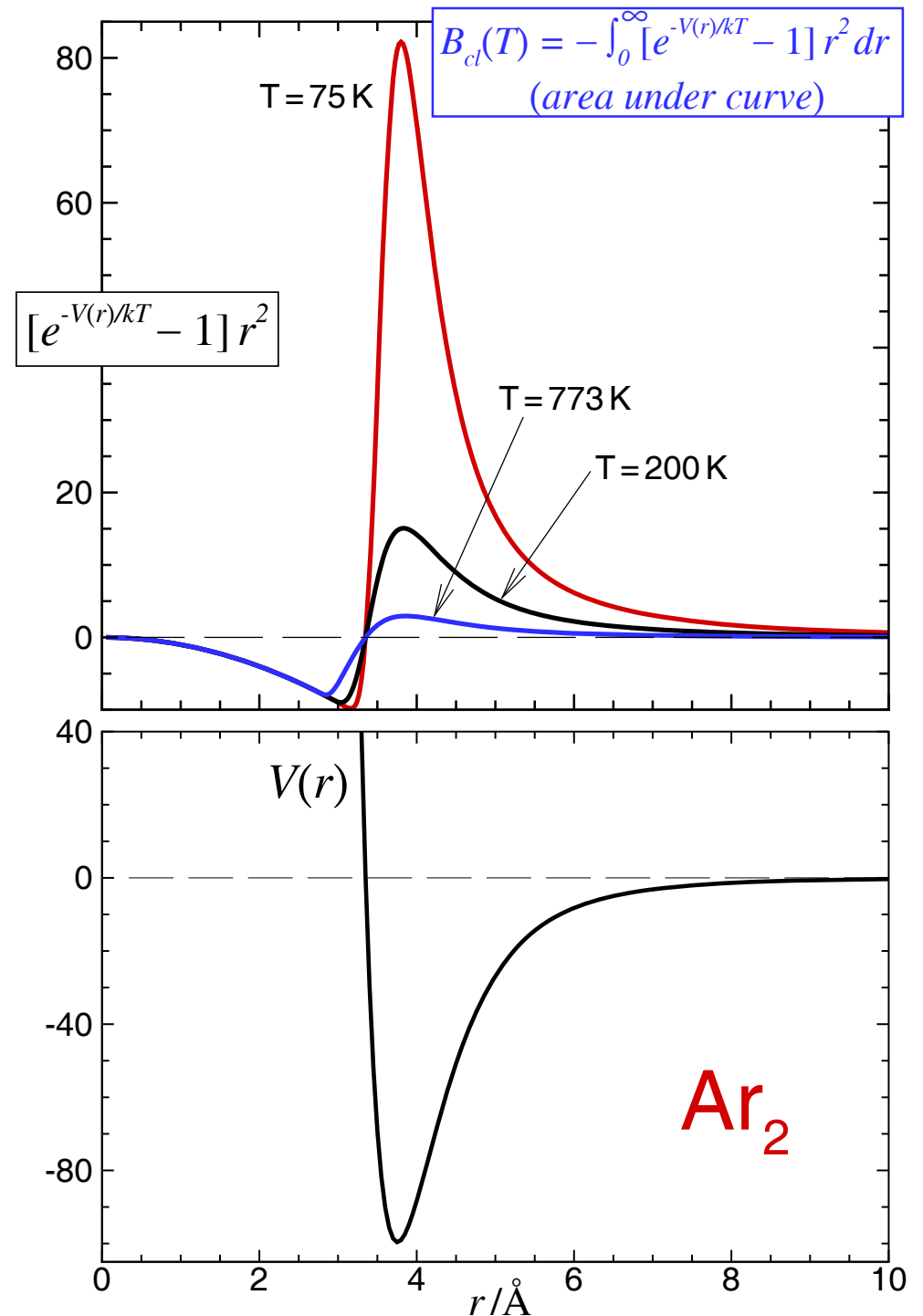
$$\frac{\partial B(T)}{\partial p_j} = \frac{\partial B_{\text{cl}}(T)}{\partial p_j} + \left(\frac{\hbar^2}{2m k_{\text{B}}T}\right) \frac{\partial B_{\text{qm},1}(T)}{\partial p_j} + \dots\dots$$

where  $\frac{\partial B_{\text{cl}}(T)}{\partial p_j} = \frac{2\pi \tilde{N}_A}{k_{\text{B}}T} \int_0^\infty \frac{\partial V(r)}{\partial p_j} e^{-V(r)/k_{\text{B}}T} r^2 dr$  , ... etc.

