A DPF Analysis yields Full Analytic Potentials for the $B\,^1\Pi_{1u}$ "Barrier" States of Rb_2 and Li_2, *and* An Improved Ground-State Well Depth and Potential Energy Function for Rb_2

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Gaseous Atomic Rb has been of considerable interest in recent years

- as a medium for laser-cooling experiments
- as the material used for the first demonstration of Bose-Einstein condensation in a dilute medium
- as a medium for studying Feschbach resonances in ultra-cold atomic collisions

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Developing a proper understanding of such phenomena, and predicting related properties, such as binary collision parameters for ultracold mixed-isotope collisions and mixed isotope Bose–Einstein condensation, all depend upon having *an accurate knowledge of the potential energy functions* governing the behaviour of colliding Rb atoms.

However ...

Ab initio calculations for this system are quite challenging . . .

- In 2001, Park *et al.*[1] reported new large-scale CI calculations using spin-averaged relativistic effective core potentials to determine an improved ground-state potential, but its well depth was 166 cm^{-1} too shallow.

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Empirical analyses for this state are in better shape, as . . .

- the most most recent 2000[8] and 2010[9] studies are in excellent agreement, yielding well-depth estimates, respectively, of 3993.53($\pm$0.06) cm^{-1} and 3993.593($\pm$0.003) cm^{-1} that agree to within their mutual uncertainties.

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- ***the present work intends to supplant that analysis !***

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- We shall test the efficacy of the new modified version of the "DELR" model used for the $B\,^1\Pi_u$ "barrier-state" potential of Li_2.[23]

[23] Y. Huang and R,J, Le Roy, *J. Chem. Phys.* **119**, 7398 (2003).

Methodology:

Direct Potential Fits consist of the following steps:

- assume an analytic functional form for the potential energy function of every electronic state involved in the spectra,
- obtain/generate/estimate plausible initial estimates for the parameters defining each of the relevant potentials,
- for the upper and lower level of every spectral transition, solve the radial Schrödinger equation to determine its eigenvalue $E_{v,J}$ to an accuracy an order of magnitude higher than the precision of the data associated with that level,
- employ the radial wavefunctions $\psi_{v,J}(r)$ obtained when solving for each of the vibration/rotational levels to calculate the exact partial derivatives of its eigenvalue with respect to all parameters p_k defining the potential energy function for that state:

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

- Use the partial derivatives in a 'standard' non-linear least-squares-fit program to optimize the values of all potential function parameters.

Tools:

- Program `betaFIT` [24] generates initial trial potential function expansion parameters from a set of RKR or *ab initio* turning points
- Program `dPotFit` [25] generates the synthetic spectra and performs least-squares fits to parameterized potential energy functions.

Functional Form for regular Single-Minimum Potentials

The Morse/Long-Range (MLR) Potential.

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

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

in which $$u_{\rm LR}(r) \;\equiv\; \sum_{i=1}^{last} D_{m_i}(r)\, \frac{C_{m_i}}{r^{m_i}} \;\simeq\; \frac{C_{m_1}}{r^{m_1}} + \frac{C_{m_2}}{r^{m_2}} + \ldots$$

where $D_{m_i}(r)$ are 'damping functions' that approach 1 as $r \to \infty$,

and $\beta(r) = y_p(r)\,\beta_\infty + [1 - y_p(r)] \sum_j \beta_j \{y_q(r)\}^j$, with $y_q(r) \equiv \frac{r^q - (r_{\rm ref})^q}{r^q + (r_{\rm ref})^q}$.

[24] see `http://leroy.uwaterloo.ca/programs/`

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Functional Form for "barrier" Potentials

