

Uncertainties in Properties Calculated from Fitted Potential Energy Functions

and

~~Determining Potential Energy Functions from Fits to Bound \rightarrow Continuum Intensity Data~~

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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.

However, *this offers little help with:*

- collisional properties including virial coefficients, diffusion, thermal conductivity and other transport properties, and various scattering cross sections

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

But *How do we determine such potentials ?*

Ans. ... from *Least-Squares Fits to Experimental Data*

{ For 3-D Van der Waals molecules since 1974, and for diatomics since ~ 1990 }

- Simulate experimental data as properties $F_i(\{p_j\})$ of some parametrized analytic potential energy function $V(r; \{p_j\})$
- Calculate the partial derivatives of each value of each property w.r.t. each potential function parameter: $\partial F_i(\{p_j\})/\partial p_k$
- Compare predictions with experiment, and optimize potential parameters via an iterative (*non-linear*) least-squares fit
- For spectroscopic transition energies this is relatively straightforward, since the data are level energy differences $F_i = E(v', J') - E(v'', J')$, and the partial derivatives of a level energy w.r.t. parameters p_k required for fitting may readily be generated using the Hellmann-Feynman theorem:

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

- In diatomic molecule data analysis this approach is (almost) becoming ‘routine’.

But what are the uncertainties associated with such potentials, and with properties calculated from them ?

Part of the answer to this question is certainly straightforward:

- the correlated uncertainties in the parameters determined in the fit tell us about those uncertainties
- *but tell us what ?? ... and how ??*

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- *but tell us what ?? ... and how ??*

Statistics texts tell us that: If a property $F(\{p_j\})$ is defined by a set of M parameters $\{p_j\}$ that were determined from a least-squares fit that yielded parameter uncertainties $\{u(p_j)\}$ and the $M \times M$ correlation matrix \mathbf{C} , the uncertainty in the value of $F(\{p_j\})$ is:

$$u(F) = \sqrt{\mathbf{D}^t \cdot \mathbf{C} \cdot \mathbf{D}}$$

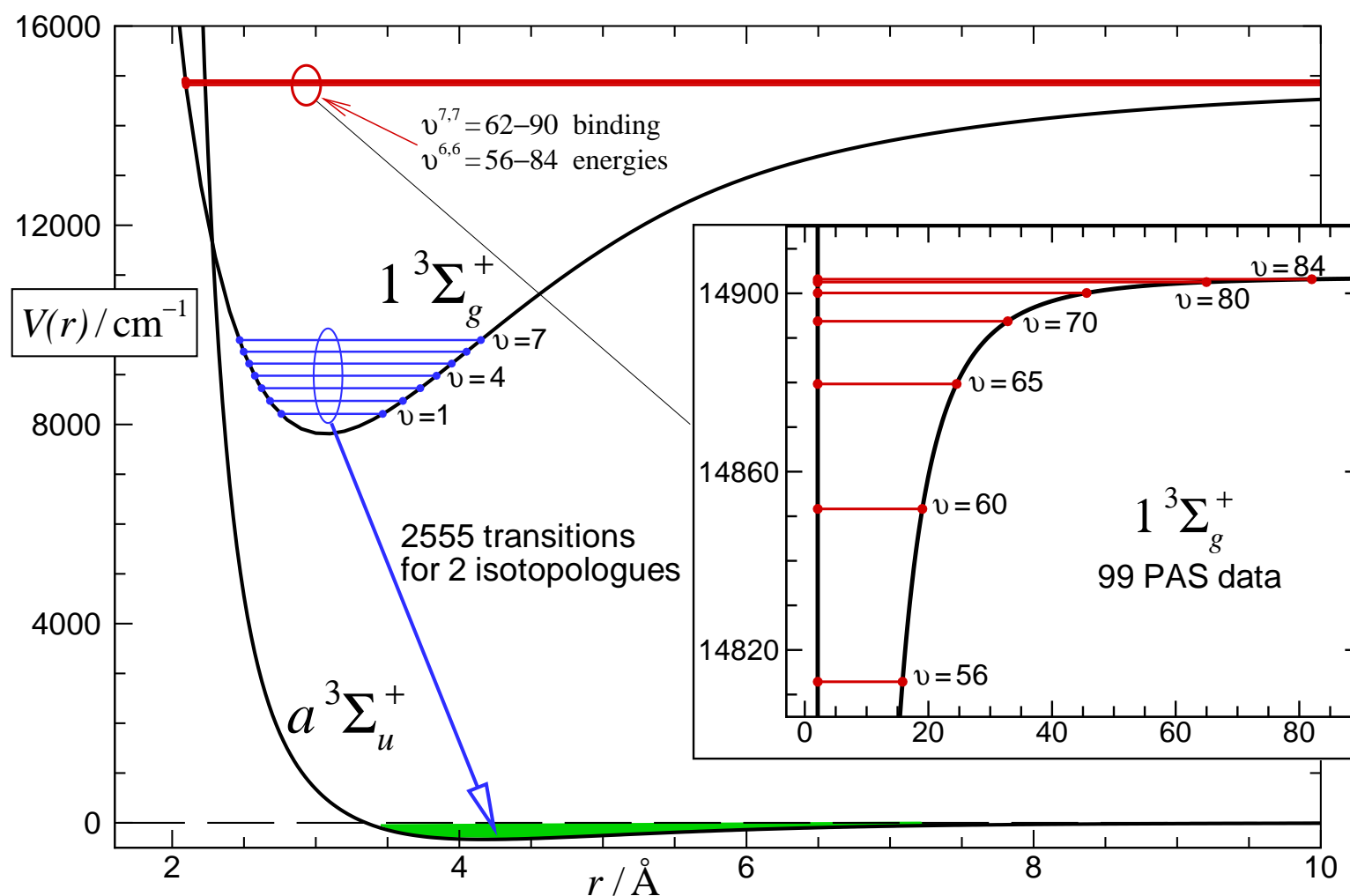
where \mathbf{D} is an $M \times 1$ column matrix of elements $D_k = u(p_k) \times \frac{\partial F(\{p_j\})}{\partial p_k}$ and \mathbf{D}^t is its transpose (a $1 \times M$ row matrix).

This technique may readily be applied to calculate uncertainties in the potential function itself $u\{V(r; \{p_j\})\}$ or its eigenvalues $u\{E(v, J; \{p_j\})\}$, since the required partial derivatives are readily available.

For example, a recent fit to high quality spectroscopic data for the $1^3\Sigma_g^+$ state of Li_2 was used to determine an analytic ‘MLR’ potential energy function for this state

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

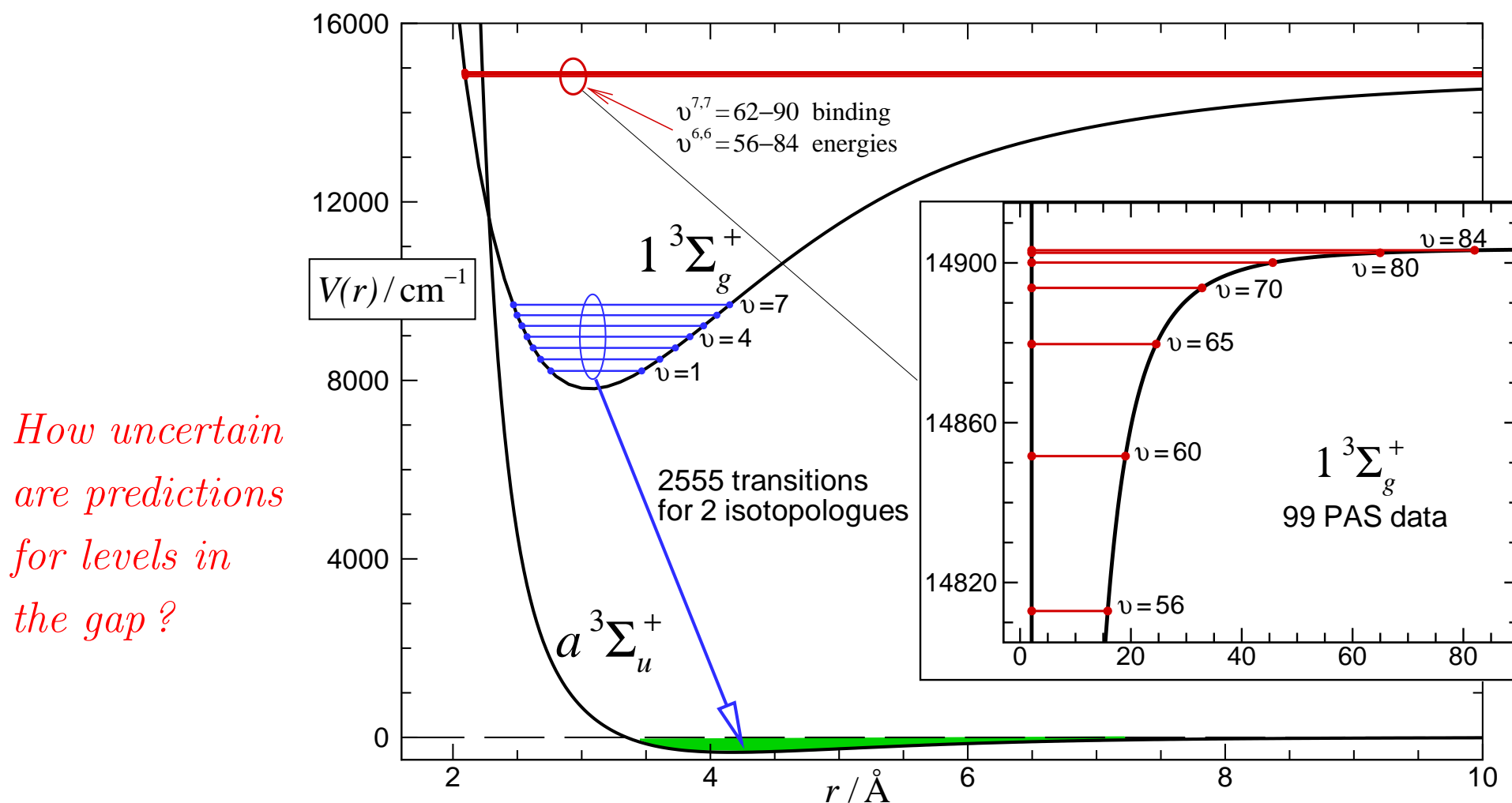
that bridged a large gap between measurements for levels near the bottom of the well, and for levels lying *very* near dissociation.