Virial coefficients depend on an average of a function of the potential.

At *low temperatures* their values are dominated by the attractive potential well, and at *high temperatures* by the repulsive potential wall.

Their ‘non-local’ dependence on the potential function means that unless one has accurate  $B(T)$  values extending over a very wide temperature range, their values will not be very sensitive to the shape of the potential.



# How do we simultaneously fit to data of different types ?

## Types of data considered in these analyses

type	magnitude	uncertainty
microwave	0.2 to 0.6 cm <sup>-1</sup>	10 <sup>-8</sup> to 3 × 10 <sup>-7</sup> cm <sup>-1</sup>
high-resolution UV	~ 77 000 cm <sup>-1</sup>	0.001 to 0.005 cm <sup>-1</sup>
medium-resolution UV (rotat. resolved)	~ 100 000 cm <sup>-1</sup>	0.02 to 0.2 cm <sup>-1</sup>
low-resolution UV (band heads)	~ 80000 cm <sup>-1</sup>	0.2 to 0.3 cm <sup>-1</sup>
virial coefficients	-400 to +17 $\left[\frac{\text{cm}^3}{\text{mol}}\right]$	0.1 to 6 $\left[\frac{\text{cm}^3}{\text{mol}}\right]$

## Answer:

Fit minimizes the overall “*dimensionless root-mean-square residual*”

$$\text{DRMSD} \equiv \overline{dd} = \sqrt{\frac{1}{N_{\text{dat}}} \sum_{i=1}^{N_{\text{dat}}} \left( \frac{y_{\text{calc}}(i) - y_{\text{obs}}(i)}{u_i} \right)^2}$$

*Note:* we can also characterize the quality of agreement with subsets of data by generating values of  $\overline{dd}(\text{MW})$  or  $\overline{dd}(\text{virials})$  or ...

# Data for rare gas pairs considered to date.

	Ne	Ar	Kr	Xe
Ne	virial coefft. high-res UV ( $v = 0 - 1$ )	virial coefft. MW: $v = 0$	virial coefft. MW: $v = 0$	virial coefft. MW: $v = 0$
Ar	—	virial coefft. med-res UV ( $v = 0 - 5$ )	virial coefft. MW: $v = 0$	virial coefft. high-res UV ( $v = 0 - 1$ ) MW: $v = 0$
Kr	—	—	virial coefft. med-res UV ( $v = 0 - 2$ ) low-res UV ( $v = 0 - 9$ )	virial coefft. MW: $v = 0$
Xe	—	—	—	virial coefft. high-res UV ( $v = 0 - 1$ ) low-res UV ( $v = 0 - 9$ )

**Results for Ne-Kr:** fitting parameters are  $\mathfrak{D}_e$ ,  $r_e$  and exponent coefficients  $\beta_i$

# expon. param.	# data	$\overline{dd}$ (MW)	$\overline{dd}$ (virials)	$\overline{dd}$ (total)	$\mathfrak{D}_e/\text{cm}^{-1}$	$r_e / \text{\AA}$
<b>All data – MW and virials</b>						
1	48	0.423	3.312	2.110	49.84(3)	3.65046(6)
2	48	0.553	1.511	1.043	47.74(34)	3.65202(23)
3	48	0.442	1.525	1.019	<b>47.96(35)</b>	<b>3.65209(29)</b>
4	48	0.403	1.493	0.990	48.27(48)	3.6492(15)
<b>MW data alone</b>						
1	29	0.418	—	0.418	49.84(1)	3.65046(1)
2	29	0.412	—	0.412	49.48(84)	3.65074(59)
<b>Virial data alone</b>						
1	19	—	1.493	1.493	22.(58)	5.2(48)
<b>Aziz's HFD-B potential</b>						
	29	<b>15776.</b>	$\sim 1.5$	—	49.82	3.6196