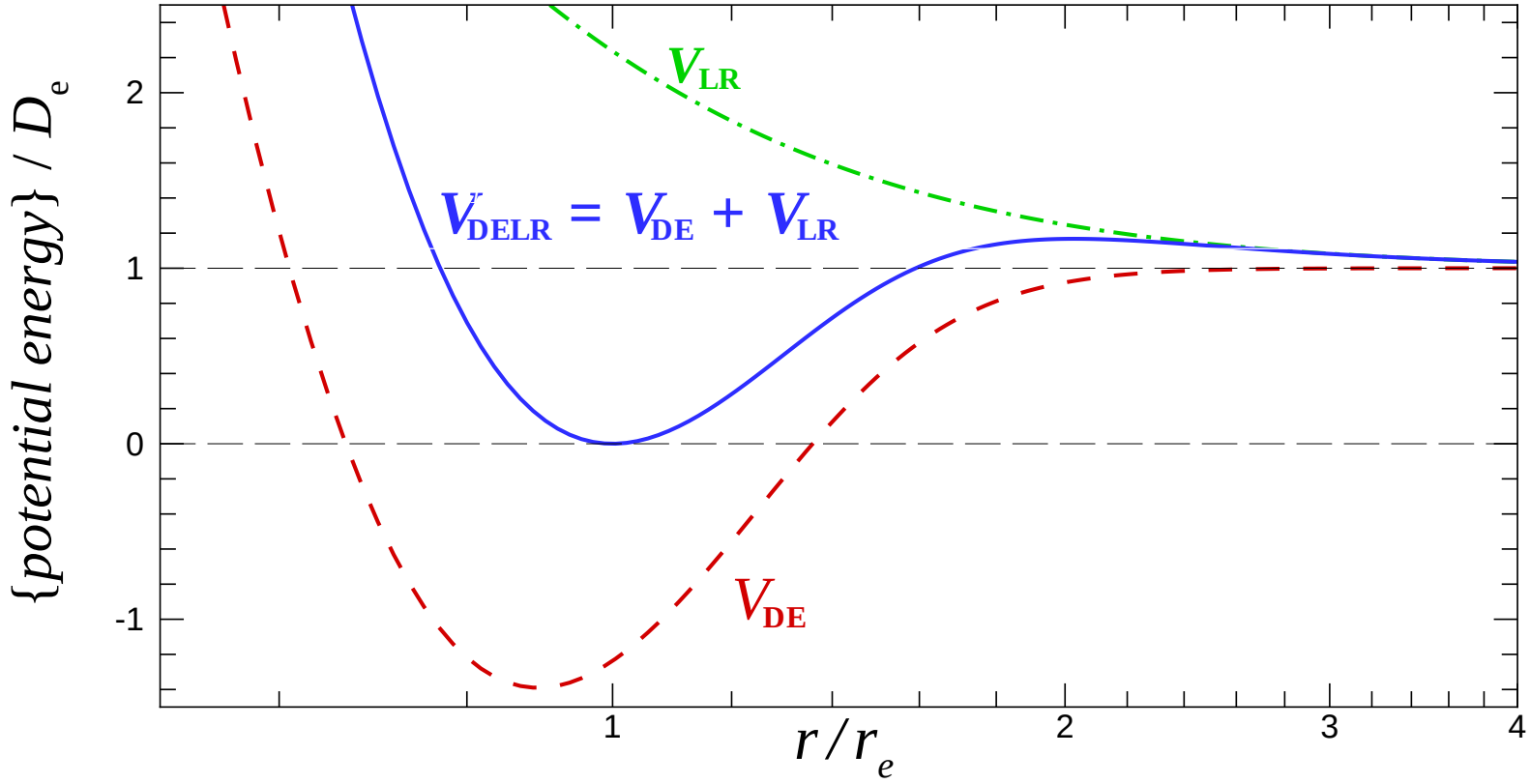
The Double-Exponential/Long-Range (DELR) Potential.

$$V_{\rm DELR}(r) \;=\; \Big[\, {\rm A}\, {\rm e}^{-2\,\beta({\rm y_q})({\rm r}-{\rm r_e})} \;-\; {\rm B}\, {\rm e}^{-2\,\beta({\rm y_q})({\rm r}-{\rm r_e})} \;+\; \mathfrak{D}_{\rm e} \,\Big] \;-\; u_{\rm LR}(r)$$

$$\xrightarrow{r \,\gg\, r_e} \;\; \mathfrak{D}_e \;-\; u_{\rm LR}(r) \;\simeq\; \mathfrak{D}_e \;-\; \frac{C_{m_1}}{r^{m_1}} \;-\; \frac{C_{m_2}}{r^{m_2}} \;-\; \ldots$$

with $\quad {\rm A} \;=\; \mathfrak{D}_{\rm e} \;-\; {\rm u_{LR}(r_e)} \;+\; {\rm u'_{LR}(r_e)}/\beta({\rm r_e})$

and $\quad {\rm B} \;=\; \mathfrak{D}_{\rm e} \;-\; 2\,{\rm u_{LR}(r_e)} \;+\; {\rm u'_{LR}(r_e)}/\beta({\rm r_e})$



