Incorporating 'Damping Functions' into the Morse/Long-Range Potential Function Form Improves both Long-Range and Very Short-Range Behaviour

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Question: ***How may we best summarize what we know about a molecule ?***

- structural properties such as bond length(s), bond strength, equilibrium force constants

- spectroscopic properties: transition energies and relative intensities in pure rotation, vibration-rotation and electronic spectroscopy, and the number and energies of unobserved levels

  Since the dawn of quantum mechanics, the central paradigm of spectroscopic data analysis was to explain the patterns of observed transition energies in terms of expressions for molecular level energies as functions of vibrational and rotational quantum numbers.

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Answer: ***By a compact, flexible, analytic potential energy function !***

But . . . . . . ***How do we determine that potential ?***

'Direct Potential Fits'

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

- Simulate level energies as eigenvalues of some parametrized analytic potential energy function $V(r;\{p_j\})$

- Partial derivatives of observables w.r.t. parameters p_j required for fitting are generated readily using the Hellmann-Feynmann 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
- readily accounts for Born-Oppenheimer breakdown (BOB), and/or for Λ-doubling or $^2\Sigma$ splittings, in terms of radial functions

Challenge ... to develop analytic potential function forms

* flexible enough to fully represent extensive high-resolution data
* robust and 'well behaved' (no spurious extrapolation behaviour)
* compact and portable – defined by 'modest' no. of parameters
* incorporating appropriate physical limiting behaviour

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At long range, all molecular interactions become

$$V(r) \simeq \mathfrak{D} - \frac{C_{m_1}}{r^{m_1}} - \frac{C_{m_2}}{r^{m_2}} - \ldots\ldots$$

so we want a function which incorporates this behaviour.

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Morse/Long-Range (MLR) *Potential*

If we define $u_{\rm LR}(r) = \dfrac{C_{m_1}}{r^{m_1}} + \dfrac{C_{m_2}}{r^{m_2}} + \ldots$ we can write

$$\boxed{V_{\rm MLR}(r) = \mathfrak{D}_e \left\{ 1 - \frac{u_{\rm LR}(r)}{u_{\rm LR}(r_e)}\, e^{-\beta(r)\cdot y_p(r)} \right\}^2}$$

$$\xrightarrow{r \gg r_e} \mathfrak{D}_e - \left(\frac{2\,\mathfrak{D}_e\, e^{-\beta_\infty}}{u_{\rm LR}(r_e)}\right) u_{\rm LR}(r) = \mathfrak{D}_e - \frac{C_{m_1}}{r^{m_1}} - \frac{C_{m_2}}{r^{m_2}} - \ldots$$

in which $\beta(r) = \beta_{\rm MLR}(r) = \beta_\infty\, y_p(r) + [1 - y_p(r)] \displaystyle\sum_{i=0}^{N} \beta_i\, y_p(r)^i$

where $\beta_\infty \equiv \beta(r{=}\infty) = \ln\{2\,\mathfrak{D}_e / u_{\rm LR}(r_e)\}$

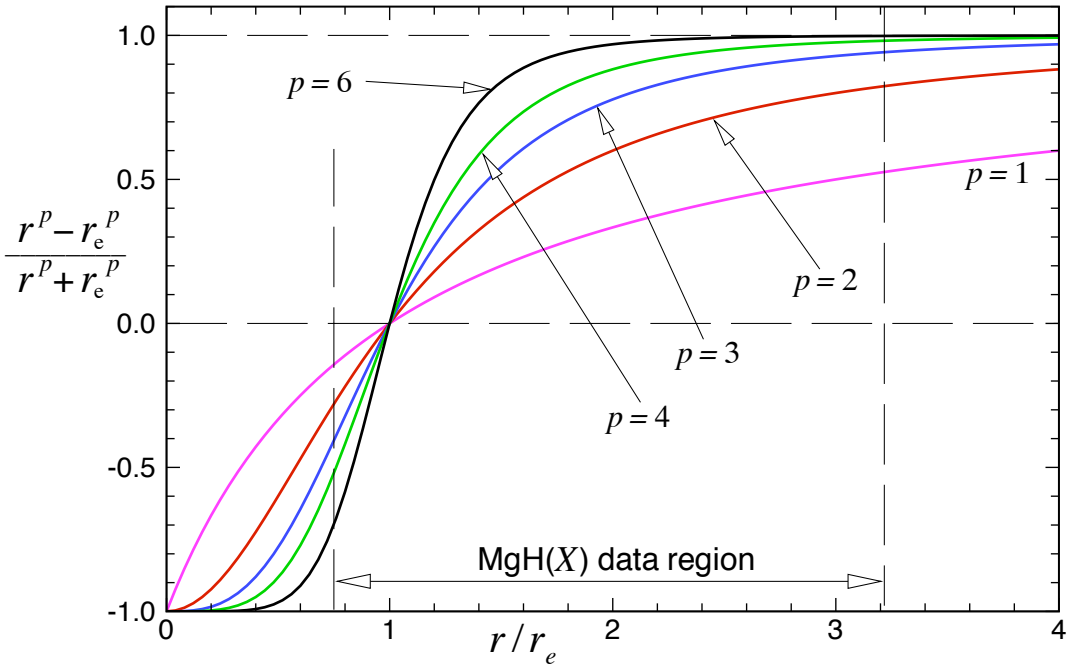
Improving the model – minding our p's and q's

e.g., For $X(^2\Sigma^+)$-state MgH including 2 terms in $u_{\rm LR}(r)$ (C_6 & C_8) means we must set $p \geq 4$. But in this case:

- $y_p(r)$ is very flat and close to 1.0 over much of the domain

$\Rightarrow$ a very high-order polynomial required to describe variation of exponent coefficient $\beta(r)$

$\Rightarrow$ polynomial would have very large coefficients of alternating sign!



