New Ways of Treating Data for Diatomic Molecule 'Shelf' and Double-Minimum States

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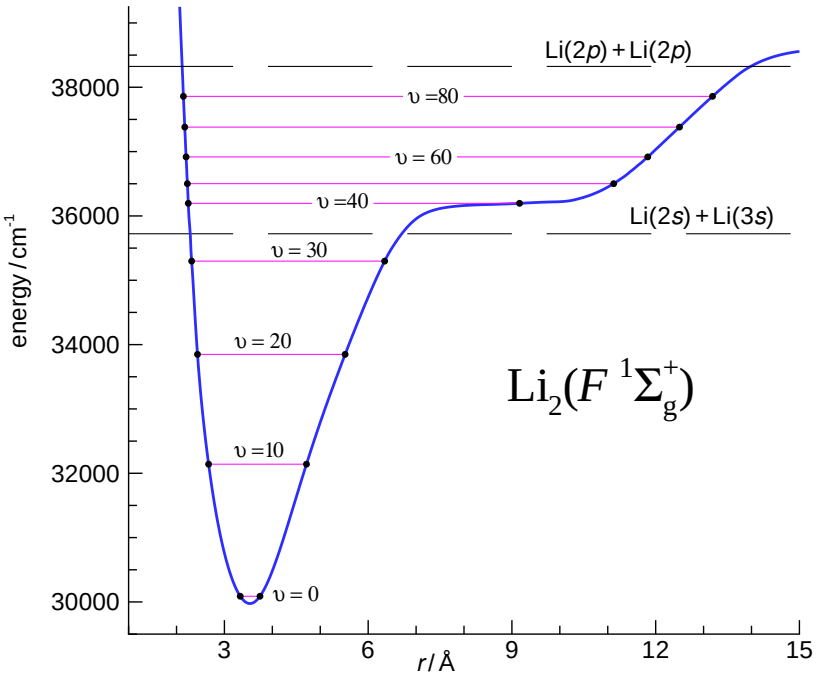