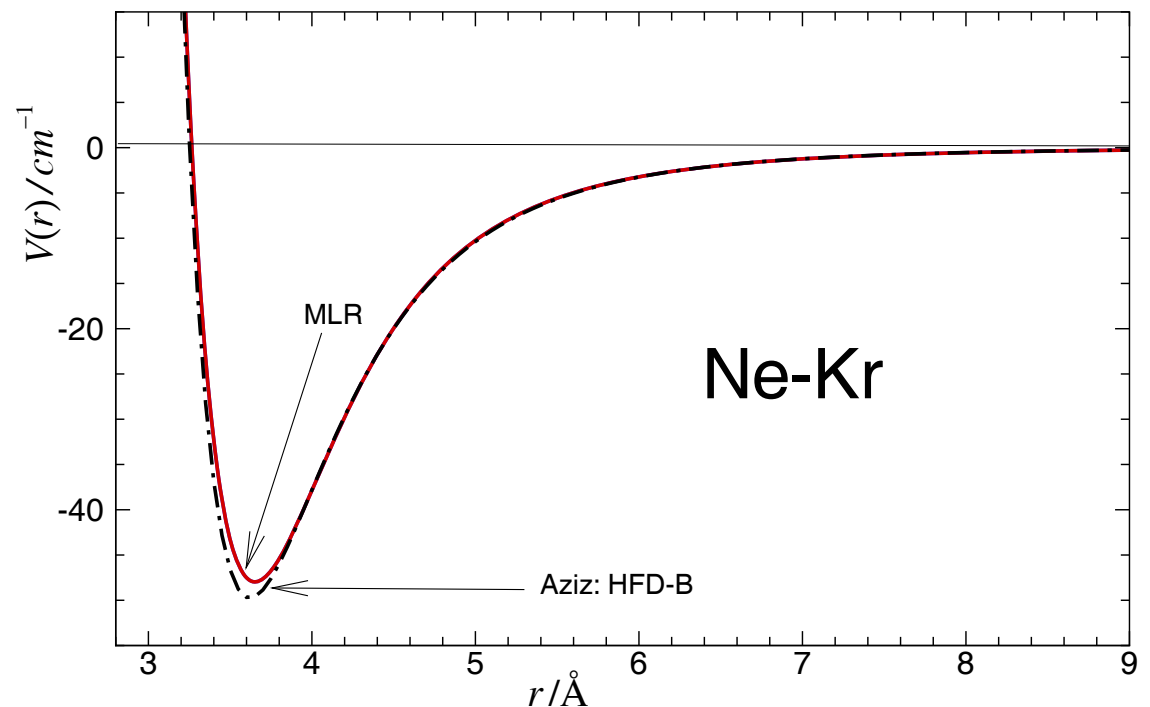
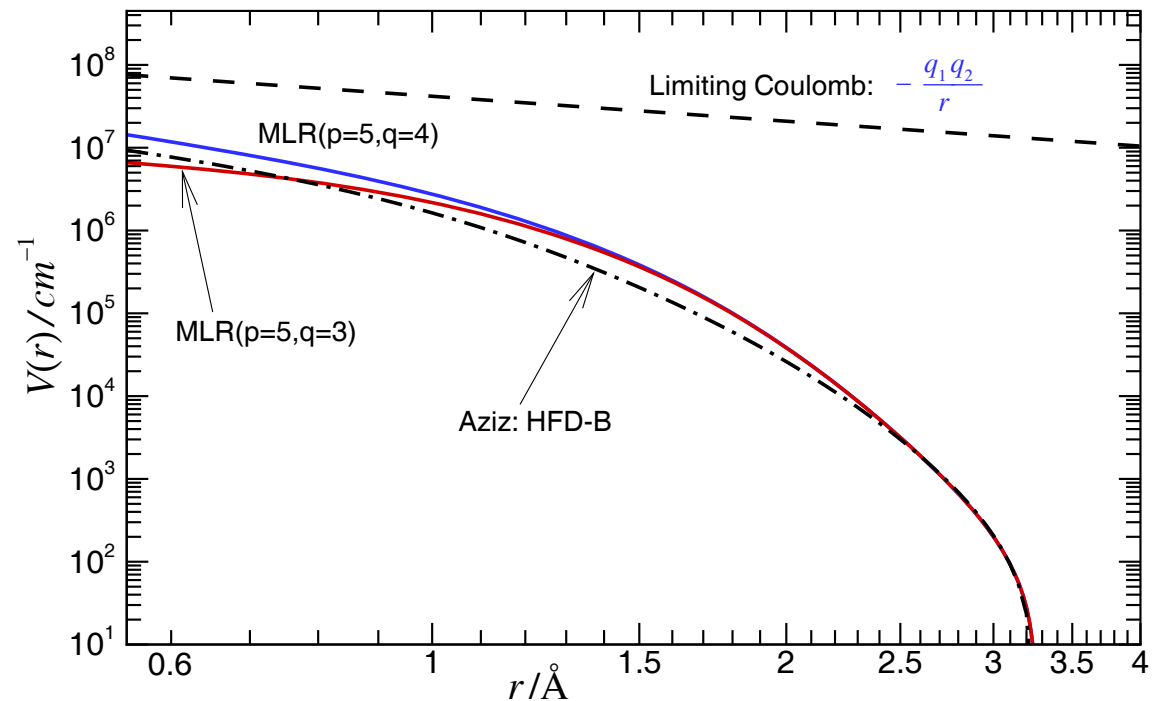
Compare our potential  
with that of Aziz.