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	$\mathrm{MLR}_{4,4}(6;18)$
$\mathfrak{D}_e/\mathrm{cm}^{-1}$	11104.7(3)
$r_e/$Å	1.729682(5)
$r_{\rm ref}/$Å	r_e
C_6/cm^{-1}Å^6	2.793×10^5
C_8/cm^{-1} Å^8	3.475×10^6
C_{10}/cm^{-1} Å^{10}	—
damping	***none***
$\{p,\,q\}$	$\{4,\,4\}$
β_0	-2.33867308
β_1	-0.7759113
β_2	-1.210606
β_3	-0.541097
β_4	-0.45237
β_5	0.15537
β_6	-0.2325
β_7	2.6224951×10^3
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β_{16}	-2.6852×10^7
β_{17}	9.26×10^6
β_{18}	-1.44×10^6
$\overline{dd}$	0.783

Improving the model – minding our p's and q's

e.g., For $X(^2\Sigma^+)$-state MgH including 3 terms in $u_{\rm LR}(r)$ (C_6, C_8 & C_{10}) means we must set $p \geq 5$. But in this case:

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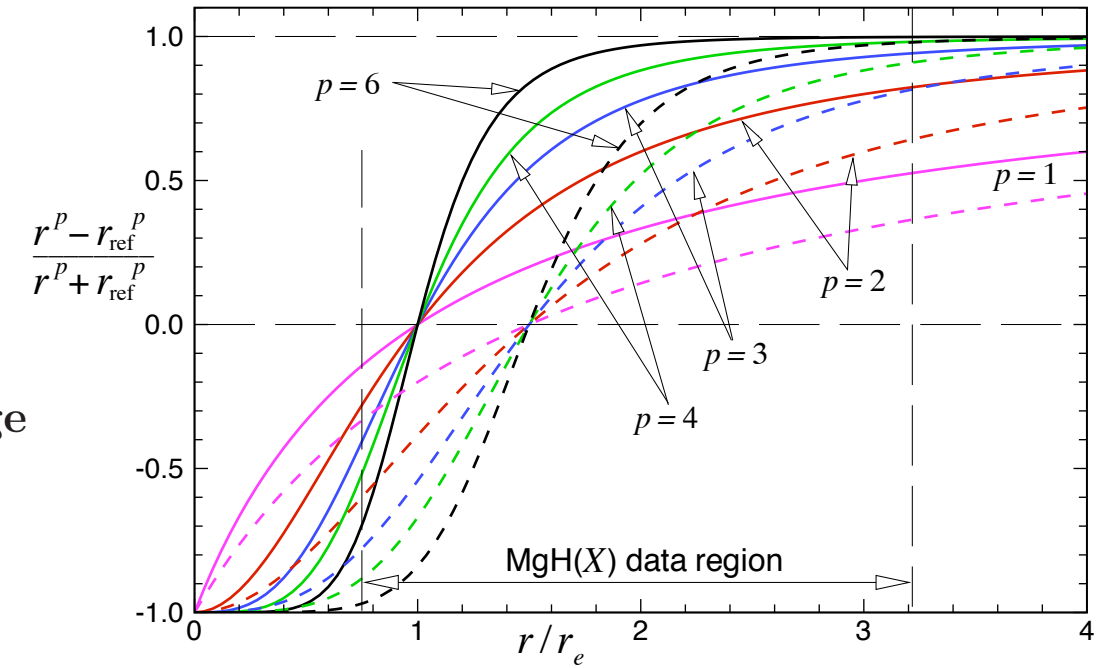

So introduce $\quad y_p^{\rm ref} = \dfrac{r^p - r_{\rm ref}{}^p}{r^p + r_{\rm ref}{}^p}$

and then define

$$\beta_{p,q}^{\rm ref}(r) \equiv y_p^{\rm ref}(r)\ \beta_\infty + \left[1 - y_p^{\rm ref}(r)\right] \sum_{i=0}^{N} \beta_i \left[y_q^{\rm ref}(r)\right]^i$$

p must be bigger than the ***difference*** *between the highest and lowest inverse powers in $u_{\rm LR}(r)$, and hence it is relatively large, but q can be smaller, which makes it a better expansion variable!*

Improving the model – minding our p's and q's

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	$\mathrm{MLR}_{4,4}(6;18)$	$\mathrm{MLR}_{5,4}(12)$
$\mathfrak{D}_e/\mathrm{cm}^{-1}$	11104.7(3)	11104.90(4)
$r_e/$Å	1.729682(5)	1.7296838(2)
$r_{\rm ref}/$Å	r_e	2.3
C_6/cm^{-1}Å^6	2.793×10^5	2.7755×10^5
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C_{10}/cm^{-1} Å^{10}	—	4.614×10^7
damping	***none***	***none***
$\{p,\,q\}$	$\{4,\,4\}$	$\{5,\,4\}$
β_0	-2.33867308	-2.48904461
β_1	-0.7759113	0.0851382
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β_4	-0.45237	3.479727
β_5	0.15537	4.24532
β_6	-0.2325	3.04072
β_7	2.6224951×10^3	1.1153
β_8	-5.2413692×10^4	-1.8392
β_9	4.968244×10^5	-1.793
β_{10}	-2.59556525×10^6	6.634
β_{11}	9.3721667×10^6	14.63
β_{12}	-2.3536146×10^7	-1.86
β_{13}	4.190927×10^7	-22.84
β_{14}	-5.288707×10^7	-14.4
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Recall the challenge . . . to develop analytic potential function forms:

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- robust and 'well behaved' (no spurious extrapolation behaviour) $\surd$
- compact and 'portable' – defined by a 'modest' number of parameters $\surd$
- incorporating appropriate limiting long-range behaviour ! $\surd$

While our extended MLR function meets all of these requirements,
a couple of further questions should be considered.

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While our extended MLR function meets all of these requirements, a couple of further questions should be considered.