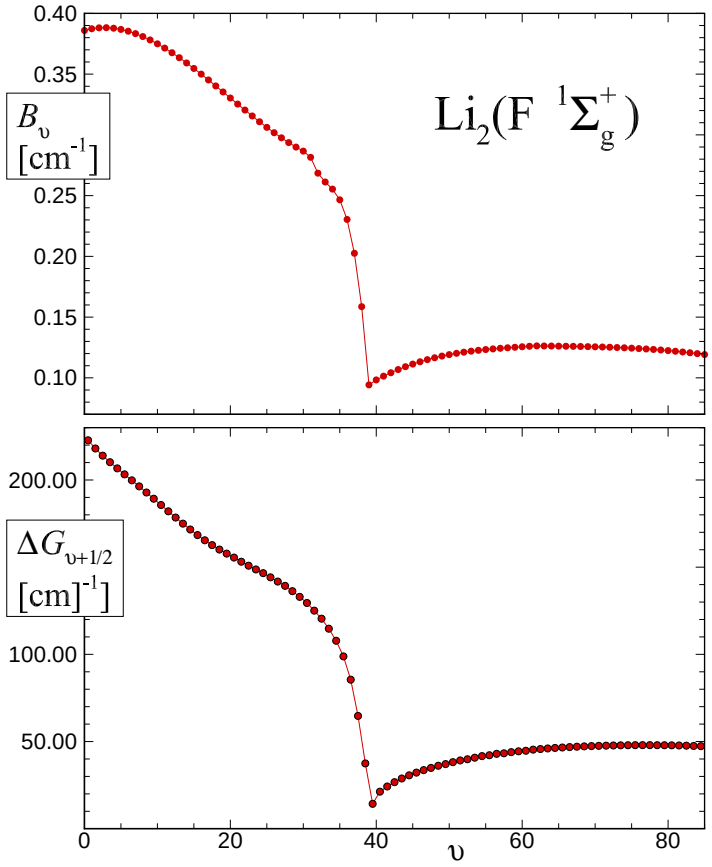
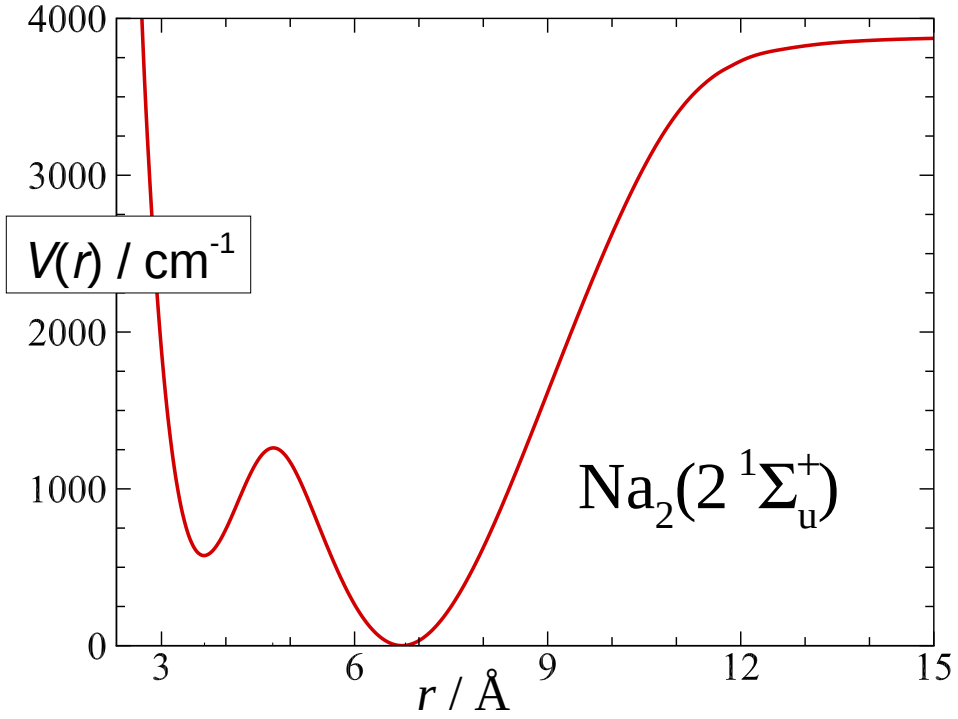
However . . . *for some types of potentials there are problems with this type of approach . . .*