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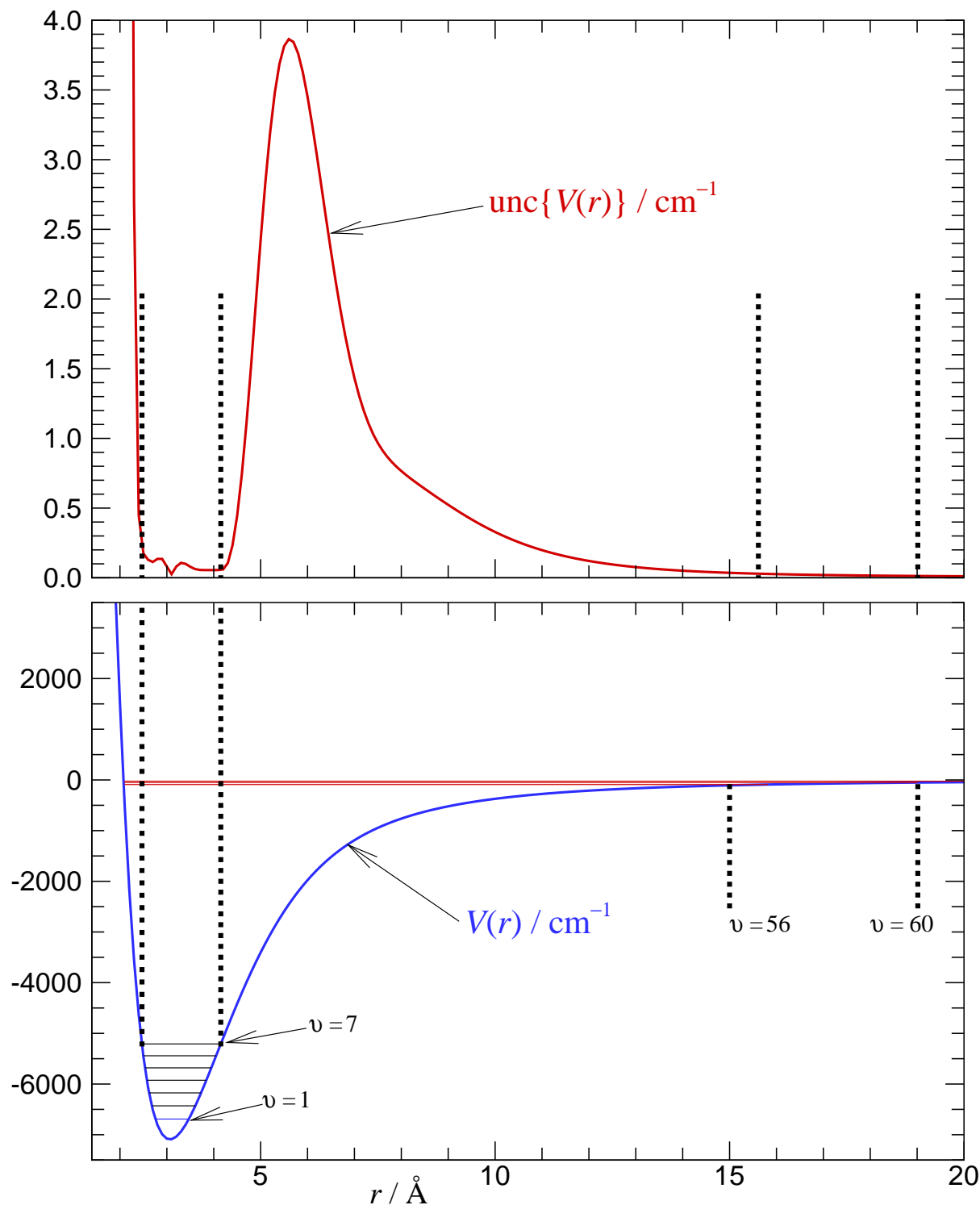
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Calculus readily yields values of the partial derivatives

$$\frac{\partial V(r; \{p_j\})}{\partial p_k},$$

while the parameter uncertainties $u(p_k)$ and correlation matrix **C** were provided by the least-squares fit, so it is straightforward to calculate the uncertainty in the potential, $unc\{V(r)\}$, as a function of r .

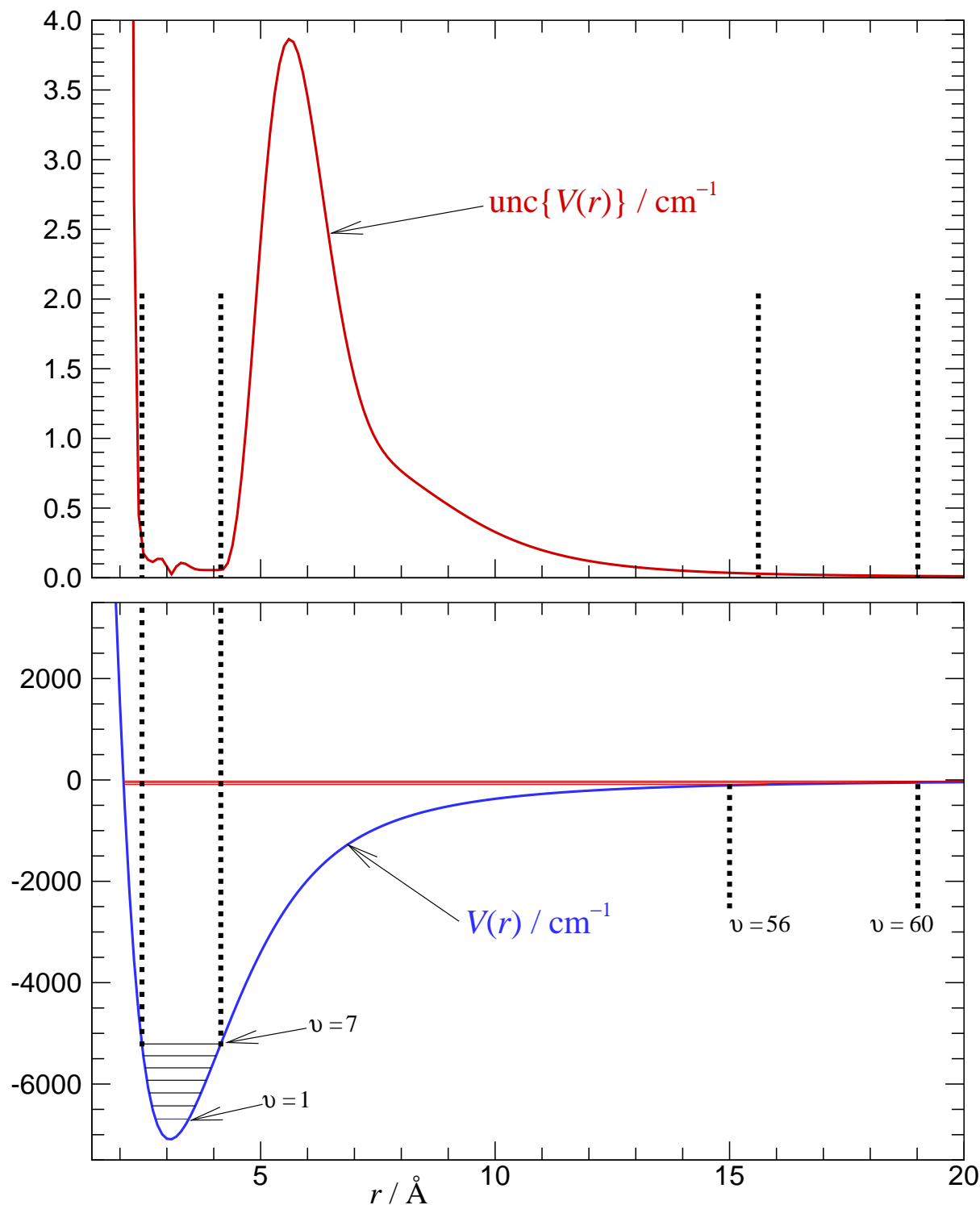


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*A nice result,
but $V(r)$ is not
an observable ...*



Very recently, new *very* high resolution ($\pm 0.000002 \text{ cm}^{-1}$) PAS experiments at UBC were searching the region $\sim 2000 - 3000 \text{ cm}^{-1}$ below dissociation, and those researchers wanted estimates of the energies and B_v values for levels in that 5000 cm^{-1} wide intermediate region (*and of their uncertainties!*).

