

**New Empirical Potential Energy Function(s)  
For the Heavier Homonuclear Rare gas pairs:  
Ne<sub>2</sub>, Ar<sub>2</sub>, Kr<sub>2</sub> and Xe<sub>2</sub>**

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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: reported  $\mathcal{D}_e$  and  $r_e$  values were sensitive to form of model potential.*
  - used model analytic potential functions which failed to incorporate theoretically known inverse-power long-range behaviour

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

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- High resolution spectroscopy not available until relatively recently (1960's)
- 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 :*

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

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

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

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\* 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  $\mathcal{D}_e$  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, virial coefficient, and transport property (viscosity, diffusion, thermal diffusion) data

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- using an objective, quantitative ‘direct-potential-fit’ procedure that fully exploits all available spectroscopic, virial coefficient, and transport property (viscosity, diffusion, thermal diffusion) 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 
$$u_{\text{LR}}(r) = \sum_m D_m(r) \frac{C_m}{r^m} = D_6(r) \frac{C_6}{r^6} + D_8(r) \frac{C_8}{r^8} + D_{10}(r) \frac{C_{10}}{r^{10}}$$

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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 ~ 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:

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

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### *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.

# *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 $\text{cm}^{-1}$	$10^{-8}$ to $3 \times 10^{-7}$ $\text{cm}^{-1}$
high-resolution UV	$\sim 77\,000$ $\text{cm}^{-1}$	0.001 to 0.005 $\text{cm}^{-1}$
medium-resolution UV (rotat. resolved)	$\sim 100\,000$ $\text{cm}^{-1}$	0.02 to 0.2 $\text{cm}^{-1}$
low-resolution UV (band heads)	$\sim 80\,000$ $\text{cm}^{-1}$	0.2 to 0.3 $\text{cm}^{-1}$
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## 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 ( $v = 0 - 11$ )

## Spectroscopic Data range for homonuclear Rg pairs

	<i>rotational resolution</i>	<i>vibrational resolution</i>
Ne <sub>2</sub>	$v = 0 - 1 \dots 90\%$ of $\mathcal{D}_e$	<i>same</i>
Ar <sub>2</sub>	$v = 0 - 5 \dots 95\%$ of $\mathcal{D}_e$	<i>same</i>
Kr <sub>2</sub>	$v = 0 - 2 \dots 38\%$ of $\mathcal{D}_e$	$v = 0 - 9 \dots 93\%$ of $\mathcal{D}_e$
Xe <sub>2</sub>	$v = 0 - 1 \dots 15\%$ of $\mathcal{D}_e$	$v = 0 - 11 \dots 82\%$ of $\mathcal{D}_e$

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***Conclude: do Ar<sub>2</sub> first !!***



## Dimensionless RMS deviations $\overline{dd}$ , for the four data types for $^{40}\text{Ar}_2$

T Range	#Data	Property	$\overline{dd}$				
			$N_\beta=2$	$N_\beta=3$	$N_\beta=3$	$N_\beta=4(tr)$	$N_\beta=4(Cou.@10^{-6}\text{\AA})$
	1397	Spectrosc.	<b>0.918</b>	<b>0.924</b>	<b>0.922</b>	<b>0.929</b>	<b>0.929</b>
75 – 700 K	166	Press. Vir.	[2.440]	<b>1.698</b>	<b>1.877</b>	<b>1.889</b>	<b>1.861</b>
90 – 450 K	59	Acous. Vir.	[44.969]	[7.622]	<b>2.373</b>	<b>2.410</b>	<b>2.372</b>
	1622	Fit total	[8.654]	<b>1.773</b>	<b>1.139</b>	<b>1.149</b>	<b>1.141</b>
78 – 2500 K	557	Transport	[1.715]	[1.268]	[1.268]	<b>1.146</b>	[1.412]
	2207	Overall	[7.517]	[1.173]	[1.173]	<b>1.148</b>	<b>1.216</b>
		$\mathcal{D}_e$	99.63(6)	99.58(5)	99.49(5)	99.49(5)	99.49(5)
		$R_e$	3.762(3)	3.767(3)	3.767(2)	3.768(3)	3.768(3)

## Comparison with predictions from previously PEFs for Ar<sub>2</sub>

T Range	#Data	Property	$\overline{dd}$				
			$N_{\beta=4}(tr)$	VJHB <sup>1</sup>	PS <sup>2</sup>	Aziz <sup>3</sup>	TT <sup>4</sup>
	1397	Spectrosc.	<b>0.929</b>	0.937	1.014	0.964	3.080
75 – 700 K	166	Press. Vir.	<b>1.889</b>	1.913	1.698	2.049	7.518
90 – 450 K	59	Acous. Vir.	<b>2.410</b>	2.479	5.696	15.299	117.897
	1622	Fit total	<b>1.149</b>	1.164	1.537	3.122	22.794
78 – 2500 K	557	Transport	<b>1.416</b>	1.153	1.086	1.732	4.481
	<u>2207</u>	Overall	<b>1.148</b>	1.161	1.435	2.832	19.796
		$\mathcal{D}_e$	99.49(5)	99.48	99.35(32)	99.55	99.64
		$R_e$	3.768(3)	3.762	3.762	3.757	3.757