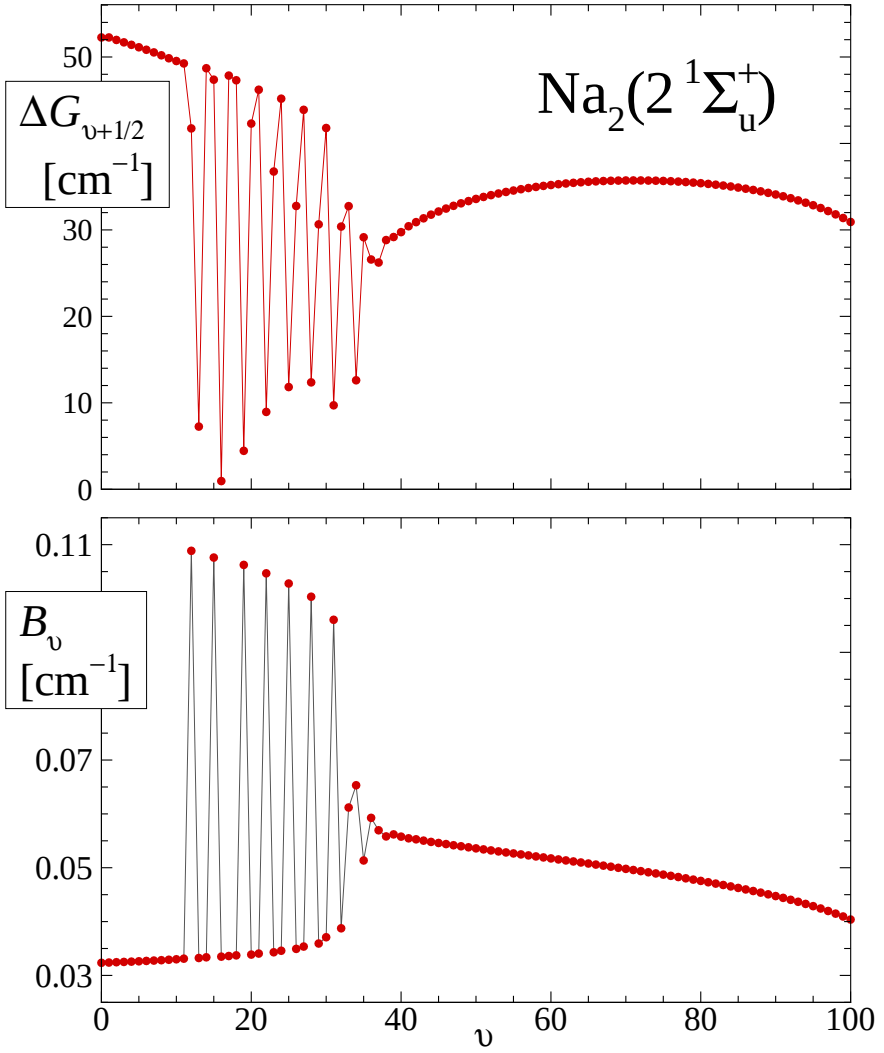
(a) for 'shelf-state' potentials





(b) for double-minimum potentials





- large B_v values are for inner well levels
- small B_v values and large $\Delta G_{v+1/2}$ values are for levels of the outer well
- small (and very small) $\Delta G_{v+1/2}$ values arise from accidental near-coincidence of adjacent inner- and outer-well levels

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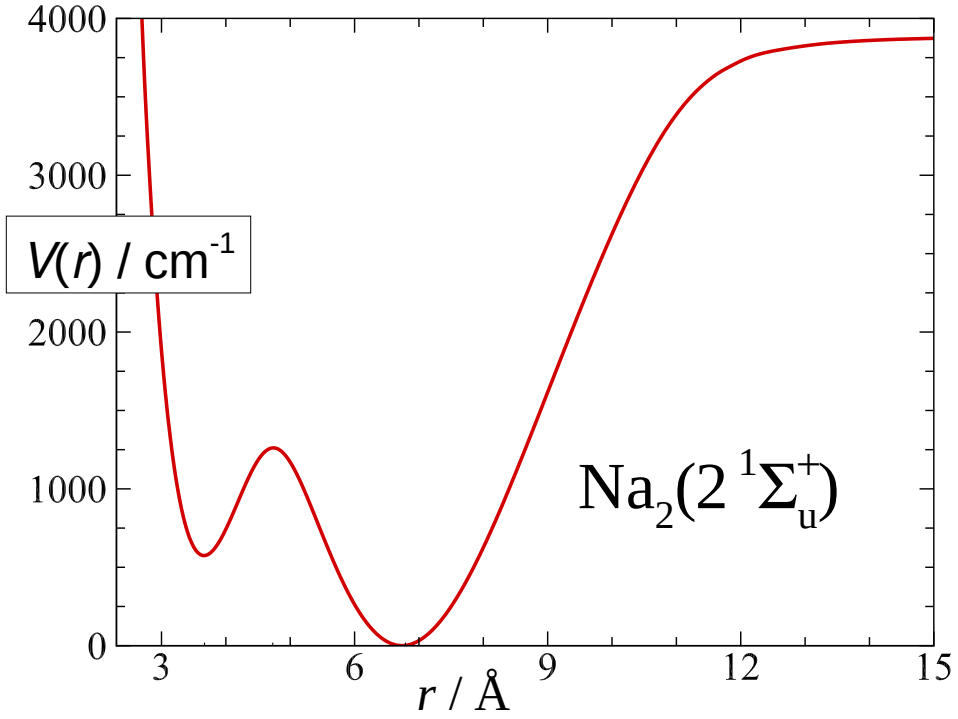