Check that the short-range  
extrapolation behaviours of  
these potentials are realistic.

As  $r \rightarrow 0$  potential  
dominated by Coulomb  
repulsion of the nuclei.

$$V(r) \rightarrow -\frac{q_1 q_2}{r}$$

*Looking good !*



## Results to date !

Compare our fitted potential parameters (first entry for each case) with those of Aziz (*in italic font*).

	Ne		Ar		Kr		Xe	
	$\mathfrak{D}_e$	$r_e$	$\mathfrak{D}_e$	$r_e$	$\mathfrak{D}_e$	$r_e$	$\mathfrak{D}_e$	$r_e$
Ne	29.31(14)	3.099(10)	47.26(53)	3.4799(6)	47.95(35)	3.6523(3)	52.65(61)	3.8914(4)
	<i>29.36</i>	<i>3.091</i>	<i>46.98</i>	<i>3.489</i>	<i>49.75</i>	<i>3.621</i>	<i>51.58</i>	<i>3.861</i>
Ar	—	—	99.63(2)	3.7557(4)	117.0(2)	3.8955(3)	129.8(4)	4.0958(3)
			<i>99.55</i>	<i>3.7557</i>	<i>116.28</i>	<i>3.8810</i>	<i>131.10</i>	<i>4.0668</i>
Kr	—	—	—	—	139.57(21)	3.993(35)	160.87(33)	4.2036(1)
					<i>139.84</i>	<i>4.0080</i>	<i>162.28</i>	<i>4.1740</i>
Xe	—	—	—	—	—	—	192.14(52)	4.3761(7)
							<i>196.56</i>	<i>4.3656</i>

Compare  $\overline{dd}(\text{spectroscopy})$  for present fitted potentials with those of Aziz (*in italic font*).

	Ne		Ar		Kr		Xe	
	present	<i>Aziz</i>	present	<i>Aziz</i>	present	<i>Aziz</i>	present	<i>Aziz</i>
Ne	0.126	<i>0.190</i>	3.799	<i>1.8</i> ×10 <sup>5</sup>	0.420	<i>1.6</i> ×10 <sup>4</sup>	0.143	<i>1.6</i> ×10 <sup>4</sup>
Ar	—	—	1.052	<i>3.30</i>	1.450	<i>7.6</i> ×10 <sup>3</sup>	0.545	<i>2.0</i> ×10 <sup>3</sup>
Kr	—	—	—	—	1.211	<i>2.723</i>	0.0808	<i>7.7</i> ×10 <sup>3</sup>
Xe	—	—	—	—	—	—	0.330	<i>18.90</i>

## *Preliminary Conclusions*

- Our direct fits to the combination of available spectroscopic data with virial coefficient data give realistic potentials whose  $\mathcal{D}_e$  and  $r_e$  values are in reasonable agreement with those for the best previous empirical potentials
- Predictions of modern spectroscopic data generated from the older empirical potentials are often many orders of magnitude worse than for our new potentials.
- For most systems, the short range extrapolation behaviour of our new MLR potentials is physically reasonable, and as good as that for Aziz's potentials.