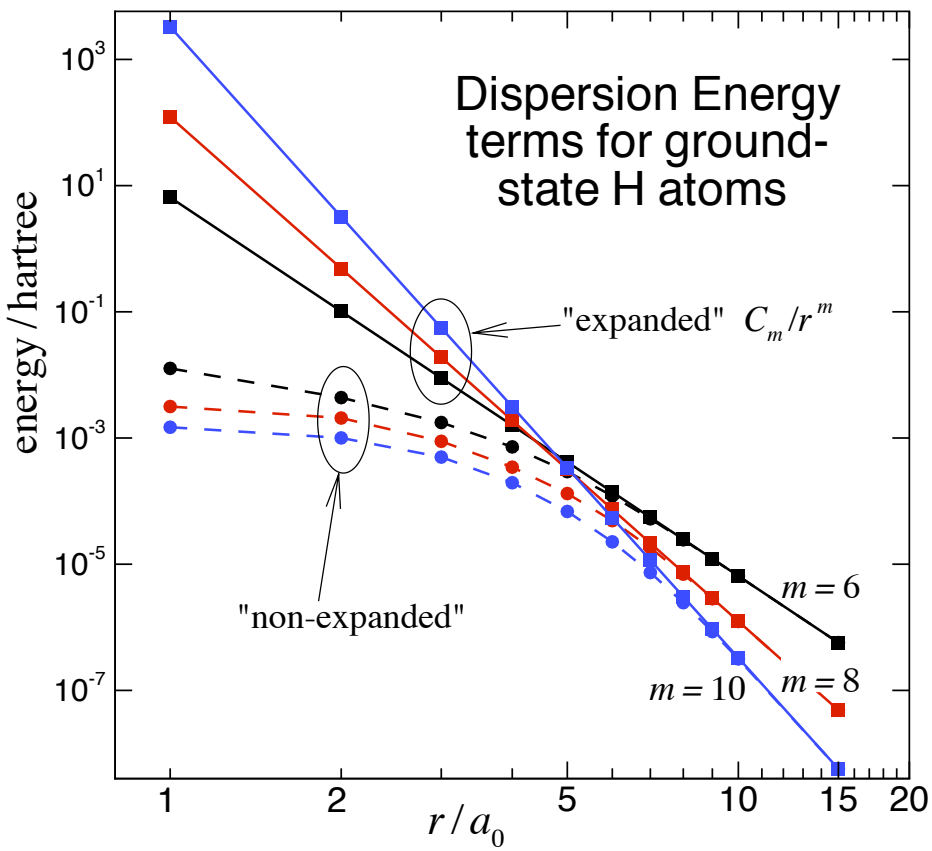
- **What about 'damping' of the inverse-power long-range terms due to overlap of the electron distributions of the interacting atoms ?**
- **What about the limiting short-range behaviour ?**

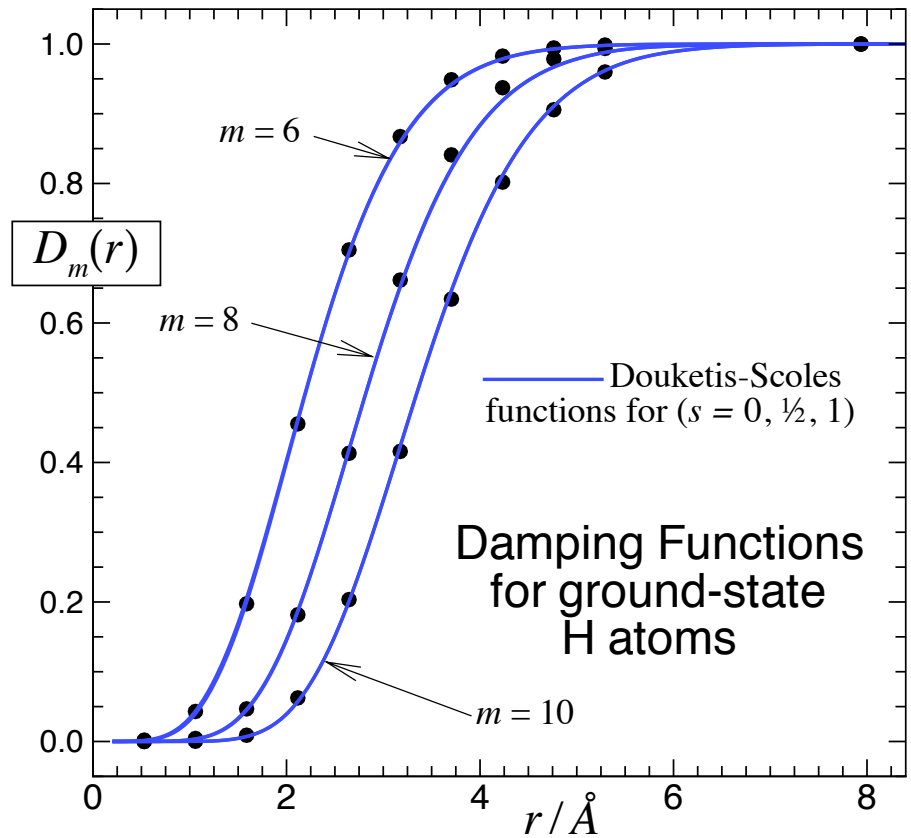
Many years ago Bill Meath taught us that overlap of the electron distributions of interacting atoms means that long-range potentials should actually include 'damping functions'. This is readily incorporated into the MLR form by defining

$$u_{\mathrm{LR}}(r) \;=\; D_{m_1}(r)\,\frac{C_{m_1}}{r^{m_1}} \;+\; D_{m_2}(r)\,\frac{C_{m_2}}{r^{m_2}} \;+\; \ldots$$

But what are these damping functions like ?

Consider Kreek-Meath calculations for two ground-state H atoms.





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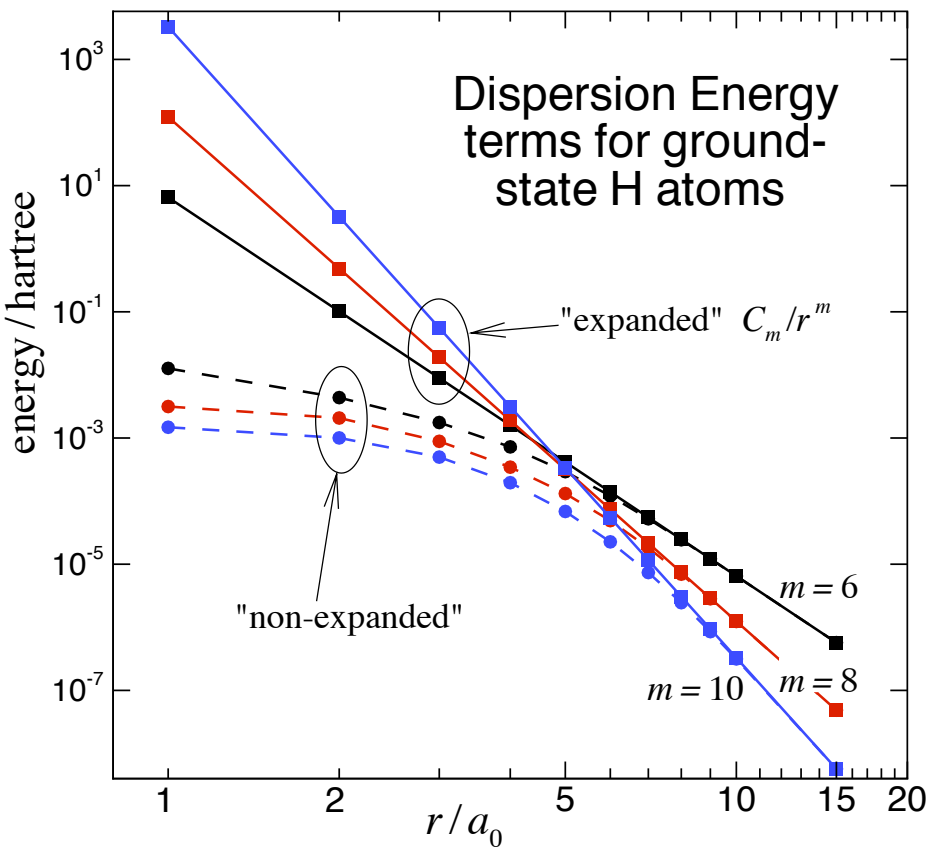