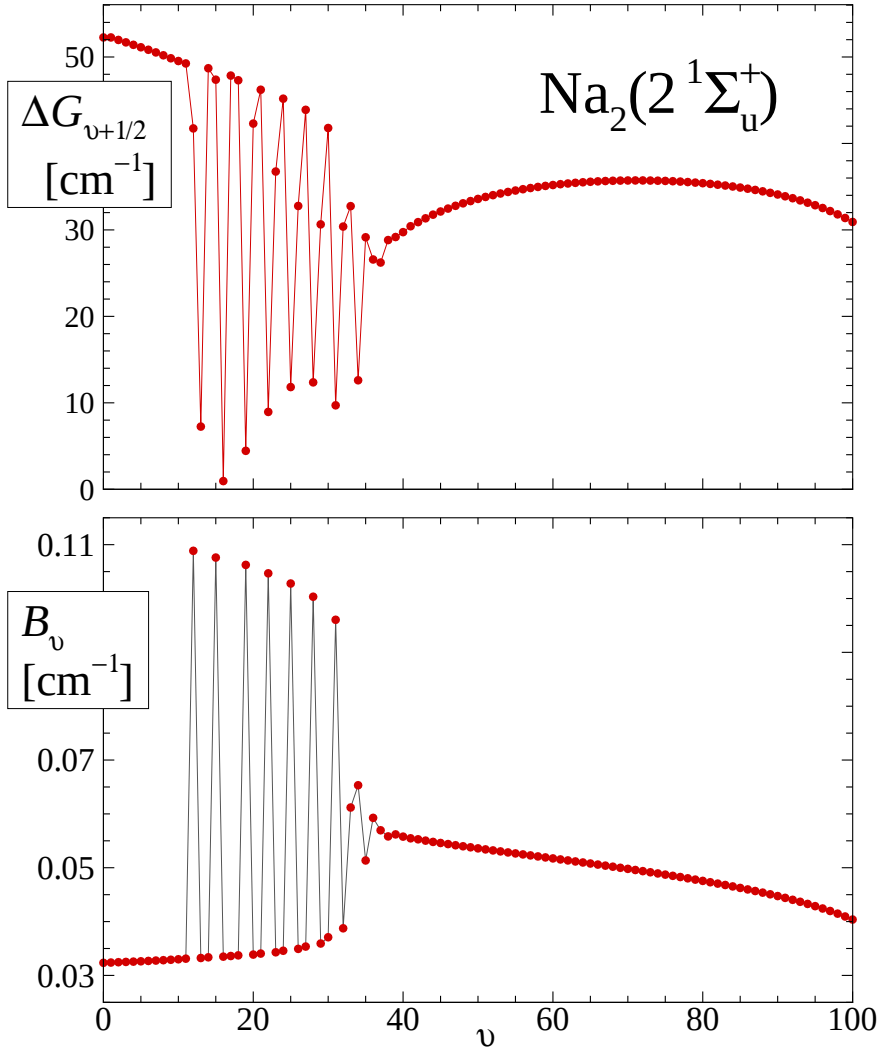

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Conclude: ***treating*** $G(v)$ ***and*** B_v ***as functions of*** v ***is not practical***

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- Calculate the partial derivatives of each value of each property w.r.t. each potential function parameter: $\partial F_i(\{p_j\})/\partial p_k$
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$$\frac{\partial E(v,J)}{\partial p_k} = \left\langle \psi_{v,J} \left| \frac{\partial V(r;\{p_j\})}{\partial p_k} \right| \psi_{v,J} \right\rangle$$

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. . . but how should we represent analytic potential functions for shelf- or double-minimum states ??

1. Pashov's 'Spline-Pointwise' Potential (SPP) form

* $V(r)$ is represented by a cubic spline through a set of specified points
* The energies at those points are the fitting parameters
* Attach analytic long- and short-range functions at *ad hoc* distances r_{out} and r_{in}, with parameters chosen to to give smooth joins

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Advantages

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Disadvantages

- Third derivatives discontinuous at all spline points. Higher-order derivatives do not exist anywhere.
- Requires a large number of parameters/spline points ($\gtrsim 50$), each specified to many significant digits, making it inconvenient to copy and use.
- Discontinuous high derivatives at attachment to the extrapolation regions

2. Prefer a Global Analytic Morse-like 'MLR' function

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

$*$ in which the exponent radial variable $(r - r_e)$ is replaced by $y_p^{\rm eq}(r) = \dfrac{r^p - {r_e}^p}{r^p + {r_e}^p}$

$*$ the exponent coefficient function $\beta(r)$ is the constrained polynomial expansion:

$$\beta(r) \;=\; \beta_\infty\, y_p^{\rm ref}(r) \;+ [1 - y_p^{\rm ref}(r)] \sum_{i=0}^{N_\beta} \beta_i [y_q^{\rm ref}(r)]^i$$

in which the coefficients β_i are the shape/fitting parameters, $y_{q/p}^{\rm ref}(r) = \dfrac{r^{q/p} - r_{\rm ref}^{q/p}}{r^{q/p} r + r_{\rm ref}^{q/p}}$

$*$ $u_{\rm LR}(r) \;=\; \displaystyle\sum_{i=1}^{last} D_{m_i}(r)\, \frac{C_{m_i}}{r^{m_i}}$ defines the long-range behaviour