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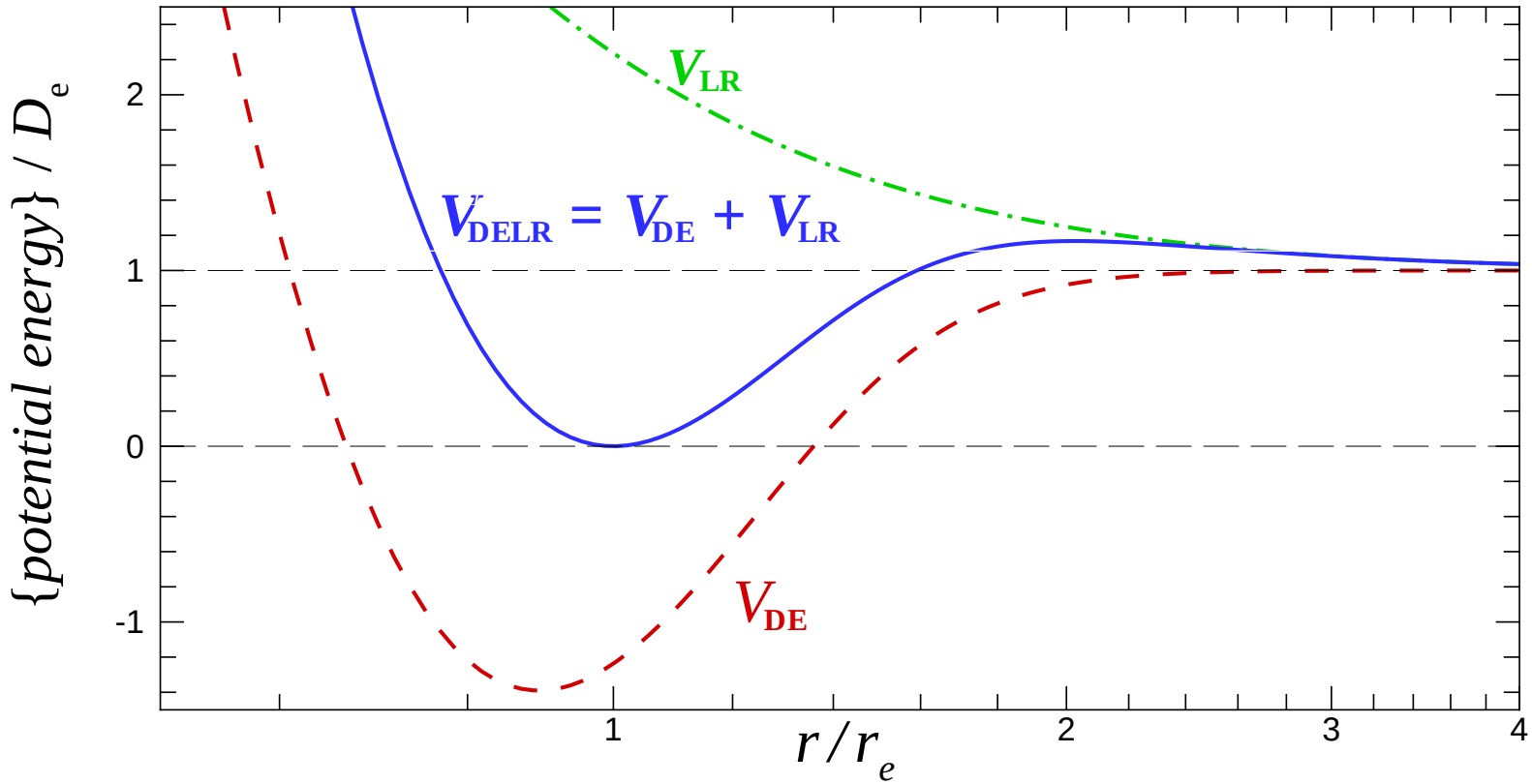