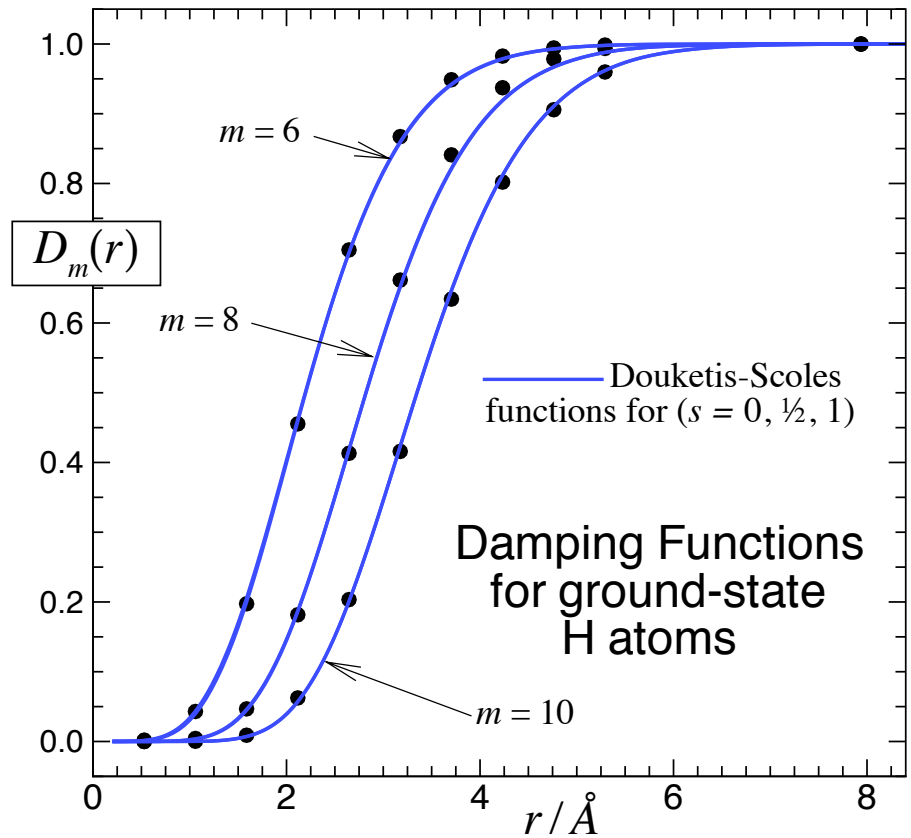

But . . . the functional form chosen for the $D_m(r)$ functions has implications regarding the short-range behaviour of MLR potentials . . . . . .

Write MLR function in expanded form and consider its ***very small*** r behaviour

$$V_{\mathrm{MLR}}(r) \quad = \quad \mathfrak{D}_e \left\{ 1 - 2 \left(\frac{u_{\mathrm{LR}}(r)}{u_{\mathrm{LR}}(r_e)} \right) e^{-\beta(r)\cdot y_p(r)} + \left(\frac{u_{\mathrm{LR}}(r)}{u_{\mathrm{LR}}(r_e)} \right)^2 e^{-2\,\beta(r)\cdot y_p(r)} \right\}$$

$$\xrightarrow{r \text{ very small}} \quad \mathfrak{D}_e \left(\frac{u_{\mathrm{LR}}(r)}{u_{\mathrm{LR}}(r_e)} \right)^2 e^{+2\,\beta(r=0)} \quad \propto \quad \{ u_{\mathrm{LR}}(r) \}^2$$

Thus, if $u_{\rm LR}(r)$ is a simple inverse-power sum such as (say)

$$u_{\rm LR}(r) \;=\; \frac{C_6}{r^6} \;+\; \frac{C_8}{r^8} \;+\; \frac{C_{10}}{r^{10}}$$

then at very small distances $V_{\rm MLR}(r) \;\propto\; \dfrac{1}{r^{20}}$ which is unphysically steep!

However **... if the long-range term includes damping functions, then at very small distances this $V_{\rm MLR}(r) \;\propto\; \left(\frac{D_{10}(r)}{r^{10}}\right)^2$ and the limiting short-range behaviour of the potential is defined by the nature of those damping functions!**

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<u>The Tang-Toennies form</u> (1984) $D_m^{\rm TT}(r) = 1 + e^{-b^{\rm tt} r} \sum_{k=0}^{m} \frac{(b^{\rm tt}\, r)^k}{k!}$ ***is not acceptable***

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<u>The Douketis-Scoles-Marchetti-Zen-Thakkar form</u> (1982) $D_m^{\rm DS}(r) \;=\; \left(1 - e^{-\frac{b^{\rm ds}\, r}{m} - \frac{c^{\rm ds}\, r^2}{\sqrt{m}}}\right)^m$

***is acceptable* since as $r \to 0$, $\frac{D_m^{\rm DS}(r)}{r^m} \to \{\text{constant}\}$ and hence $V_{\rm MLR}(r) \to \{\text{constant}\}$**

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However, within an MLR potential, an even better damping function is the

<u>Modified Douketis-Scoles-M-Z-T form</u> (2009) $D_m^{\rm mDS}(r) \;=\; \left(1 - e^{-\frac{b^{\rm mds}\, r}{m} - \frac{c^{\rm mds}\, r^2}{\sqrt{m}}}\right)^{m-s}$