PHYSICAL REVIEW A **87**, 052505 (2013)

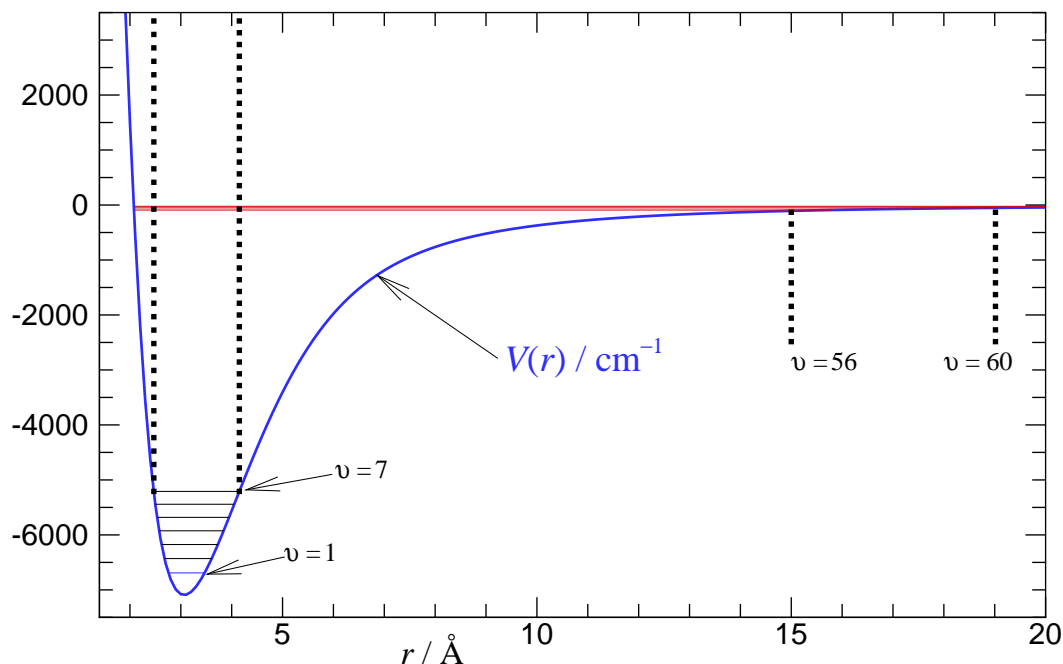
High-resolution photoassociation spectroscopy of the ${}^6\text{Li}_2 \ 1^3\Sigma_g^+$ state

Mariusz Semczuk,¹ Xuan Li,² Will Gunton,¹ Magnus Haw,¹ Nikesh S. Dattani,³
Julien Witz,¹ Arthur K. Mills,¹ David J. Jones,¹ and Kirk W. Madison¹

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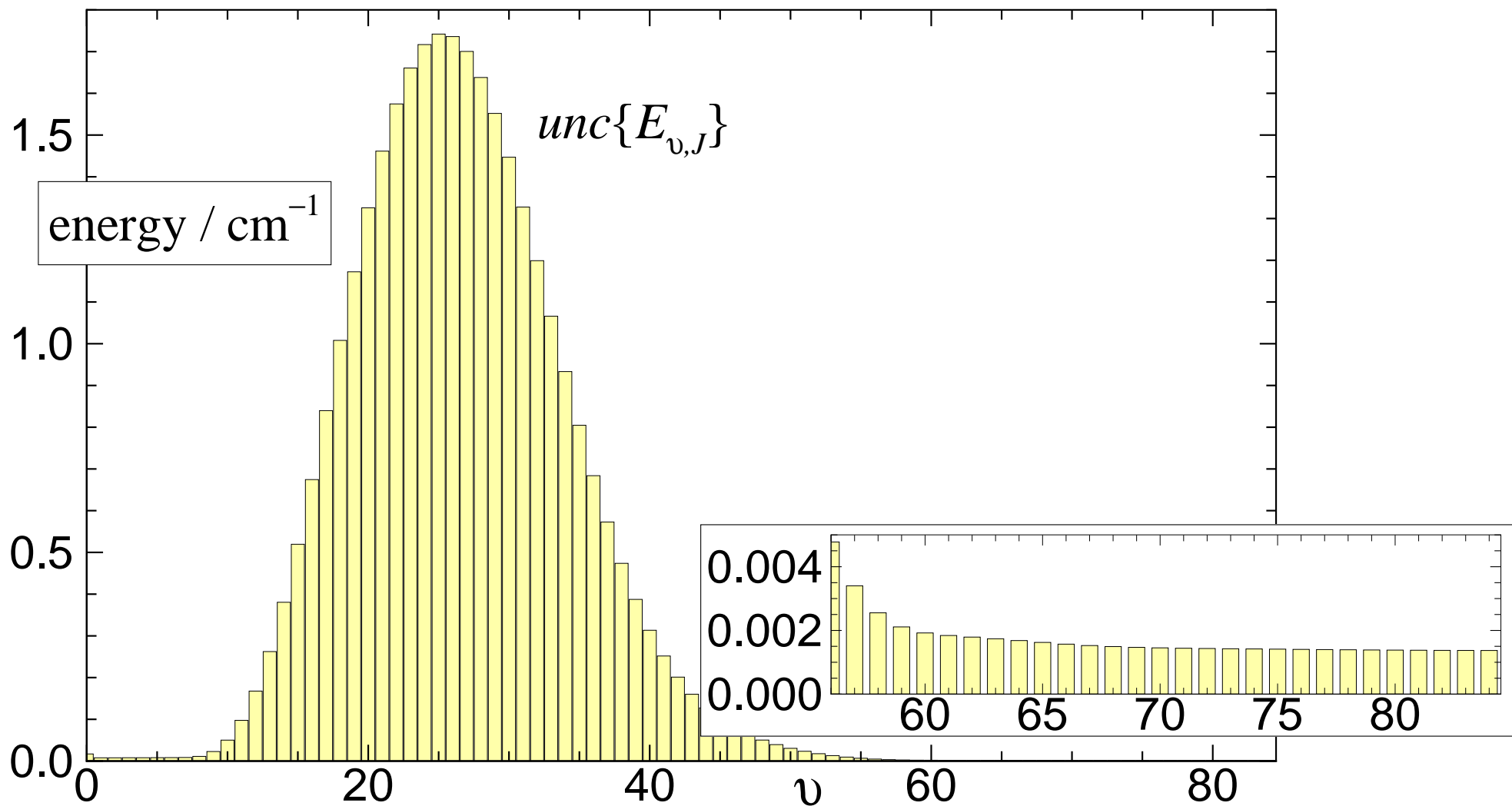
For the *level energies*, addressing this need is straightforward, since the fit that determined the optimum model for the potential gave predictions

- for the energies of the ‘missing’ levels,
- for the parameter uncertainties $\{u(p_k)\}$, and
- for the correlation matrix of the fit \mathbf{C} ,

while the required partial derivatives may be generated readily using the

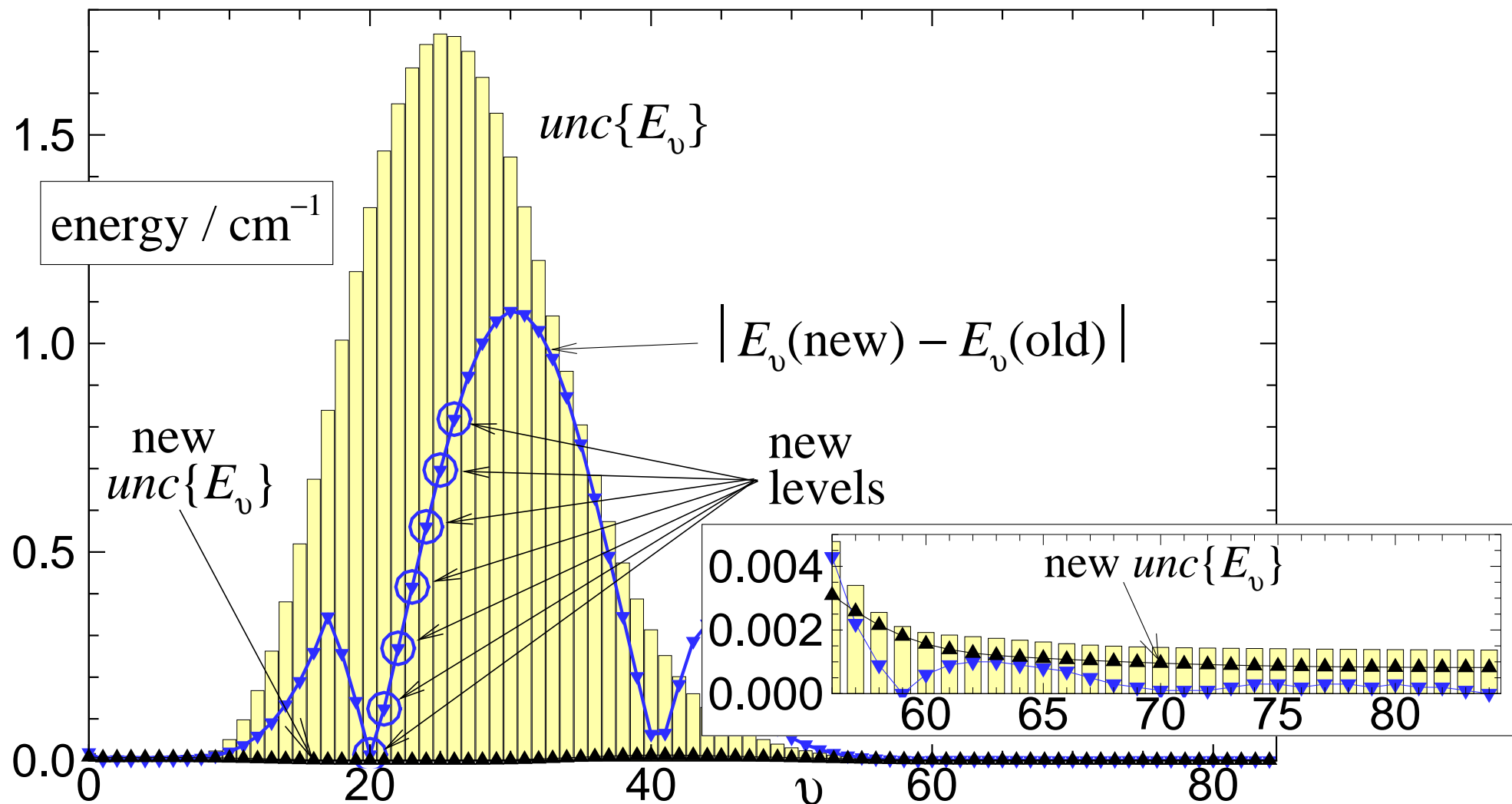
Hellmann-Feynman theorem expression $\frac{\partial E(v,J)}{\partial p_k} = \left\langle \psi_{v,J} \left| \frac{\partial V(r;\{p_j\})}{\partial p_k} \right| \psi_{v,J} \right\rangle$.

Here we show the level energy uncertainties predicted from the original (2011) fitted potential that was based on data for $v = 1 - 7$ and $v = 56 - 84$.