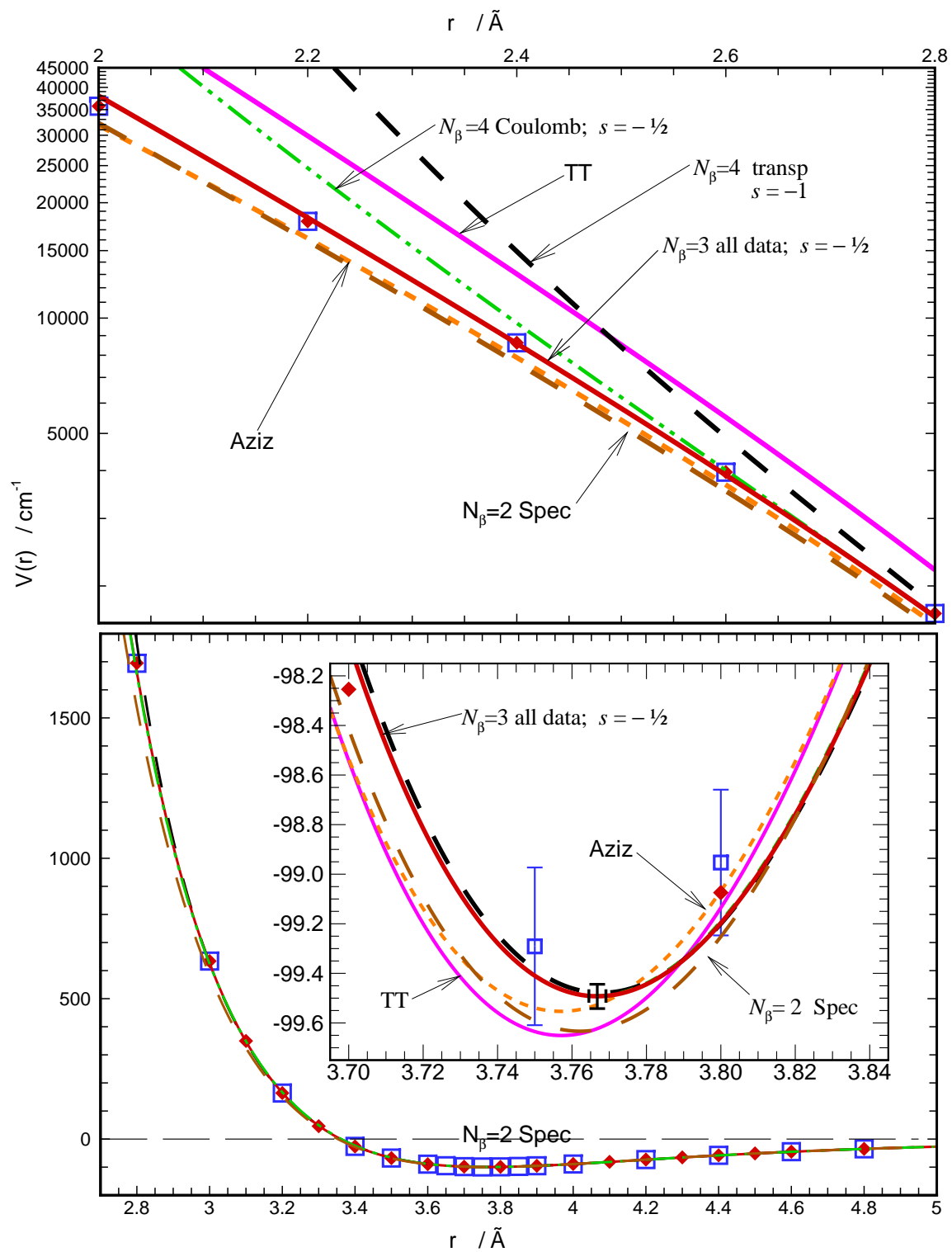
<sup>1</sup> E. Vogel, B. Jäger, R. Hellmann and E. Bich, *Mol. Phys.* **108**, 3335 (2010); *{ab initio}*.

<sup>2</sup> K. Patkowski and K. Szalewicz, *J. Chem. Phys.* **133**, 094304 (2010); *{ab initio}*.

<sup>3</sup> R.A. Aziz, *J. Chem. Phys.* **99**, 4518 (1993); *{empirical manual fit}*

<sup>4</sup> K.T. Tang and J.P. Toennies, *J. Chem. Phys.* **118**, 4876 (2003); *{model using copied  $\mathcal{D}_e$  &  $R_e$ }*

*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	
	$\mathcal{D}_e$	$r_e$	$\mathcal{D}_e$	$r_e$	$\mathcal{D}_e$	$r_e$	$\mathcal{D}_e$	$r_e$
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	—	—	99.49(5)	3.767(2)	117.0(2)	3.8955(3)	129.8(4)	4.0958(3)
			<i>99.55</i>	<i>3.757</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	$1.8 \times 10^5$	0.420	$1.6 \times 10^4$	0.143	$1.6 \times 10^4$
Ar	—	—	0.929	<i>0.964</i>	1.450	$7.6 \times 10^3$	0.545	$2.0 \times 10^3$
Kr	—	—	—	—	1.211	<i>2.723</i>	0.0808	$7.7 \times 10^3$
Xe	—	—	—	—	—	—	0.330	<i>18.90</i>

## *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.
  - Acoustic virial coefficients provide a critical property to include . . . discriminates sharply between models
  - Analogous studies of the other Rare Gas pairs are under way
-