$*$ and the explicit constraint

$$\lim_{r\to\infty} \beta(r) \;\equiv\; \beta_\infty \;=\; \ln\left\{ \frac{2\,\mathfrak{D}_e}{u_{\rm LR}(r_e)} \right\}$$

algebraically *requires* the potential to have the long-range form

$$V(r) \;\simeq\; \mathfrak{D}_e \;-\; u_{\rm LR}(r)$$

2. Global Analytic Morse/Long-Range (MLR) function

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

Advantages

- Incorporates physically meaningful quantities $\mathfrak{D}_e$, r_e, and the C_{m_i} as explicit fitting parameters in the algebraic form, as well as the $\{\beta_i\}$
- Function and derivatives to all order are smooth everywhere
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Disadvantages

- High inter-parameter correlation
- Difficulty accounting for abrupt changes in shape encountered in shelf- and double-minimum potentials

Can we combine the best features of both forms ?

3. The Spline-Exponent-MLR (SE-MLR) form

Same MLR structure, except that instead of being represented by a constrained polynomial, the exponent coefficient $\beta(r)$ is defined as a spline function through a specified set of values $\{\beta_k\}$, which are the fitting parameters. It can be written as:

$$\beta(r) = \sum_{k=1}^{N} S_k(r) \cdot \beta\left(y_q^{\text{ref}}(r_k)\right) = \sum_{k=1}^{N} S_k(r) \cdot \beta_k$$

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How do we apply the SE-MLR?

1. Choose parameters q, p, and r_{ref} to define radial variables $y_q^{\text{ref}}(r)$ and $y_p^{\text{eq}}(r)$
2. Place the N spline points $y_q^{\text{ref}}(r_k)$
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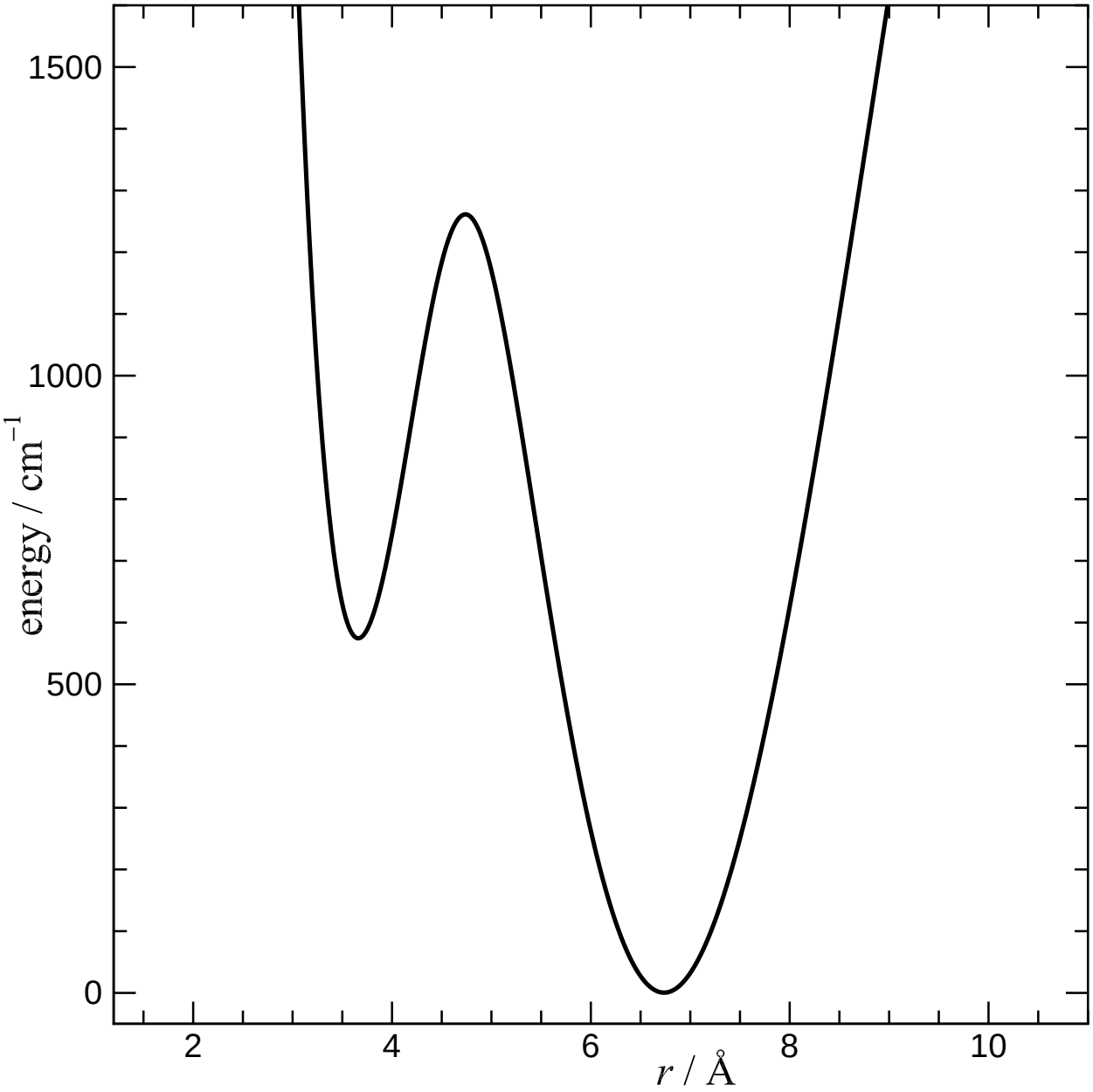
However, *for any form, the central step of a fitting procedure is*