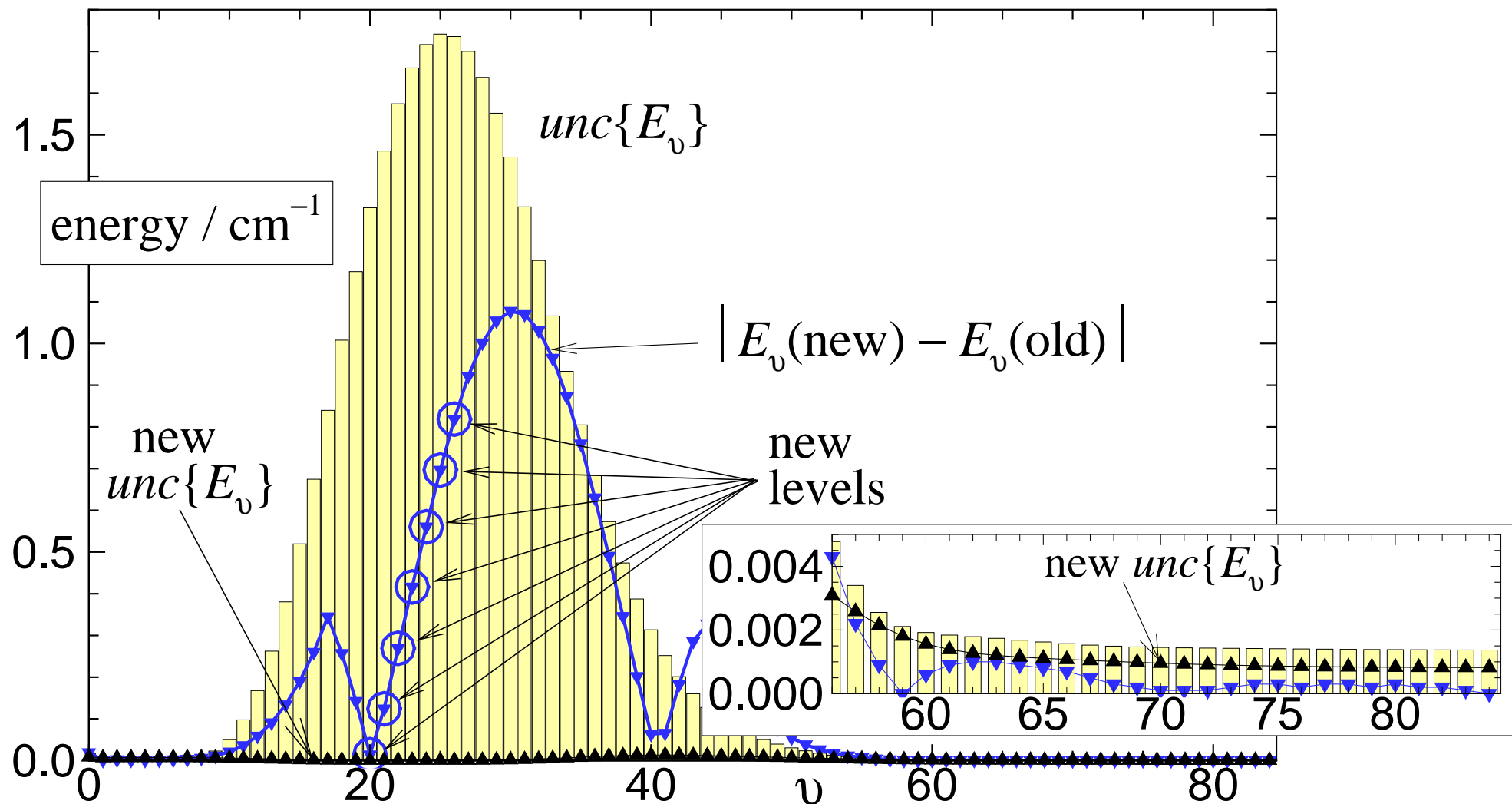
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Now, compare those predictions to the changes $|E_{v,J}(\text{new}) - E_{v,J}(\text{old})|$ when the fit was repeated while including the new (2013) data for $v = 20 - 26$.



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Conclude: *these predicted uncertainties are realistic!*

However ... predicting the uncertainties in B_v values is not straightforward, because the partial derivatives $\partial B_v / \partial p_k$ are not obtained directly. In particular, from the definition of

$$B_v \equiv \frac{\hbar^2}{2\mu} \left\langle \psi_{v,0}(r) \left| \frac{1}{r^2} \right| \psi_{v,0}(r) \right\rangle$$

we see that

$$\frac{\partial B_v}{\partial p_k} = 2 \left(\frac{\hbar^2}{2\mu} \right) \left\langle \frac{\partial \psi_{v,0}(r)}{\partial p_k} \left| \frac{1}{r^2} \right| \psi_{v,0}(r) \right\rangle$$

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but **how do we determine** $\frac{\partial \psi_{v,0}(r)}{\partial p_k}$??

Ans: The proper way to determine $\frac{\partial \psi(v,0)}{\partial p_k}$ and hence $\frac{\partial B_v}{\partial p_k}$ starts (*as do most things in my universe*) with the radial Schrödinger equation

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2 \psi_{v,J}(r)}{\partial r^2} + \left[V(r) + \frac{\hbar^2 [J(J+1)]}{2\mu r^2} - E_{v,J} \right] \psi_{v,J}(r) = 0$$

Applying the operator $\partial / \partial p_k$, defining $\psi_{v,J}^{(k)}(r) \equiv \frac{\partial \psi_{v,J}(r)}{\partial p_k}$,

and separating off terms involving $\psi_{v,J}(r)$ from those involving $\psi_{v,J}^{(k)}(r)$, we obtain

$$\begin{aligned}
-\frac{\hbar^2}{2\mu} \frac{\partial^2 \psi_{v,J}^{(k)}(r)}{\partial r^2} + \left[V(r) + \frac{\hbar^2[J(J+1)]}{2\mu r^2} - E_{v,J} \right] \psi_{v,J}^{(k)}(r) \\
= \left[\frac{\partial E_{v,J}}{\partial p_k} - \frac{\partial V(r)}{\partial p_k} \right] \psi_{v,J}(r)
\end{aligned}$$

The homogeneous left-hand side of this equation has exactly the same form as the original Schrödinger equation, while the right-hand side is known, since solution of the Schrödinger equation gave us the wavefunction $\psi_{v,J}(r)$, and the Hellman-Feynman theorem gave us a value for $\partial E_{v,J}/\partial p_k$

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This linear inhomogeneous differential equation has exactly the same form as the one encountered in Hutson's perturbation theory method for calculating the leading centrifugal distortion constants (see [*J.Phys.B* **14**, 851 (1981)]), except that in that case the inhomogeneous part was $\frac{2\mu}{\hbar^2} \left(B_v - \frac{\hbar^2}{2\mu r^2} \right) \psi_{v,J}(r)$.

Thus, it was a straightforward matter to revise/adapt **Tellinghuisen's** subroutine for calculating distortion constants to solve the above equation for $\psi_{v,J}^{(j)}(r)$, and thence to calculate the $\partial B_v/\partial p_k$, and hence to generate values of $unc(B_v)$.

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But why do we care about the uncertainties $unc(B_v)$??

High-resolution photoassociation spectroscopy of the ${}^6\text{Li}_2$ $1^3\Sigma_g^+$ state

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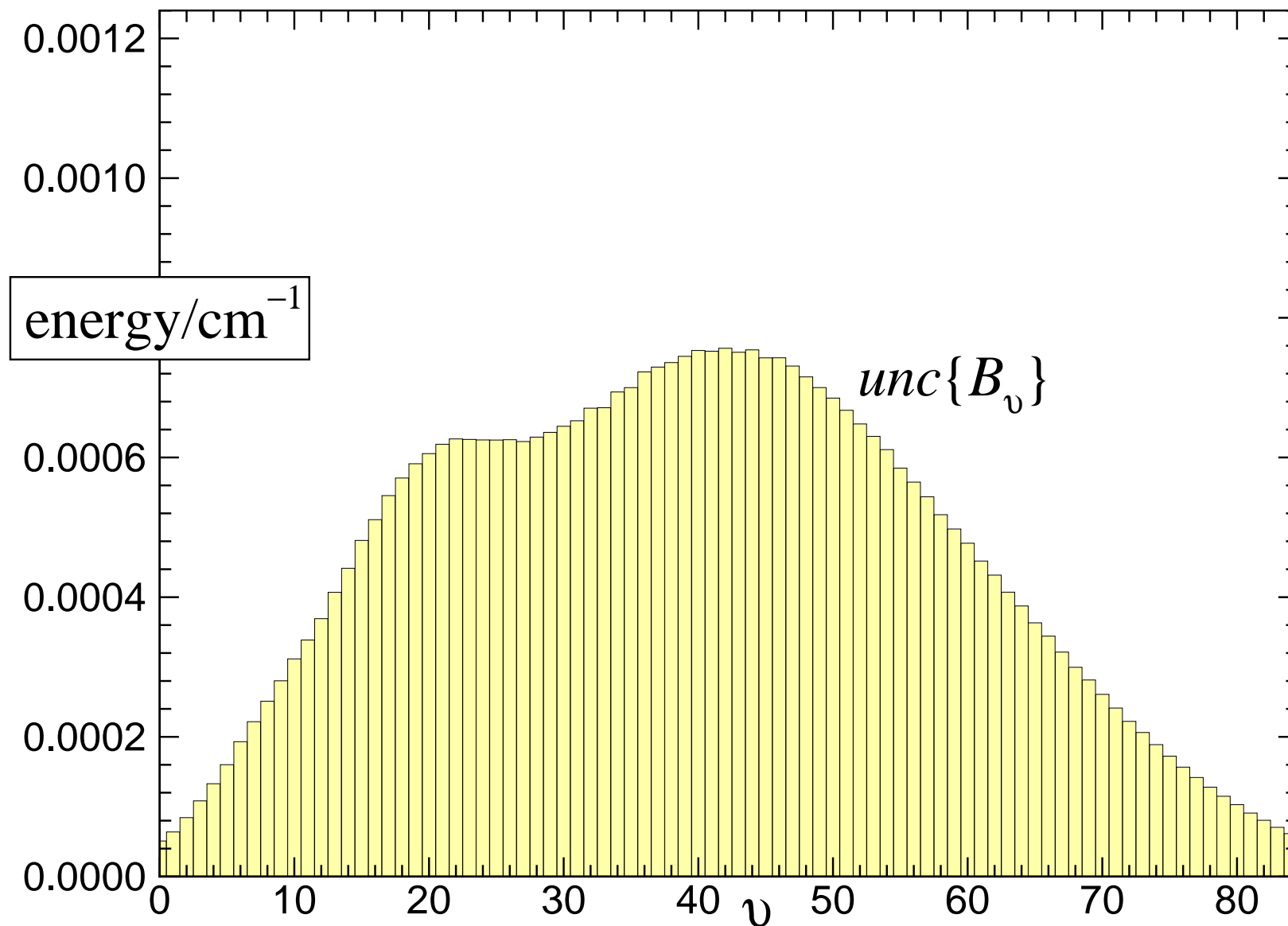
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These very high resolution experiments ($\pm 0.00002 \text{ cm}^{-1}$) resolve splittings due to spin-spin and spin-rotation interactions.