*\* However ... this is not always the case!*

**Results for Xe<sub>2</sub>:** fitting parameters are  $\mathfrak{D}_e$ ,  $r_e$  and exponent coefficients  $\beta_i$

# expon. param.	# data	$\overline{dd}$ (hi-res UV)	$\overline{dd}$ (low-res UV)	$\overline{dd}$ (virials)	$\overline{dd}$ (total)	$\mathfrak{D}_e/\text{cm}^{-1}$	$r_e/\text{\AA}$
<b>All data – High and Low Resolution UV and virials</b>							
1	231	4.875	7.863	5.632	5.354	174.4(28)	4.394(17)
2	231	2.400	6.253	6.007	3.446	172.8(18)	4.391(11)
3	231	0.362	1.093	0.947	0.557	<b>191.76(68)</b>	<b>4.3775(18)</b>
4	231	0.363	1.095	0.919	0.555	192.07(85)	4.3776(18)
<b>High Resolution UV and virial data alone</b>							
1	205	4.977	—	4.179	4.912	172.7(27)	4.389(16)
2	205	2.020	—	5.277	2.483	171.6(14)	4.3860(81)
3	205	0.363	—	0.930	0.443	192.28(87)	4.3774(15)
4	205	0.364	—	0.785	0.419	198.5(28)	4.3768(14)
<b>Virial data alone</b>							
1	18	—	—	0.311	0.311	294.(5)	3.915(12)
2	18	—	—	0.309	0.309	298.(18)	3.905(54)
<b>Aziz's HFD-B potential</b>							
		<b>20.17</b>	<b>0.818</b>	—	—	196.54	4.3656