- Simulate experimental data as properties $F_i(\{p_j\})$ of a parametrized analytic potential energy function $V(r;\{p_j\})$

How do we locate an arbitrary (v, J) level of a double-minimum potential ?



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1. locate lowest PEF minimum

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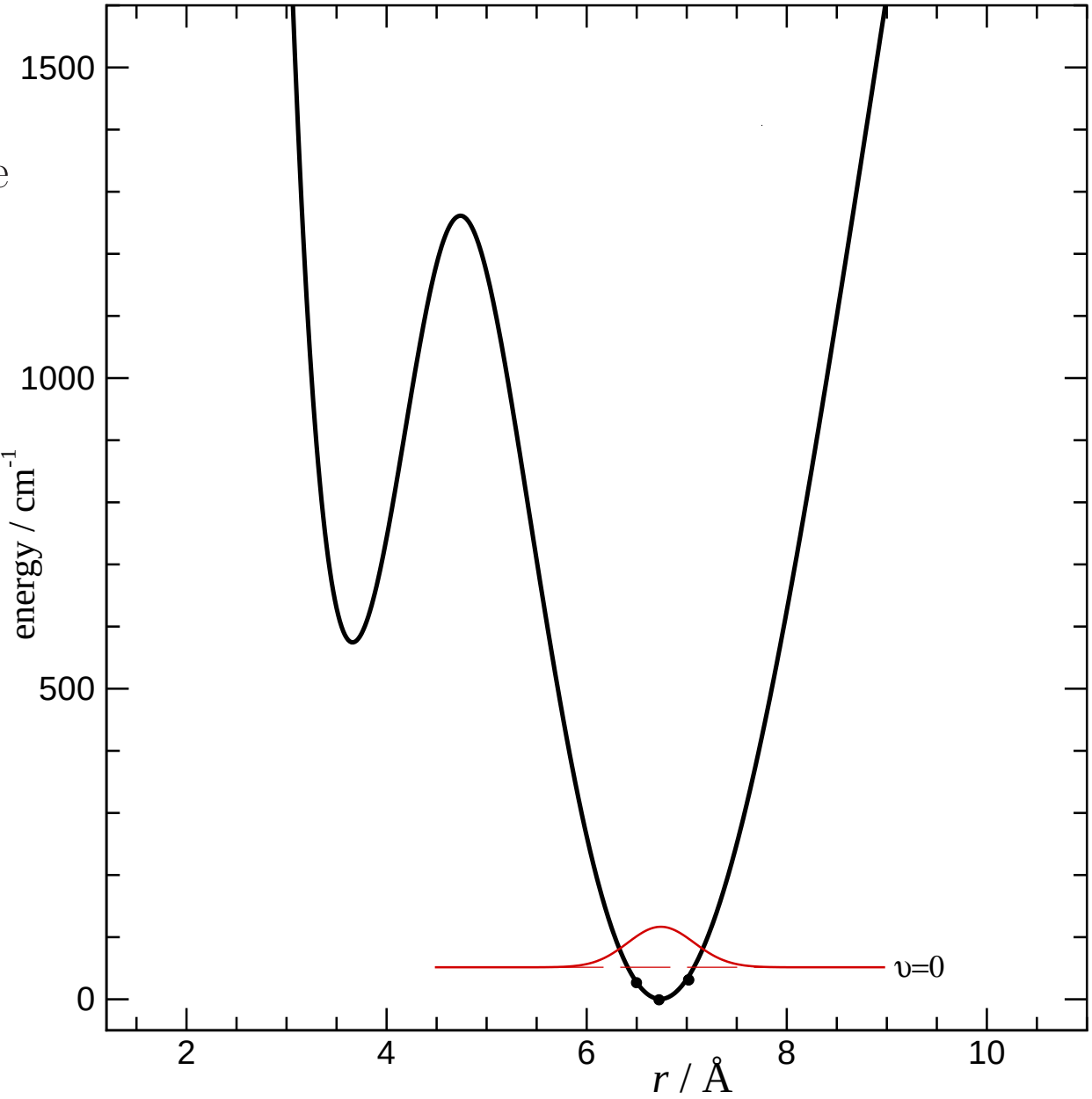