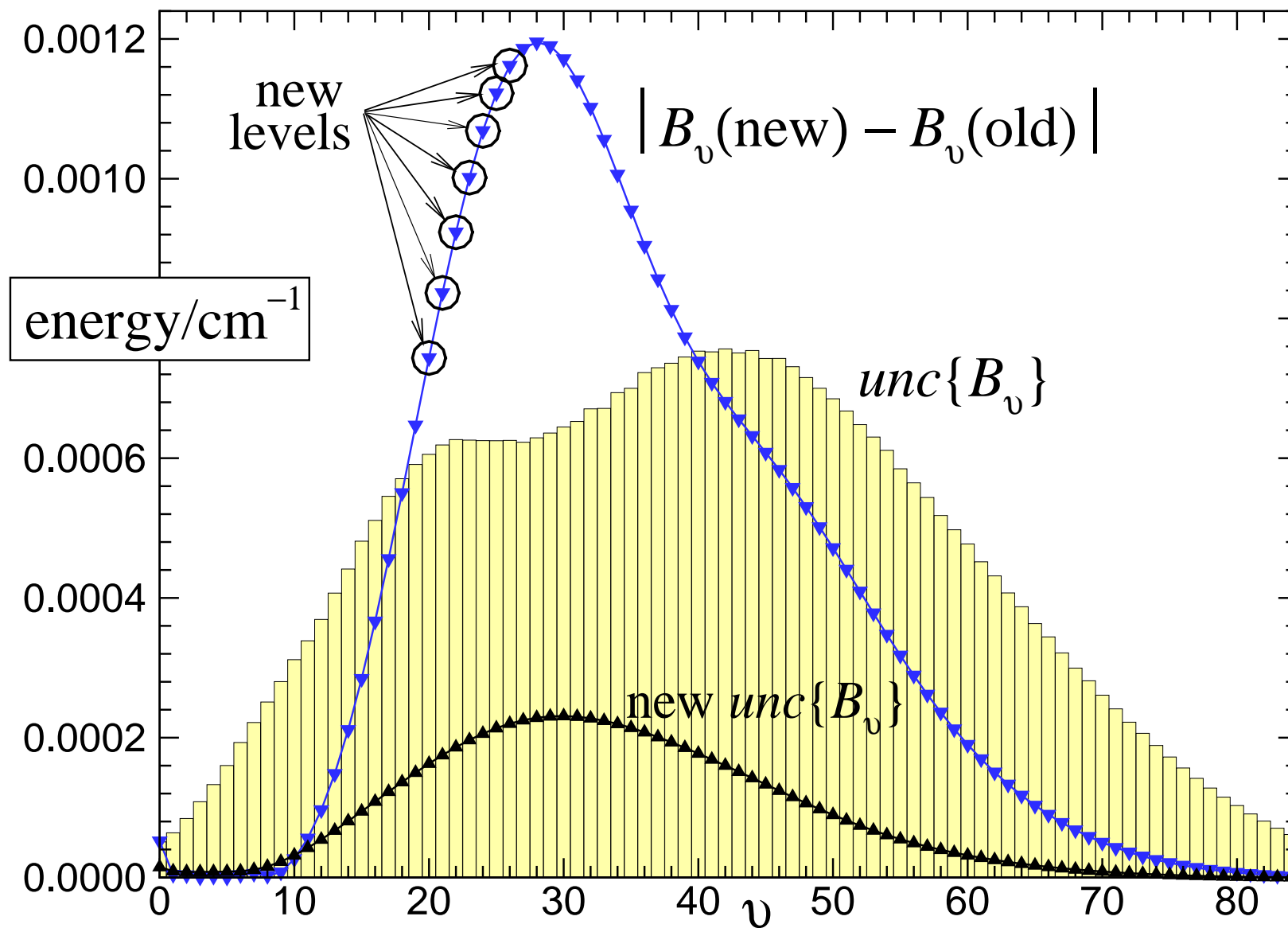
$$\begin{aligned} F_{J=N+1} &= B_v N(N+1) + (2N+3)B_v - \lambda_v \\ &\quad - \sqrt{(2N+3)^2 B_v^2 + \lambda_v^2 - 2\lambda_v B_v + \gamma_v(N+1)}, \\ F_{J=N} &= B_v N(N+1), \\ F_{J=N-1} &= B_v N(N+1) - (2N-1)B_v - \lambda_v \\ &\quad + \sqrt{(2N-1)^2 B_v^2 + \lambda_v^2 - 2\lambda_v B_v - \gamma_v N}, \end{aligned} \tag{1}$$

However, the uncertainties in the spin-spin and spin-rotation constants λ_v and γ_v determined from these equations depend on the uncertainty in B_v !

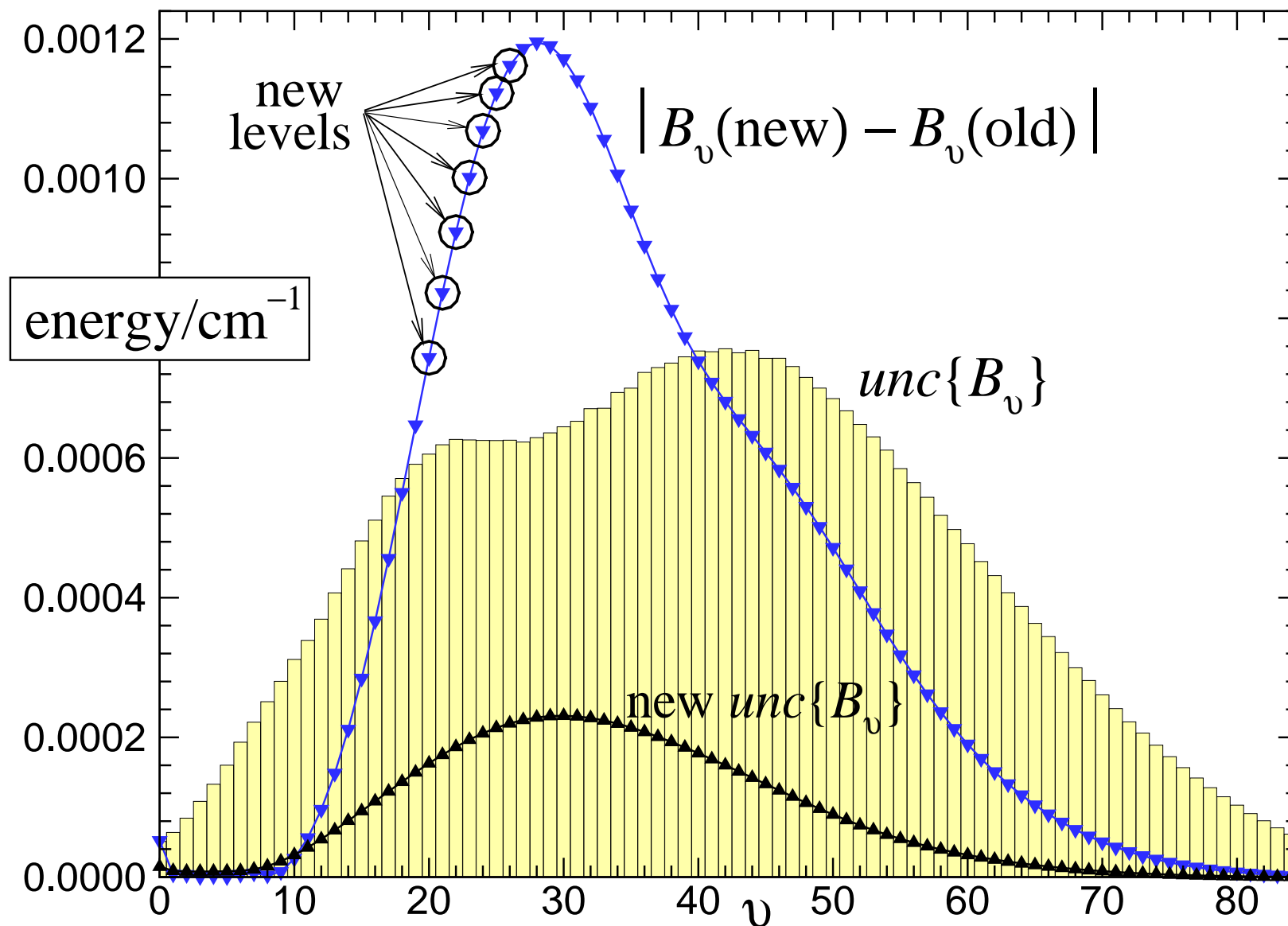
Uncertainties in B_v values calculated from a fitted potential energy function may now be generated using partial derivatives $\partial B_v / \partial p_k$ calculated from the $\psi_{v,J}^{(k)}(r)$!



Let us test these predictions of $unc(B_v)$ by comparing them with changes in the B_v values upon including the new (2013) $v = 20 - 26$ Li_2 data in the fit.