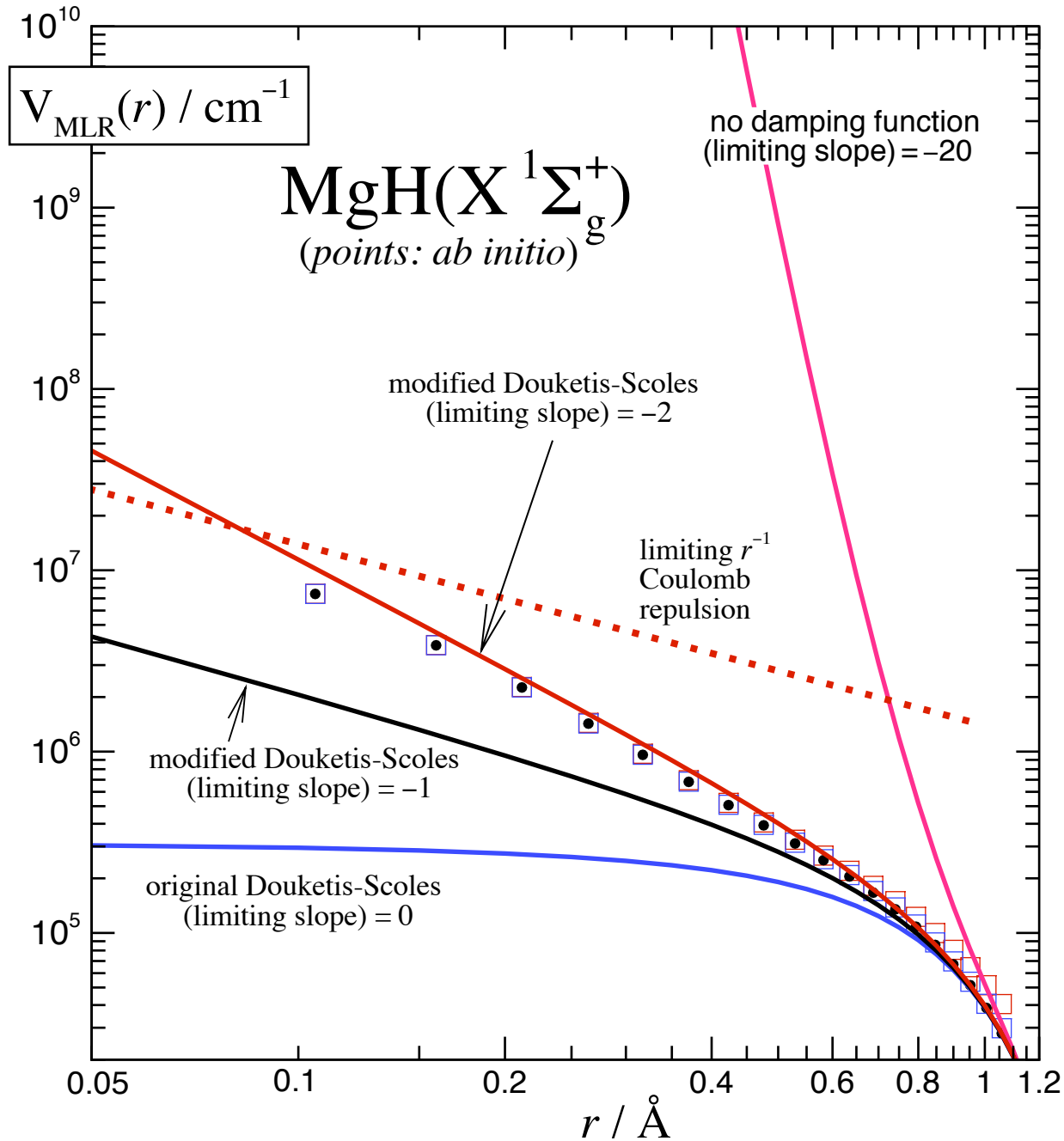
is recommended since at very small distances $\frac{D_m^{\rm mDS}(r)}{r^m} \propto \frac{1}{r^s}$ and $V_{\rm MLR}^{\rm mDS}(r) \propto \frac{1}{r^{2s}}$!

In particular, $s = 1/2$ yields the theoretically predicted "united atom limit" very short-range behaviour $V_{\rm MLR}^{\rm mDS}(r) \propto 1/r$!

e.g., compare short-range extrapolation behaviour of potentials with different damping functions, determined from otherwise equivalent fits to data spanning the entire potential well of MgH.

Inclusion of long-range damping softens the $u_{\mathrm{LR}}(r)$ *contribution to the short-range repulsive wall, but has no effect on the quality of the potential in the 'data region' (the well).*

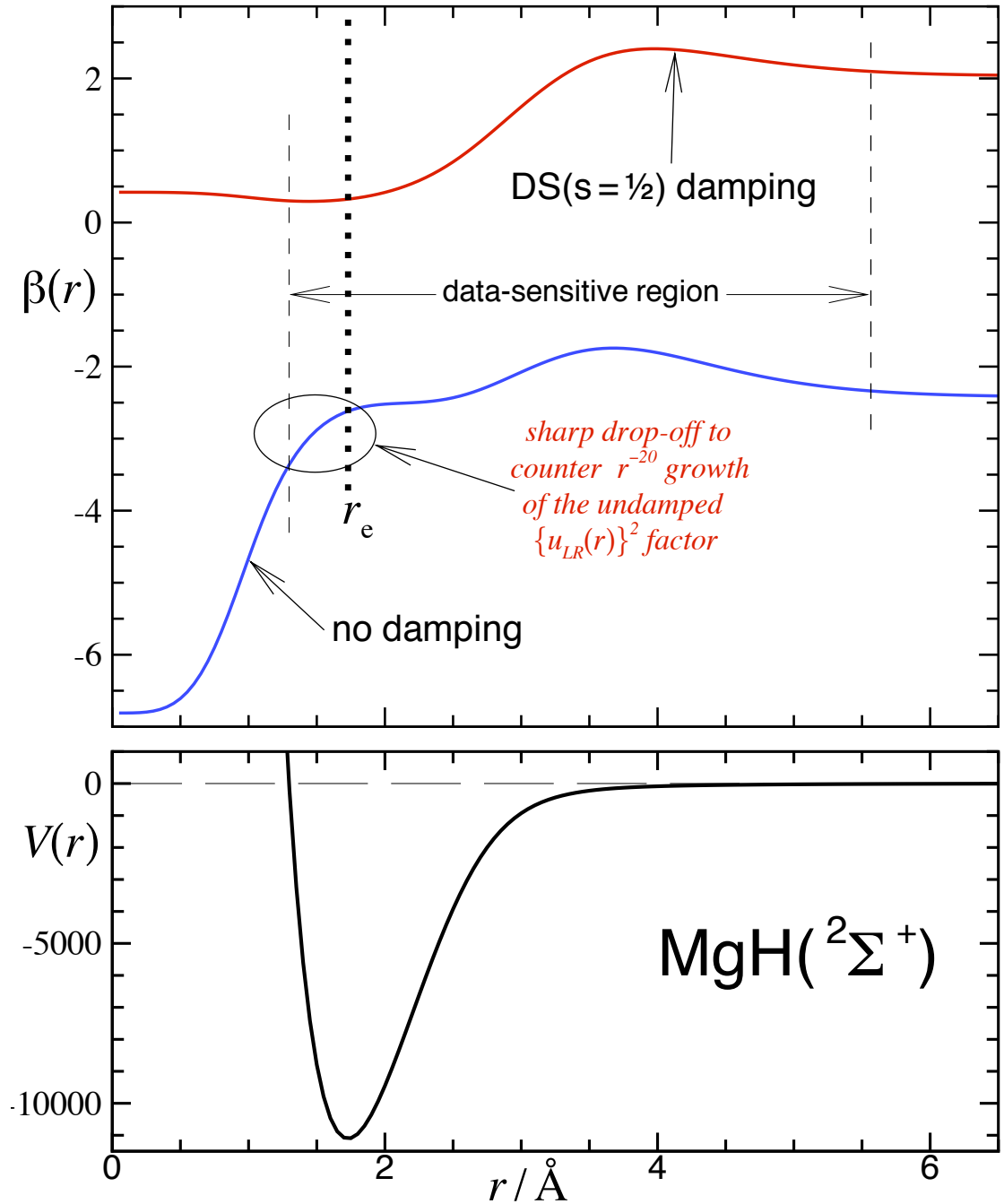
Different damping function models give different very short-range behaviour, but all agree at 'chemical energies' of up to 100 000 cm^{-1}