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In our previous study of the analogous $B\,^1\Pi_u$ state of Li_2,[26] the repulsive long-range part of the DELR potential was represented by a conventional sum of damped inverse-power term . . .

$$u_{\rm LR}(r) \equiv \sum_{i=1}^{last} D_{m_i}(r)\,\frac{C_{m_i}}{r^{m_i}} \simeq \frac{C_{m_1}}{r^{m_1}} + \frac{C_{m_2}}{r^{m_2}} + \ldots$$

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However, theory tells us that it should be represented by the middle eigenvalue of the 3×3 matrix $\mathbf{M_{LR}}(r)$:[28]

$$-\begin{pmatrix}
\sum_{n=3,6,8\ldots} D_n(r)\frac{C_n^{3\Sigma}+C_n^{1\Pi}+C_n^{3\Pi}}{3\,r^n} & \sum_{n=3,6,8\ldots} D_n(r)\frac{C_n^{3\Pi}+C_n^{1\Pi}-2C_n^{3\Sigma}}{3\sqrt{2}\,r^n} & \sum_{n=3,6,8\ldots} D_n(r)\frac{C_n^{3\Pi}-C_n^{1\Pi}}{\sqrt{6}\,r^n} \\
\sum_{n=3,6,8\ldots} D_n(r)\frac{C_n^{3\Pi}+C_n^{1\Pi}-2C_n^{3\Sigma}}{3\sqrt{2}\,r^n} & \sum_{n=3,6,8\ldots} D_n(r)\frac{C_n^{3\Pi}+C_n^{1\Pi}+4C_n^{3\Sigma}}{6\,r^n} + V_{\rm LIM} & \sum_{n=3,6,8\ldots} D_n(r)\frac{C_n^{3\Pi}-C_n^{1\Pi}}{2\sqrt{3}\,r^n} \\
\sum_{n=3,6,8\ldots} D_n(r)\frac{C_n^{3\Pi}-C_n^{1\Pi}}{\sqrt{6}\,r^n} & \sum_{n=3,6,8\ldots} D_n(r)\frac{C_n^{3\Pi}-C_n^{1\Pi}}{2\sqrt{3}\,r^n} & \sum_{n=3,6,8\ldots} D_n(r)\frac{C_n^{3\Pi}+C_n^{1\Pi}}{2\,r^n} + V_{\rm LIM}
\end{pmatrix}$$

The present work will compare these two models and determine whether the experimental data can distinguish between them!

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[27] Y. Huang and R.J. Le Roy, *J. Chem. Phys.* **119**,7398 (2003).

[28] M. Aubert-Frécon, G. Hadinger, S. Magnier and S. Rousseau, *J. Mol. Spectrosc.* **188**, 182 (1998).

Results: . . . and with 44 fitting parameters get $\overline{dd} = 1.63$ (over 30,169 data).