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again ... *we conclude that our predicted uncertainties are quite realistic!*

Part II

Determining Potential Energy Functions from Fits to Bound→Continuum Intensity Data

The Journal of Chemical Physics, Vol. 65, No. 4, 15 August 1976

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Diatom potential curves and transition moment functions from continuum absorption coefficients: $\text{Br}_2^{*†}$

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(Received 22 April 1976)

JOURNAL OF CHEMICAL PHYSICS

VOLUME 117, NUMBER 20

22 NOVEMBER 2002

1 potential, 2 potentials, 3 potentials—4: Untangling the UV photodissociation spectra of HI and DI

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7806

J. Phys. Chem. A **2004**, 108, 7806–7813

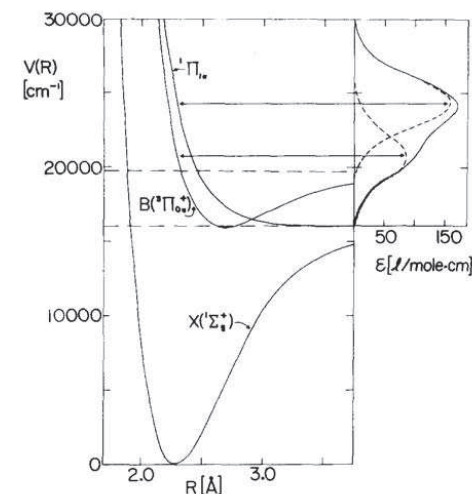
Probing Excited Electronic States Using Vibrationally Mediated Photolysis: Application to Hydrogen Iodide[†]

Jon P. Camden, Hans A. Bechtel, Davida J. Ankeny Brown, Andrew E. Pomerantz, and Richard N. Zare*

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Probing Electronic States with Photolysis

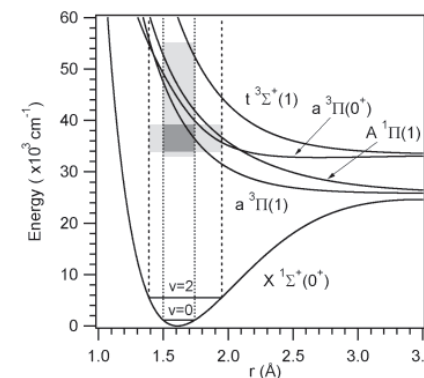


Figure 1. Empirical potential energy curves⁴³ for the lowest electronic states of HI labeled according to the historic Hund's case (a) notation.

In $\text{bound} \rightarrow \text{continuum}$ spectra, the normal observable is the thermal absorption cross-section

$$\sigma_T(\nu) = A \nu \sum_{v'', J''} F_{v'', J''}(T) \sum_u (E_u)^{-1/2} \sum_{J'} \frac{g_u S_{J''}^{J'}}{(2J'' + 1)} \mathfrak{I}(v'', J'', E_u)$$

which depends on the frequency of the light ν , the temperature of the sample T , and matrix elements between discrete-level bound-state wavefunctions $\psi_{v'', J''}(r)$ and continuum wavefunctions $\psi_{E_u, J'}(r)$ at final-state energy E_u :

$$\mathfrak{I}(v'', J'', E_u) \propto \left| \langle \psi_{v'', J''}(r) | M(r) | \psi_{E_u, J'}(r) \rangle \right|^2$$

In most cases, the potential that defines the initial-state wavefunctions $\psi_{v'', J''}(r)$ is known, and the objective is to determine the repulsive potential that determines the final-state continuum wavefunctions $\psi_{E_u, J'}(r)$.

However, to fit to measured intensities to determine an analytic final-state potential $V(r; \{p_k\})$, one requires values of the partial derivatives with respect to its parameters, and inside the various levels of summation we need to determine:

$$\frac{\partial \mathfrak{I}(v'', J'', E_u; \{p_j\})}{\partial p_k} = 2 \left| \langle \psi_{v'', J''}(r) | M(r) | \psi_{E_u, J'}(r) \rangle \right| \left\langle \psi_{v'', J''}(r) \left| M(r) \right| \frac{\partial \psi_{E_u, J'}(r; \{p_k\})}{\partial p_k} \right\rangle$$

The wavefunction partial derivatives at the core of this expression

$$\psi_{E_u, J'}^{(j)}(r; \{p_k\}) \equiv \frac{\partial \psi_{E_u, J'}(r; \{p_k\})}{\partial p_k}$$

are defined by exactly the same type of linear inhomogeneous differential equation encountered above:

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2 \psi_{v, J}^{(j)}(r)}{\partial r^2} + \left[V(r) + \frac{\hbar^2 [J(J+1)]}{2\mu r^2} - E_u \right] \psi_{v, J}^{(j)}(r) = -\frac{\partial V(r)}{\partial p_k} \psi_{v, J}(r)$$

that can be solved using the same procedure. *However*, for the bound-state case the orthogonality relation arising from the unit normalization

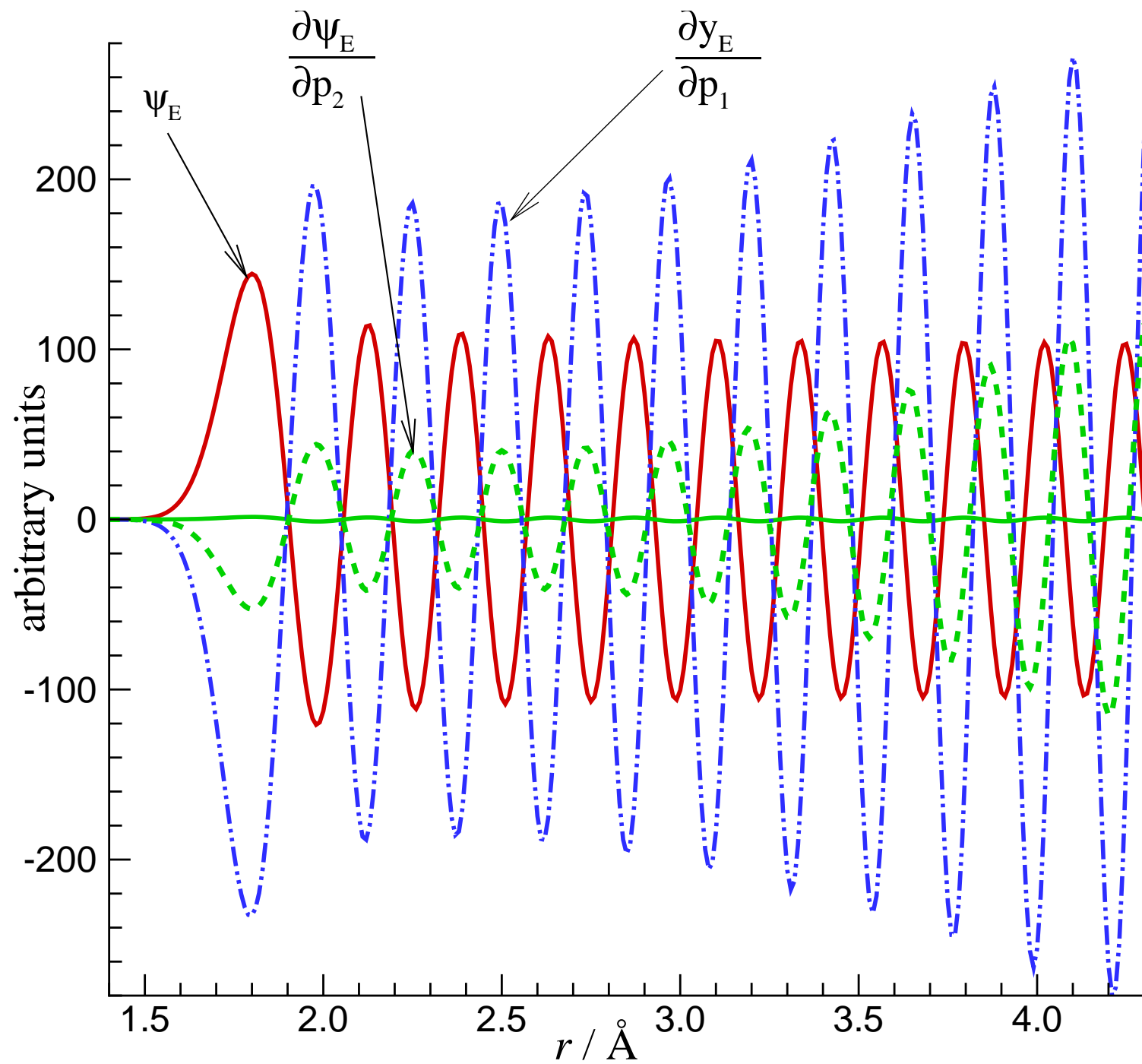
$$\langle \psi_h | \psi_h \rangle = 1$$

which means that

$$\frac{\partial \langle \psi_h | \psi_h \rangle}{\partial p} = 0 = 2 \left\langle \frac{\partial \psi_h}{\partial p} \middle| \psi_h \right\rangle$$