$$V_{\mathrm{MLR}}(r) \;=\; \mathfrak{D}_e \left\{ 1 \;-\; \frac{u_{\mathrm{LR}}(r)}{u_{\mathrm{LR}}(r_e)}\, e^{-\beta(r)\cdot y_p(r)} \right\}^2$$

Inclusion of damping functions softens the short-range growth of $u_{\mathrm{LR}}(r)$ *so the exponent coefficient* $\beta(r)$ *no longer needs to drop off sharply at small* r *to compensate for artificial* $1/r^{20}$ *growth of the* $u_{\mathrm{LR}}(r)$ *term.*

This allows the exponent coefficient $\beta(r)$ *to be represented accurately by a lower-order polynomial!*



Re. our analysis of 7453 data spanning the entire potential well of MgH($X\,^2\Sigma^+$) . . .

A model incorporating damping functions tends to require fewer exponent polynomial fitting parameters to achieve a given accuracy.

	no damping in $u_{\rm LR}(r)$		$u_{\rm LR}(r)$ damped
	MLR$_{4,4}$(6; 18)	MLR$_{5,4}$(14)	MLR$_{5,4}$(11)
$\mathfrak{D}_e$/cm^{-1}	11104.7(3)	11104.90(4)	11105.22(3)
r_e/Å	1.729682(5)	1.7296838(2)	1.7296846(1)
$r_{\rm ref}$/Å	r_e	2.3	2.55
C_6/cm^{-1}Å^6	2.793×10^5	2.7755×10^5	2.7755×10^5
C_8/cm^{-1} Å^8	3.475×10^6	3.4549×10^6	3.4549×10^6
C_{10}/cm^{-1} Å^{10}	—	4.614×10^7	4.614×10^7
damping	***none***	***none***	***YES***
$\{p,\,q\}$	{4, 4}	{5, 4}	{5, 4}
β_0	−2.33867308	−2.48904461	0.90643023
β_1	−0.7759113	0.0851382	0.2756464
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β_9	4.968244×10^5	−1.793	−5.37
β_{10}	-2.59556525×10^6	6.634	−7.06
β_{11}	9.3721667×10^6	14.63	−2.82
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β_{18}	-1.44×10^6		
$\overline{dd}$	0.783	0.762	0.776

Conclusions

Introducing damping functions into the definition of $u_{\rm LR}(r)$ in the MLR potential function form:

$$V_{\rm MLR}(r) \;=\; \mathfrak{D}_e \left\{ 1 \;-\; \frac{u_{\rm LR}(r)}{u_{\rm LR}(r_e)}\; e^{-\beta(r)\cdot y_p(r)} \right\}^2$$

with $\quad u_{\rm LR}(r) \;=\; D_{m_1}(r)\,\dfrac{C_{m_1}}{r^{m_1}} \;+\; D_{m_2}(r)\,\dfrac{C_{m_2}}{r^{m_2}} \;+\; \ldots$

- ***gives a better physical description of the long-range tail of the potential energy function***
- ***gives a physically more realistic (less steep!) short-range potential function wall***
- ***can yield a more compact (fewer parameters) model for the potential energy function***

Conclusions

Introducing damping functions into the definition of $u_{\rm LR}(r)$ in the MLR potential function form:

$$V_{\rm MLR}(r) \;=\; \mathfrak{D}_e \left\{ 1 \;-\; \frac{u_{\rm LR}(r)}{u_{\rm LR}(r_e)}\; e^{-\beta(r)\cdot y_p(r)} \right\}^2$$