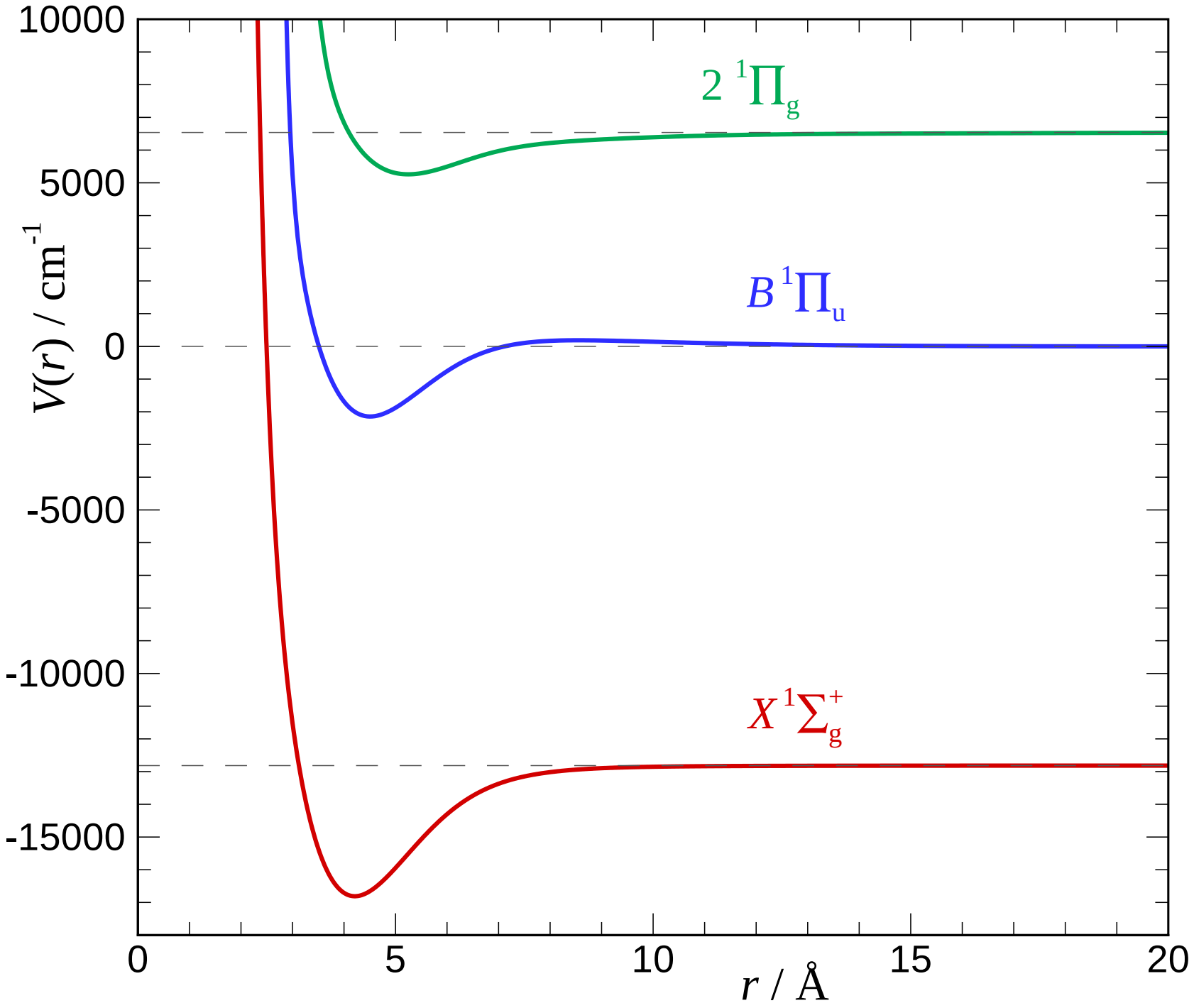
	$X\,^1\Sigma_g^+$(MLR)	$B\,^1\Pi_u$(DELR)	$2\,^1\Pi_g$(MLR)
$V_{\rm LIM}$	[−12816.545]	[0]	[6539.0665]
$\mathfrak{D}_e$	3993.618 (13)	2144.68842 (920)	1279.6087 (93)
r_e	4.209929 (41)	4.506241 (26)	5.246006 (38)
C_3^{Σ}	—	$[-5.984\times10^5]$	—
$C_3^{^1\Pi}$	—	$[-2.992\times10^5]$	—
$C_3^{^3\Pi}$	—	$[2.992\times10^5]$	—
C_5	—	—	$[8.894\times10^6]$
C_6^{Σ}	$[2.2338\times10^7]$	$[5.807\times10^7]$	—
$C_6^{^1\Pi}$	—	$[3.878\times10^7]$	$[7.1375\times10^7]$
$C_6^{^3\Pi}$	—	$[3.878\times10^7]$	—
C_8^{Σ}	$[7.6939\times10^8]$	$[1.277\times10^{10}]$	—
$C_8^{^1\Pi}$	—	$[1.528\times10^9]$	$[2.4584\times10^9]$
$C_8^{^3\Pi}$	—	$[5.672\times10^8]$	—
C_{10}	$[2.9916\times10^{10}]$	—	—
$\{p,\,q\}$	{5, 3}	{–, 3}	{5, 3}
$r_{\rm ref}$	[5.73]	[4.7]	[7.6]
β_0	0.0898006	0.7410021	0.616469
β_1	−0.74343386	0.283468	1.04582
β_2	−0.3428	0.163047	−1.617
β_3	0.67605	0.19056	−5.6496
β_4	1.1796093	0.1666	2.646
β_5	1.2845	0.148	2..41
β_6	1.3819	−1.5254	−8.
β_7	1.994	−0.689	−96.70655
β_8	1.495	4.641	−57.9
β_9	−0.7	−3.67	181.6
β_{10}	−2.	—	284.772
β_{10}	−2.28	—	120.
β_{11}	−4.1068	—	—
β_{12}	−3.55	—	—
β_{13}	−3.994	—	—
$\{p_{\rm ad},\,q_{\rm ad}\}$	$\{n/a\}$	{3, 3}	{3, 3}
u_0	—	−0.123(69)	0.20(7)
u_1	—	−1.03	−23.7
u_2	—	—	30.
u_3	—	—	20.
u_∞	—	[0.0]	[0.0]