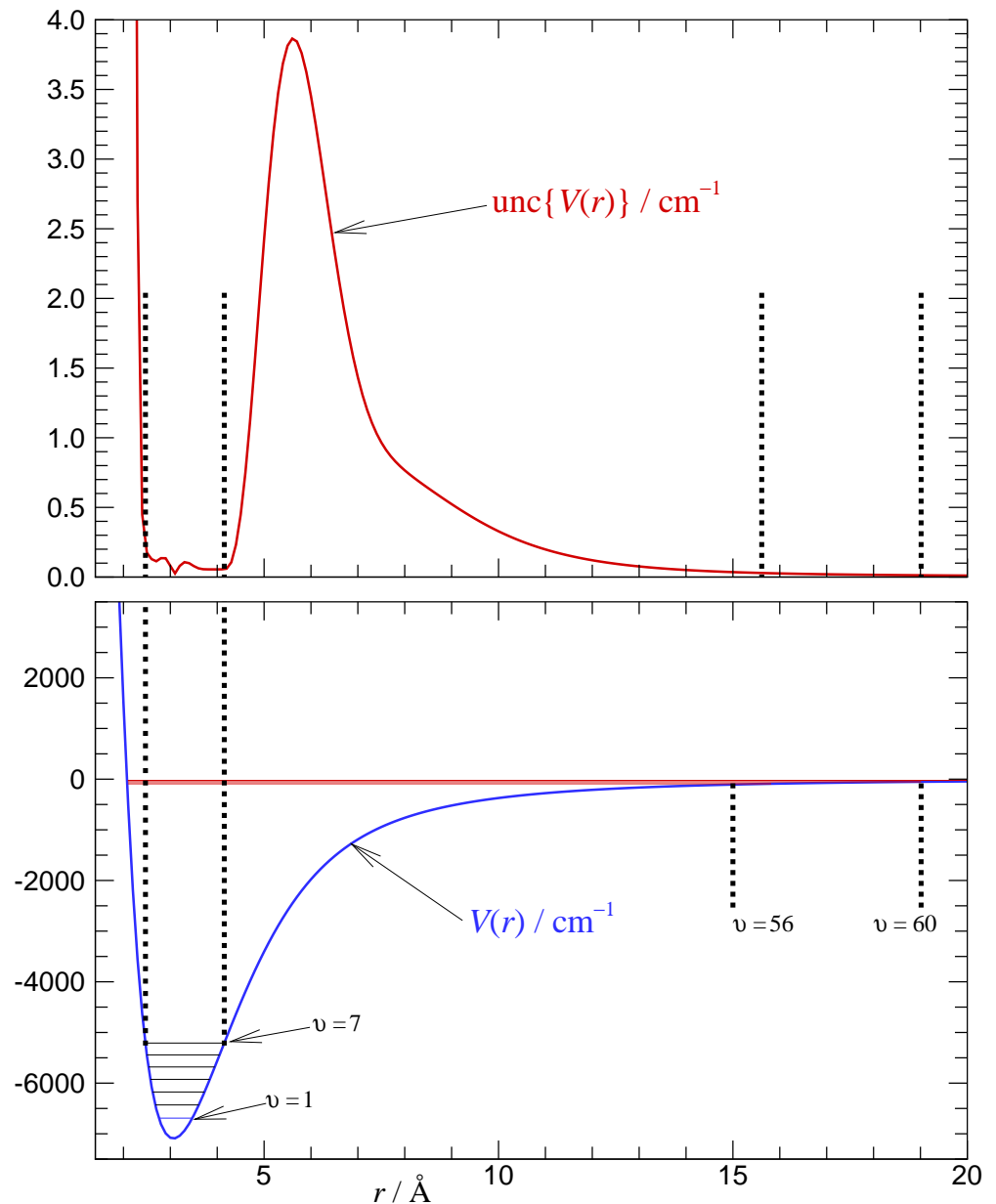
allowed us to project out the *homogeneous* contribution from the *general* solution of our *inhomogeneous* differential equation.

For continuum wavefunctions, however, **this does not work**, because the inhomogeneous term introduces a ‘phase shift’ that prevents the homogeneous solution component from simply being projected out!



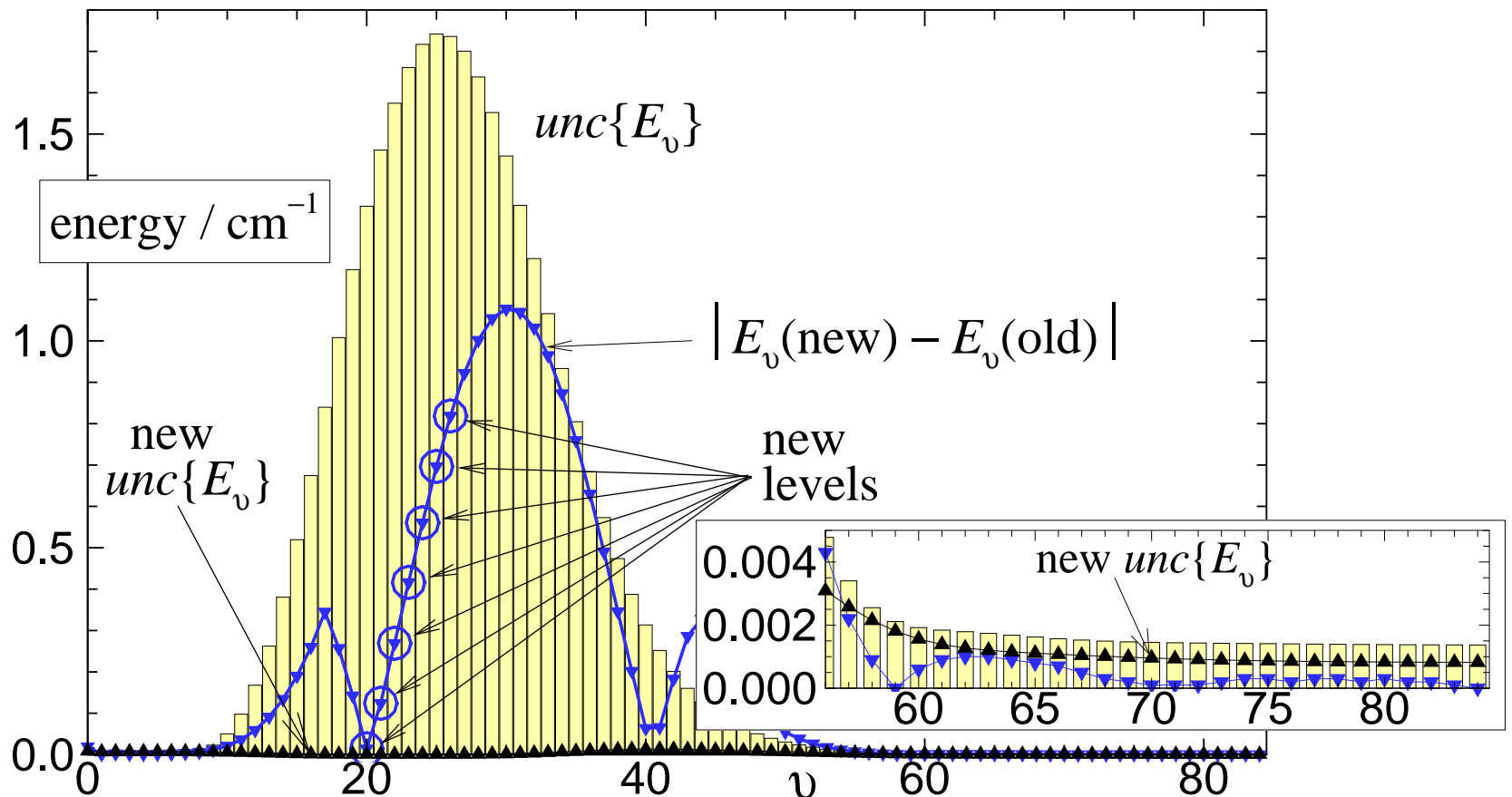
Conclusions

- Application of the expression $u(F) = \sqrt{\mathbf{D}^t \cdot \mathbf{C} \cdot \mathbf{D}}$ can yield a very illuminating understanding of the uncertainties in an analytic potential energy function determined from a fit.



Conclusions

- Application of the expression
$$u(F) = \sqrt{\mathbf{D}^t \cdot \mathbf{C} \cdot \mathbf{D}}$$
 can yield a very illuminating understanding of the uncertainties in an analytic potential energy function determined from a fit.
- Applying the above expression using Hellman-Feynman theorem partial derivatives
$$\frac{\partial E(v,J)}{\partial p_k} = \left\langle \psi_{v,J} \left| \frac{\partial V(r;\{p_k\})}{\partial p_k} \right| \psi_{v,J} \right\rangle$$
 can give very useful estimates of the uncertainties in level energies generated from a fitted potential energy function

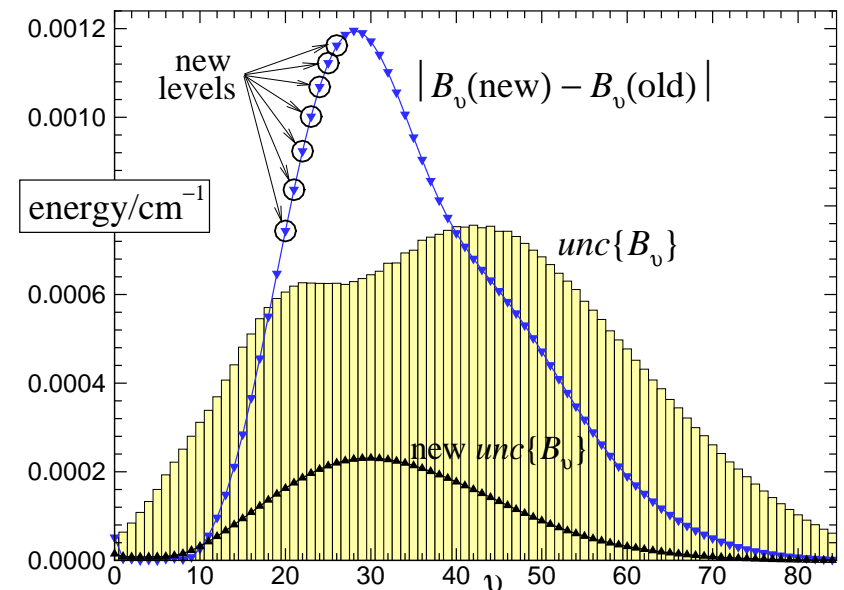


Conclusions

- Application of the expression $u(F) = \sqrt{\mathbf{D}^t \cdot \mathbf{C} \cdot \mathbf{D}}$ can yield a very illuminating understanding of the uncertainties in an analytic potential energy function determined from a fit.
- Applying the above expression using Hellman-Feynman theorem partial derivatives $\frac{\partial E(v,J)}{\partial p_k} = \left\langle \psi_{v,J} \left| \frac{\partial V(r;\{p_k\})}{\partial p_k} \right| \psi_{v,J} \right\rangle$ can give very useful estimates of the uncertainties in level energies generated from a fitted potential energy function
- Applying the above expression using wavefunction derivatives obtained by solving the *linear inhomogeneous* differential equation

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2 \psi_{v,J}^{(j)}(r)}{\partial r^2} + \left[V(r) + \frac{\hbar^2[J(J+1)]}{2\mu r^2} - E_{v,J} \right] \psi_{v,J}^{(j)}(r) = \left[\frac{\partial E_{v,J}}{\partial p_k} - \frac{\partial V(r)}{\partial p_k} \right] \psi_{v,J}(r)$$

allows us to predict the uncertainties in *any property* calculated from an expectation value or matrix element of the wavefunctions $\psi_{v,j}(r)$