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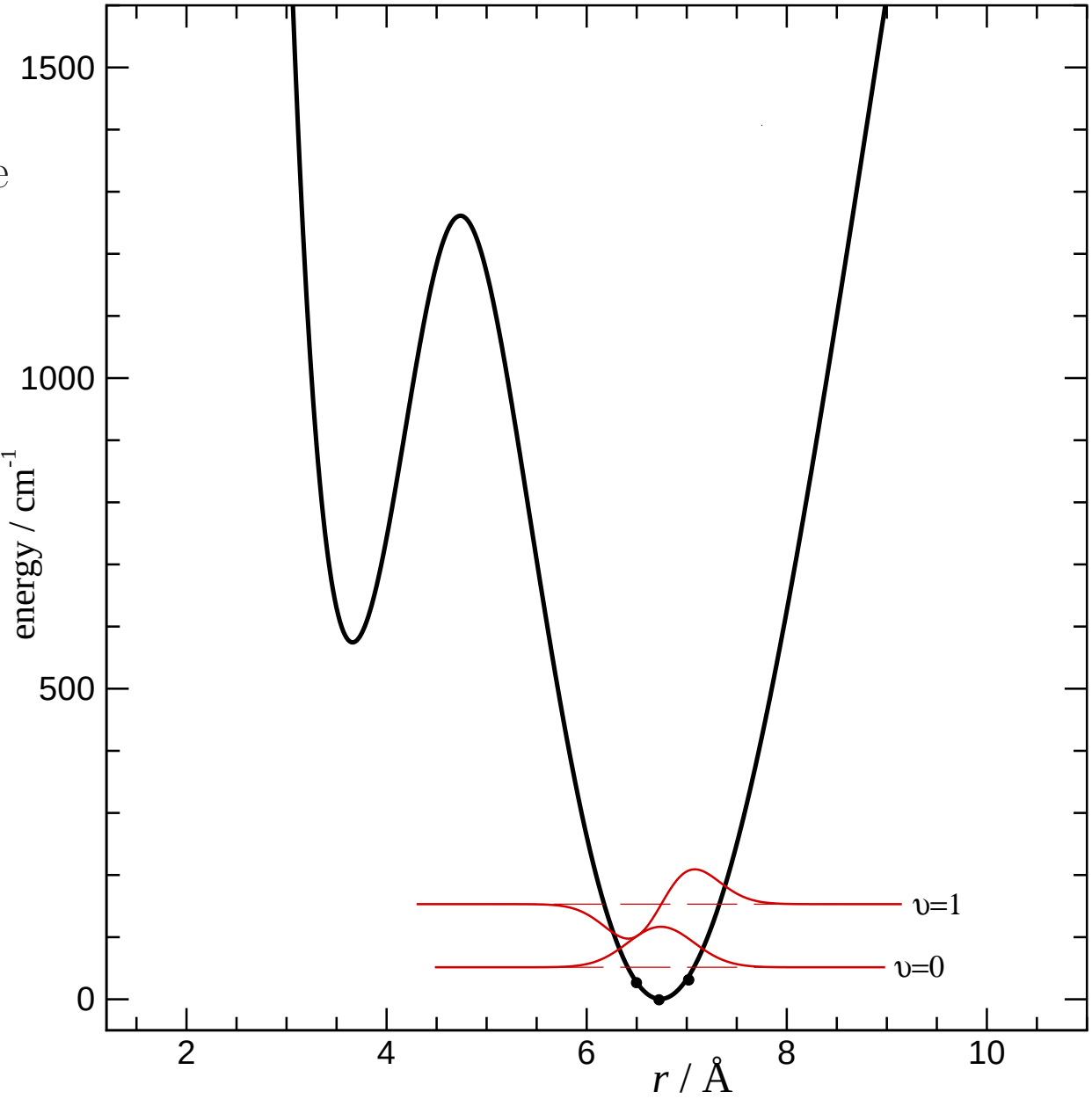