Results: Compare fitted parmeters of our MLR model for the $X\,^1\Sigma_g^+$ state with those defining the 'Hannover Polynomial Potential' (HPP) model of Strauss *et al.*[29]

	MLR(present)		HPP(Strauss)
$\mathfrak{D}_e$	3993.618 (12)		3993.593 (3)
r_e	4.209929 (4)		3.02991 (5)
β_0	0.0898006	a_0	3.993592873×10^{3}
β_1	−0.74343386	a_1	0.000000000000000000
β_2	−0.3428	a_2	$0.282069372972346137\times10^{5}$
β_3	0.67605	a_3	$0.560425000209256905\times10^{4}$
β_4	1.1796093	a_4	$-0.423962138510562945\times10^{5}$
β_5	1.2845	a_5	$-0.598558066508841584\times10^{5}$
β_6	1.3819	a_6	$-0.162613532034769596\times10^{5}$
β_7	1.994	a_7	$-0.405142102246254944\times10^{5}$
β_8	1.495	a_8	$0.195237415352729586\times10^{6}$
β_9	−0.7	a_8	$0.413823663033582852\times10^{6}$
β_{10}	−2.	a_{10}	$-0.425543284828921501\times10^{7}$
β_{10}	−2.28	a_{11}	$0.546674790157210198\times10^{6}$
β_{11}	−4.1068	a_{12}	$0.663194778861331940\times10^{8}$
β_{12}	−3.55	a_{13}	$-0.558341849704095051\times10^{8}$
β_{13}	−3.994	a_{14}	$-0.573987344918535471\times10^{9}$
		a_{15}	$0.102010964189156187\times10^{10}$
		a_{16}	$0.300040150506311035\times10^{10}$
		a_{17}	$-0.893187252759830856\times10^{10}$
		a_{18}	$-0.736002541483347511\times10^{10}$
		a_{19}	$0.423130460980355225\times10^{11}$
		a_{20}	$-0.786351477693491840\times10^{10}$
		a_{21}	$-0.102470557344862152\times10^{12}$
		a_{22}	$0.895155811349267578\times10^{11}$
		a_{23}	$0.830355322355692902\times10^{11}$
		a_{24}	$-0.150102297761234375\times10^{12}$
		a_{25}	$0.586778574293387070\times10^{11}$