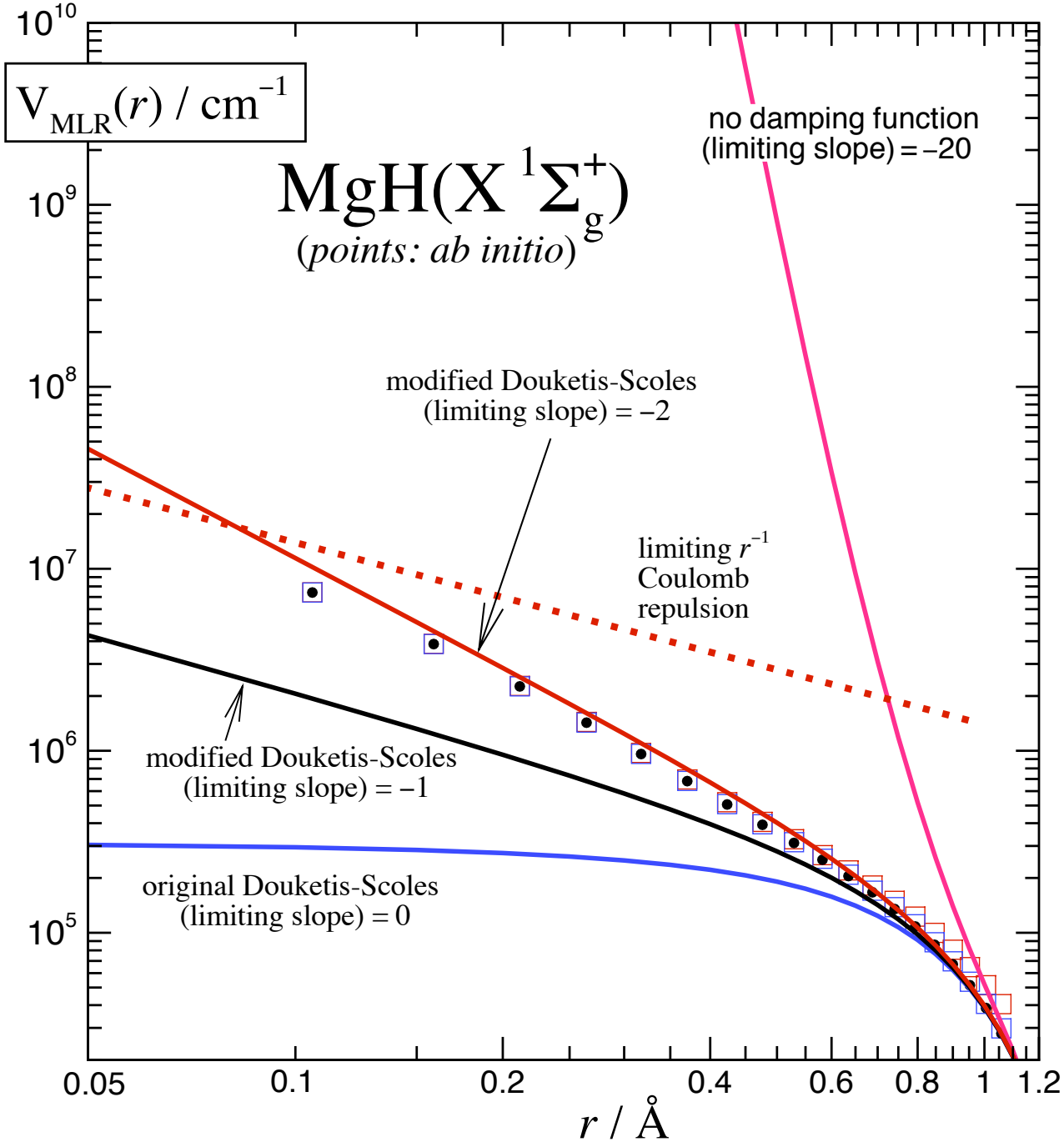
with $\quad u_{\rm LR}(r) \;=\; D_{m_1}(r)\,\dfrac{C_{m_1}}{r^{m_1}} \;+\; D_{m_2}(r)\,\dfrac{C_{m_2}}{r^{m_2}} \;+\; \ldots$

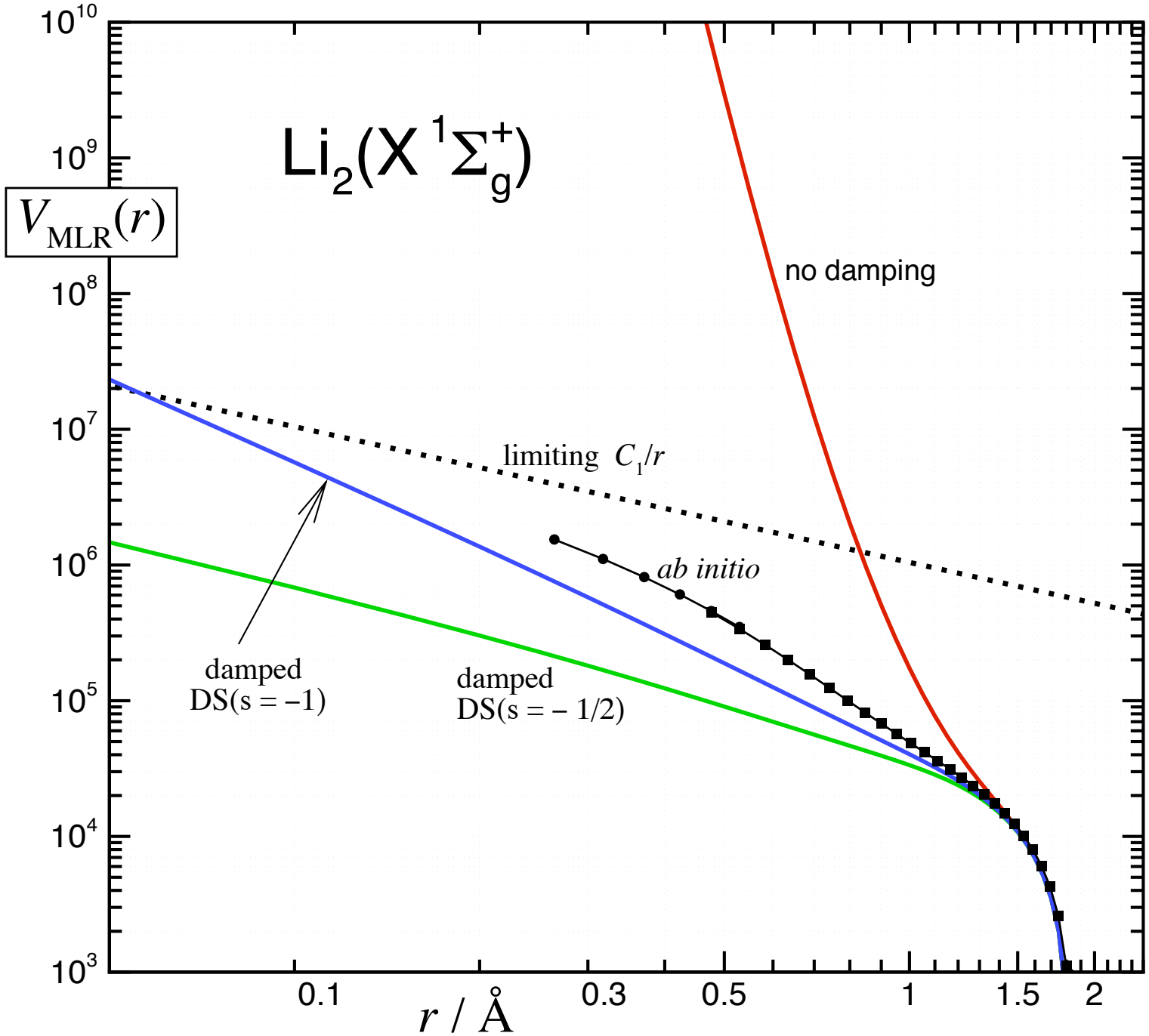
- ***gives a better physical description of the long-range tail of the potential energy function***
- ***gives a physically more realistic (less steep!) short-range potential function wall***
- ***can yield a more compact (fewer parameters) model for the potential energy function***