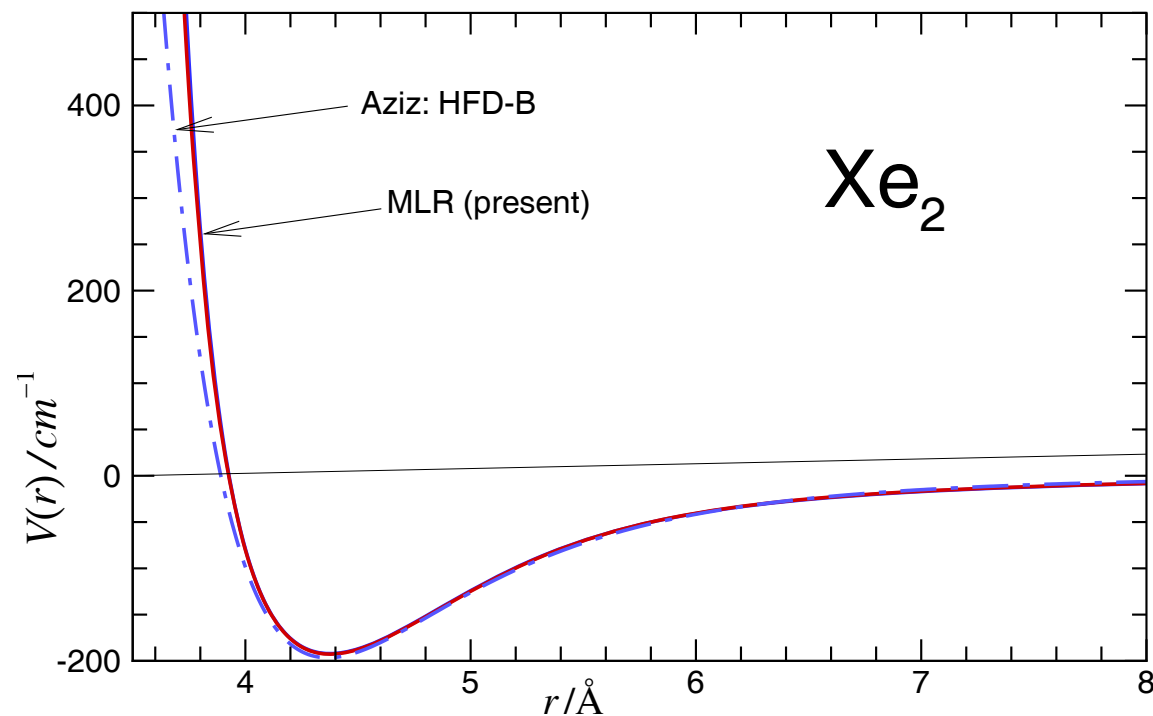
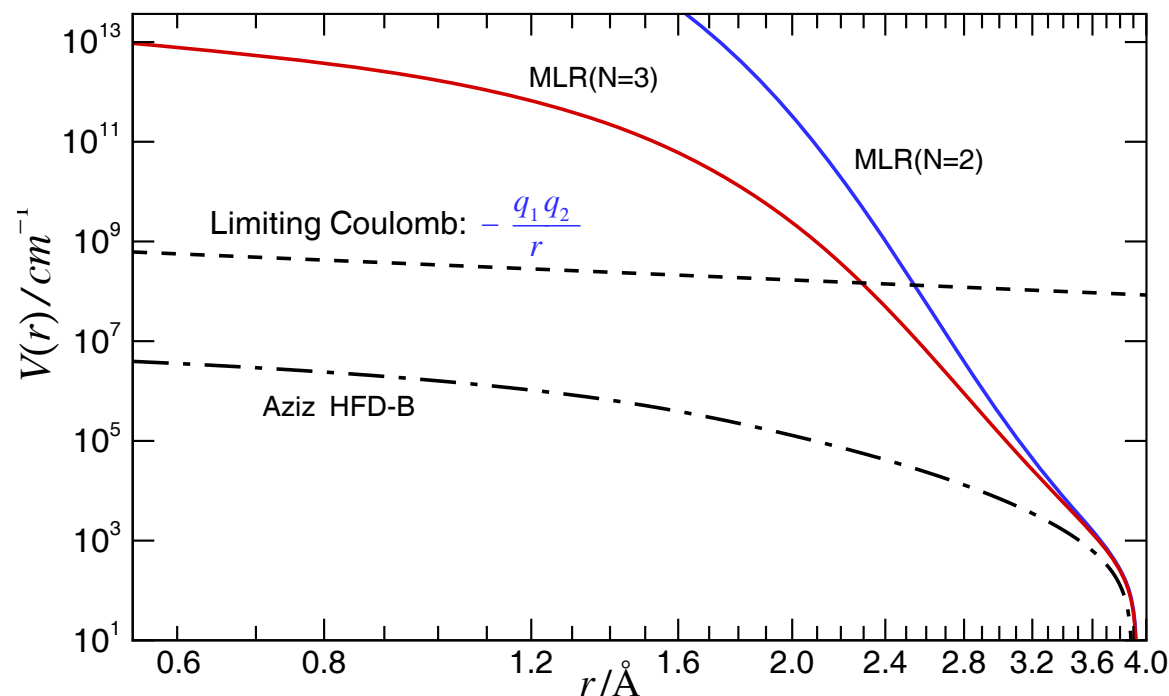
Compare our potential  
with that of Aziz.

As  $r \rightarrow 0$  potential  
dominated by Coulomb  
repulsion of the nuclei.

$$V(r) \rightarrow -\frac{q_1 q_2}{r}$$

Short-range behaviour of our  
potentials deviate significantly  
from that for Aziz's HFD-B  
*and* our very short-range  
extrapolation much too steep!

***We have a problem !***



# Conclusions !

- Our direct fits to the combination of available spectroscopic data with virial coefficient data give realistic potentials whose  $\mathfrak{D}_e$  and  $r_e$  values are in reasonable agreement with those for the best previous empirical potentials
- Predictions of modern spectroscopic data generated from the older empirical potentials are often many orders of magnitude worse than for our new potentials.
- For most systems, the short range extrapolation behaviour of our new MLR potentials is physically reasonable, and as good as that for Aziz's potentials.

*\* However ... this is not always the case !*

- The problem with the short-range behaviour of our Xe<sub>2</sub> potential reflects the fact that the spectroscopic data (mainly sensitive to the potential well) and available virial data do not accurately define the short-range potential wall.
- To address this Xe<sub>2</sub> problem and improve our treatment of the other systems, our future work will incorporate experimental transport properties (viscosity, diffusion and thermal diffusion coefficients) into our 'direct-potential-fit' data analyses.