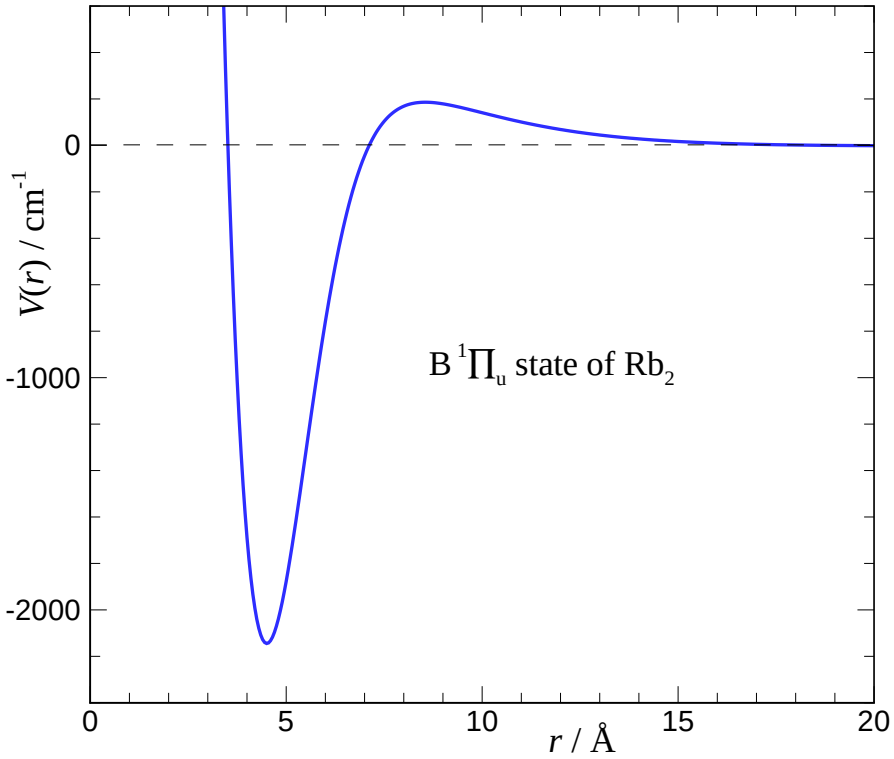
[29] C. Strauss, T. Takekoshi, F. Lang, K. Winkler, R. Grimm, J.H. Denschlag, and E. Tiemann, *Phys. Rev. A* **82**, 052514 (2010).

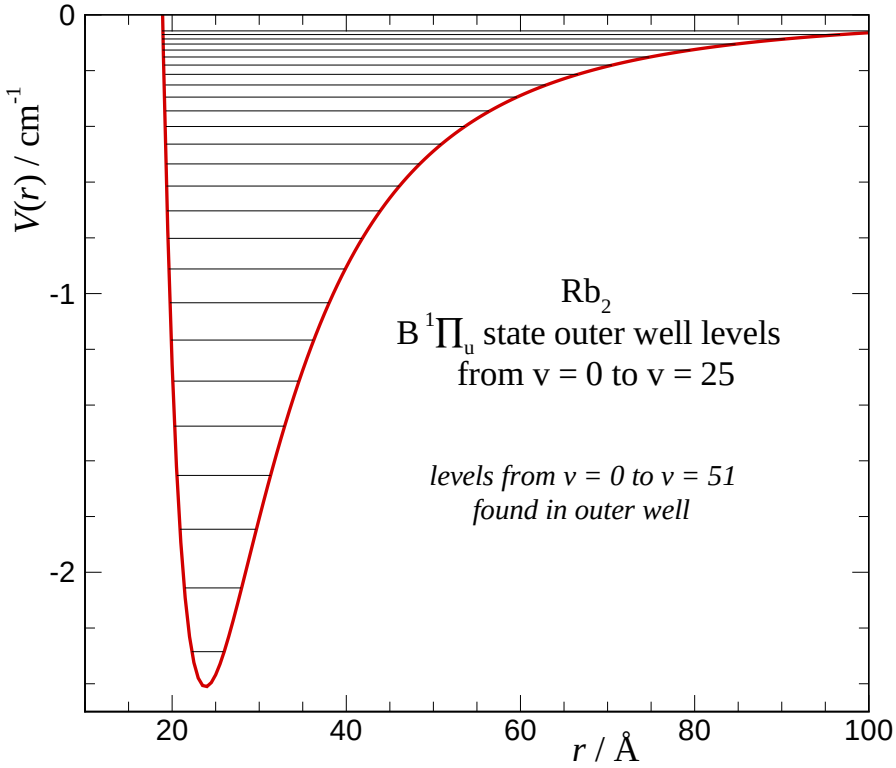
Results: Our analysis yields accurate analytic potentials for the three states!