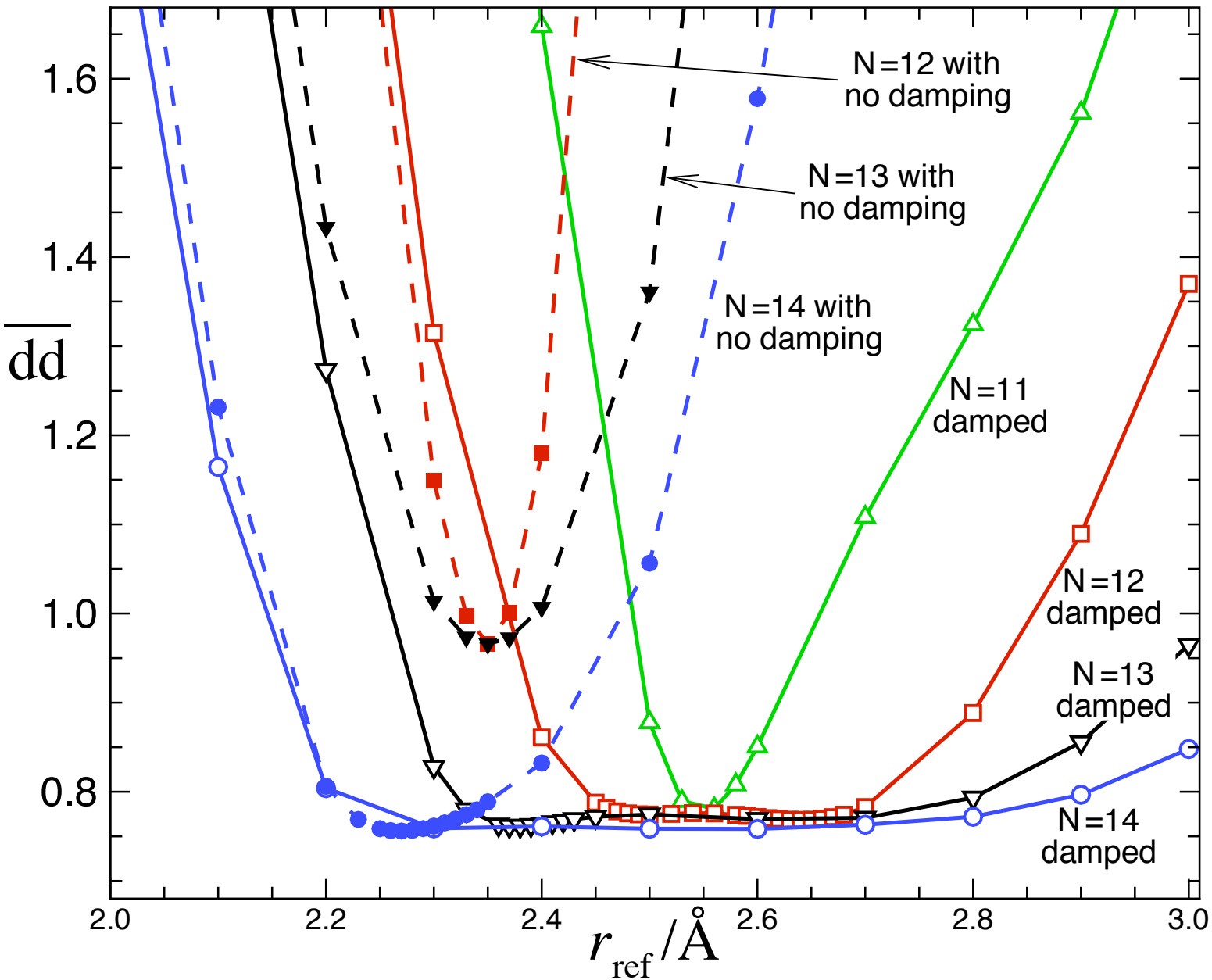
Questions to be resolved

∗ is there a unique 'best' damping function form ?

∗ can a potential using $s = -1/2$ Douketis-Scoles damping functions be constrained to give *quantitative* united-atom-limit behaviour $V(r) \simeq -\frac{Z_1 Z_2\, e^2}{4\pi\epsilon_0\; r}$?


$V_{MLR}(r)$ / cm^{-1}
MgH($X\,^1\Sigma_g^+$)
(points: ab initio)
no damping function
(limiting slope) = –20
modified Douketis-Scoles
(limiting slope) = –2
limiting r^{-1}
Coulomb
repulsion
modified Douketis-Scoles
(limiting slope) = –1
original Douketis-Scoles
(limiting slope) = 0
10^{10}
10^9
10^8
10^7
10^6
10^5
0.05
0.1
0.2
0.4
0.6
0.8
1
1.2
r / Å


$Li_2(X\,^1\Sigma_g^+)$
$V_{MLR}(r)$
no damping
limiting C_1/r
ab initio
damped
DS(s = −1)
damped
DS(s = − 1/2)
10^{10}
10^9
10^8
10^7
10^6
10^5
10^4
10^3
0.1
0.3
0.5
1
1.5
2
r / Å


N=12 with
no damping
N=13 with
no damping
N=14 with
no damping
N=11
damped
N=12
damped
N=13
damped
N=14
damped
1.6
1.4
1.2
1.0
0.8
2.0
2.2
2.4
2.6
2.8
3.0
$\overline{dd}$
r_{ref}/Å

Diatomic DPF analyses may be performed 'routinely' using

program `DPotFit` (*'Diatomic Potential Fits'*)

{ available with manual from `http://leroy.uwaterloo.ca/programs/` }

which performs DPF fits to spectroscopic data and can:

- simultaneously treat any combination of microwave, infrared, electronic, fluorescence series, tunneling level widths, & photo-association data
  - for one or multiple isotopologues
  - for one or multiple electronic states
- take account of atomic-mass dependent Born-Oppenheimer breakdown
- take account of Λ-doubling of singlet states or $^2\Sigma$ splittings
- use "*sequential rounding and re-fitting*" to automatically yield fitted parameters with a minimum number of significant digits and no loss of precision in representing data
- use Watson's "*robust*" data weighting technique to damp the effect of "outlier" observations which give anomalously large discrepancies with the model, and might unreasonably mislead a fit.
- use four types of potential forms: EMO, MLR, DELR, or polynomials.