Conclusions

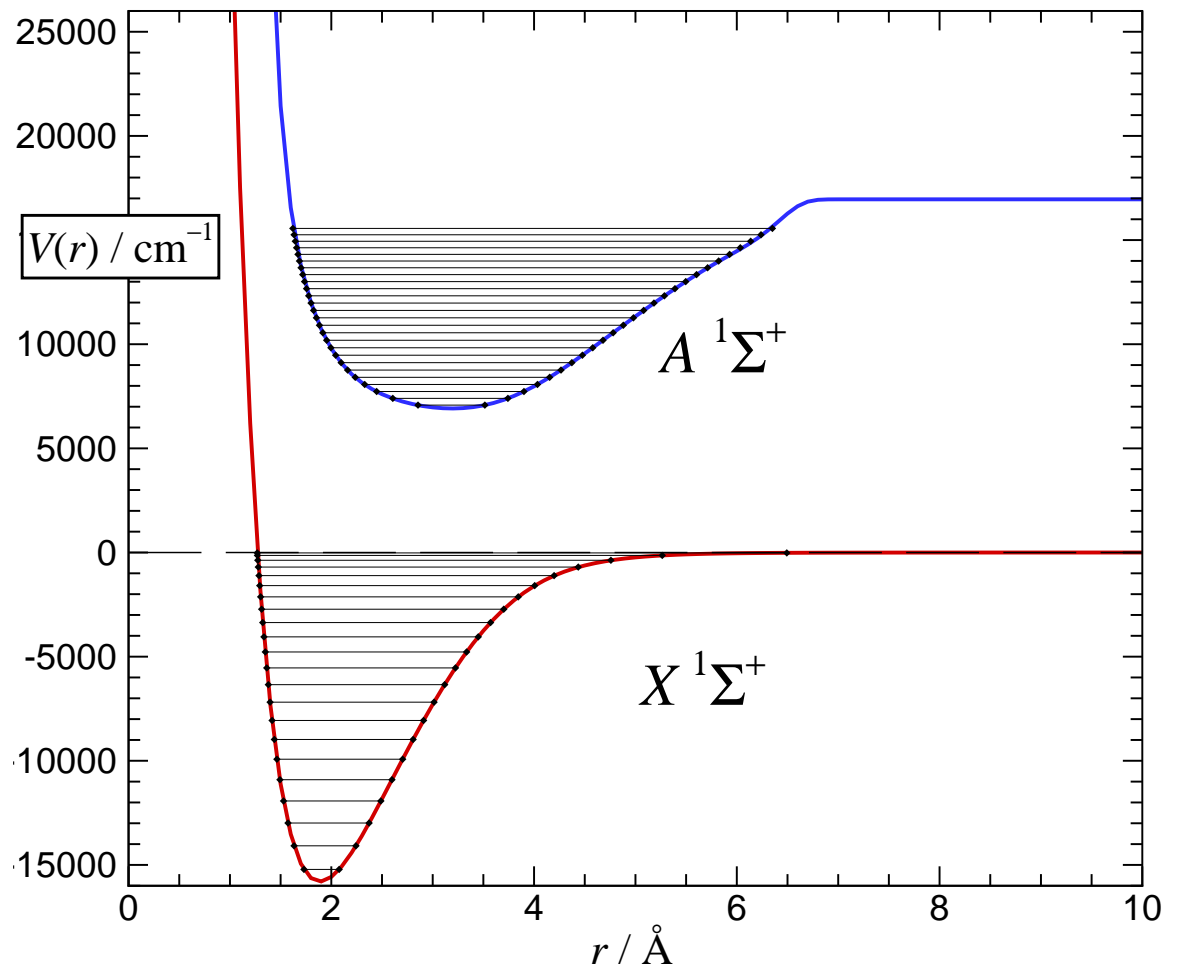
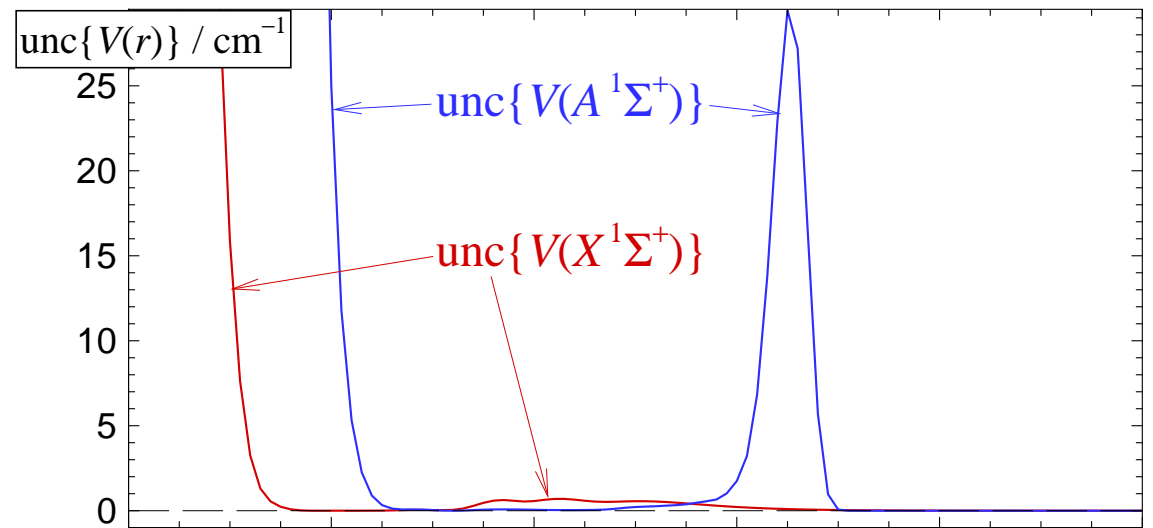
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 - Applying the above expression using Hellman-Feynman theorem partial derivatives
$$\frac{\partial E(v,J)}{\partial p_k} = \left\langle \psi_{v,J} \left| \frac{\partial V(r; \{p_k\})}{\partial p_k} \right| \psi_{v,J} \right\rangle$$
 can give very useful estimates of the uncertainties in level energies generated from a fitted potential energy function
 - Applying the above expression using wavefunction derivatives obtained by solving the *linear inhomogeneous* differential equation
$$-\frac{\hbar^2}{2\mu} \frac{\partial^2 \psi_{v,J}^{(j)}(r)}{\partial r^2} + \left[V(r) + \frac{\hbar^2 [J(J+1)]}{2\mu r^2} - E_{v,J} \right] \psi_{v,J}^{(j)}(r) = \left[\frac{\partial E_{v,J}}{\partial p_k} - \frac{\partial V(r)}{\partial p_j} \right] \psi_{v,J}(r)$$
 allows us to generate predicted uncertainties in *any property* calculated from an expectation value or matrix element of the wavefunctions $\psi_{v,J}(r)$
 - ***However, we do not (yet!) know how to use solutions of the above equation to calculate partial derivatives of matrix elements involving continuum wavefunctions.***
-

Conclusions

- Application of the expression $u(F) = \sqrt{\mathbf{D}^t \cdot \mathbf{C} \cdot \mathbf{D}}$ can yield a very illuminating understanding of the uncertainties in an analytic potential energy function determined from a fit.
- Applying the above expression using Hellman-Feynman theorem partial derivatives $\frac{\partial E(v,J)}{\partial p_k} = \left\langle \psi_{v,J} \left| \frac{\partial V(r;\{p_k\})}{\partial p_k} \right| \psi_{v,J} \right\rangle$ can give very useful estimates of the uncertainties in level energies generated from a fitted potential energy function
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Research supported by NSERC

My thanks to Dr. Nikesh Dattani and Professor Kirk Madison for raising the questions about uncertainties in calculated B_v values that instigated this project.



Recalling the NaH case
from the previous paper ...

we see that the predicted
uncertainties are indeed
large where we expect !

Our undergraduate d.e. course taught us that the *general solution* of a linear inhomogeneous differential equation is a linear combination of the ‘*particular solution*’ ψ_p with an arbitrary multiple of the associated ‘*homogeneous*’ solution

$$\psi_h$$

$$\psi_g = \psi_p + a \times \psi_h$$

For discrete bound states, the unit normalization of the wavefunction shows that

ψ_p and ψ_h must be orthogonal, since

$$\langle \psi_h | \psi_h \rangle = 1$$

then

$$\frac{\partial \langle \psi_h | \psi_h \rangle}{\partial p} = 0 = 2 \left\langle \frac{\partial \psi_h}{\partial p} \middle| \psi_h \right\rangle$$

This allowed us to take an inner product and project out the unwanted homogeneous solution component and retain only the ‘particular solution’.

For continuum wavefunctions, however, this does not work, because the inhomogeneous term introduced a ‘phase shift that prevents the homogeneous solution component from being simply projected out!

People who didn't know any better (or are lazy about coding), may calculate these derivatives by differences:

$$\frac{\partial \mathfrak{I}(v'', J'', E; \{p_k\})}{\partial p_k} \approx \frac{\mathfrak{I}(p_k + \Delta p_k, \{p_k\}_{j \neq k}) - \mathfrak{I}(p_k - \Delta p_k, \{p_k\}_{j \neq k})}{2\Delta p_k}$$

However, this approach has significant ‘overhead’ costs:

- For an M –parameter fit, the entire simulation calculation must be performed $2M + 1$ times in each cycle of the fit.
- One must fuss over the choice of the parameter increment Δp_k
 - Δp_k needs to be ‘small’ for the derivatives to be accurate
 - If Δp_k is too small, the loss of significant digits in the differences $\mathfrak{I}(p_k + \Delta p_k, \{p_k\}_{j \neq k}) - \mathfrak{I}(p_k - \Delta p_k, \{p_k\}_{j \neq k})$ reduces the accuracy
 - Because the sensitivity of the data to changes in different parameters may differ by many orders of magnitude, no simple % change rule will suffice

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Thus, we would like to be able to address this problem directly and obtain the exact partial derivatives that determine:

$$\left\langle \psi_{v'', J''}(r) \middle| M(r) \middle| \frac{\partial \psi_{E_u, J'}(r; \{p_k\})}{\partial p_k} \right\rangle$$