Results:

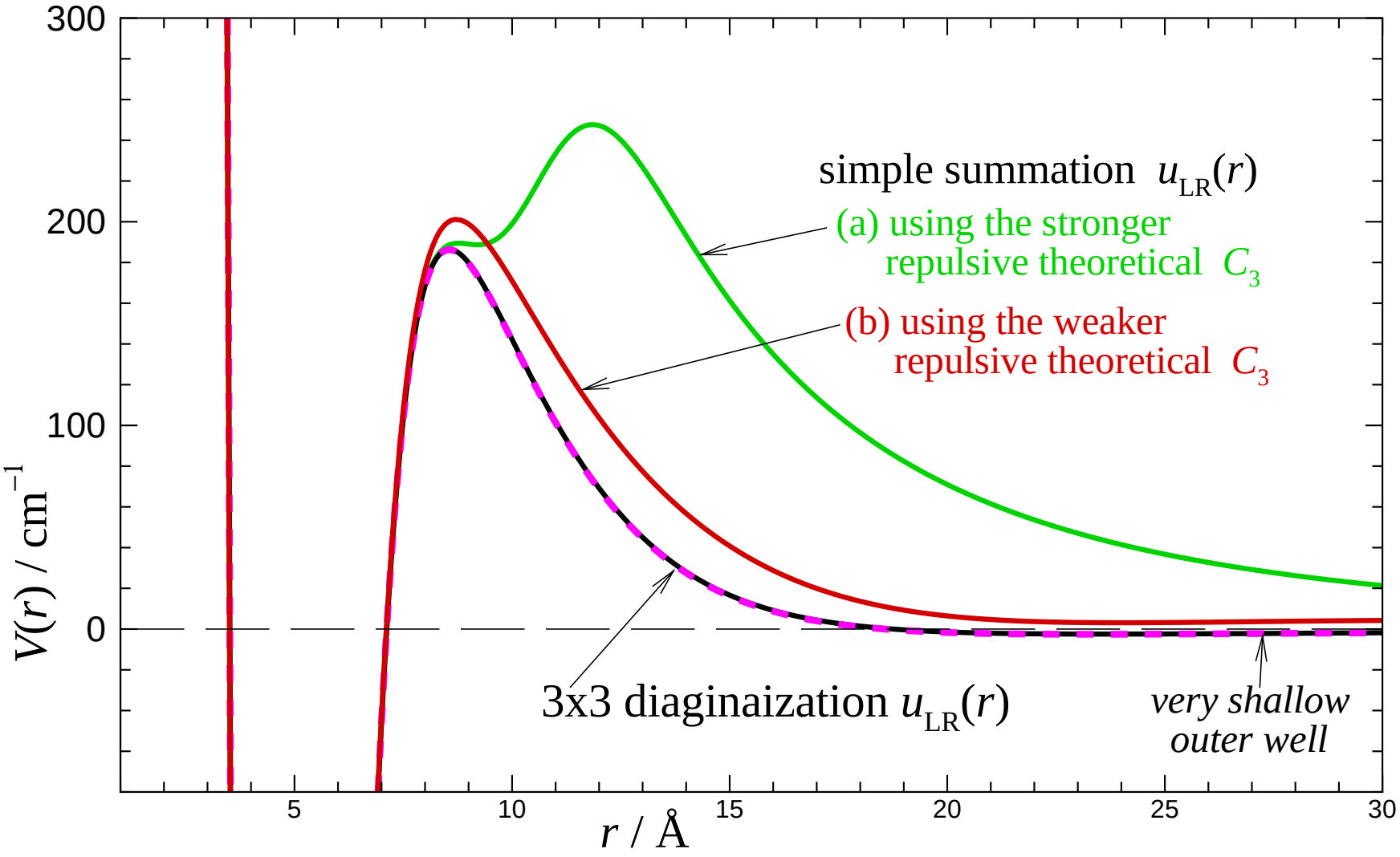
. . . and in addition to determining the $B\,^1\Pi_u$ state potential well and barrier properties, the present analysis delineates the properties of its long-predicted[30] outer well centred at 24 Å, which is found to support 51 vibrational levels!





[30] M. Movre and G. Pichler, *J. Phys. B: At. Mol. Phys.* **10**, 2631 (1977).

Results: {*Conclusions re. for* 3×3 *vs. simple sum, for* $u_{\mathrm{LR}}(r)$ *not yet fully clear . . . !* }



Conclusions:

- We have determined fully analytic PECs for the $X\,^1\Sigma_g^+$, $B\,^1\Pi_u$, and $2\,^1\Pi_g$ states of Rb_2 whose *44 fitted parameters* compactly summarize our spectroscopic knowledge of these species.

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- An isotopologue-dependent 3-parameter "effective non-adiabatic" centrifugal BOB function must be included in the model for the $B\,^1\Pi_u$ state to fully explain the data.