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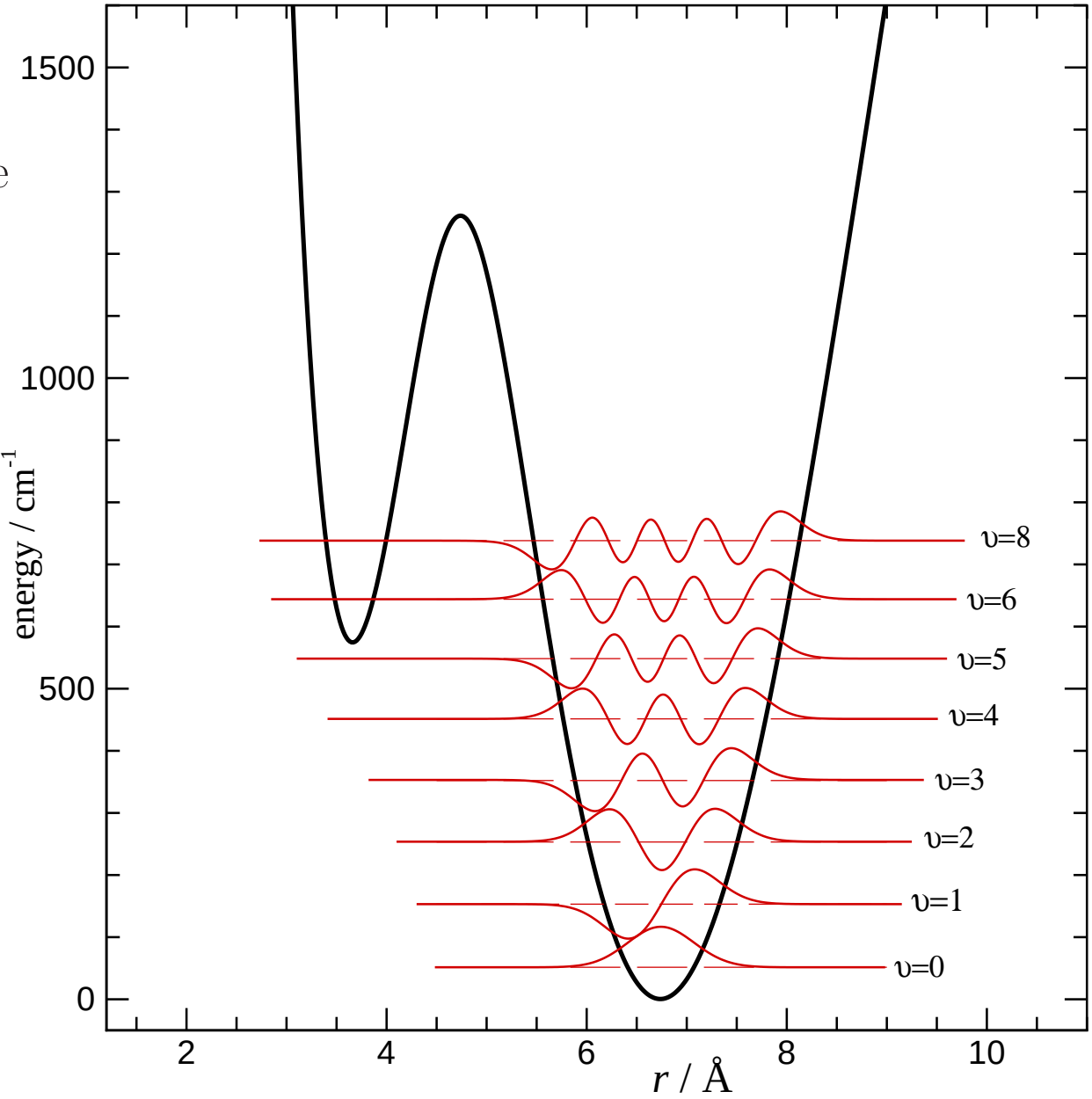
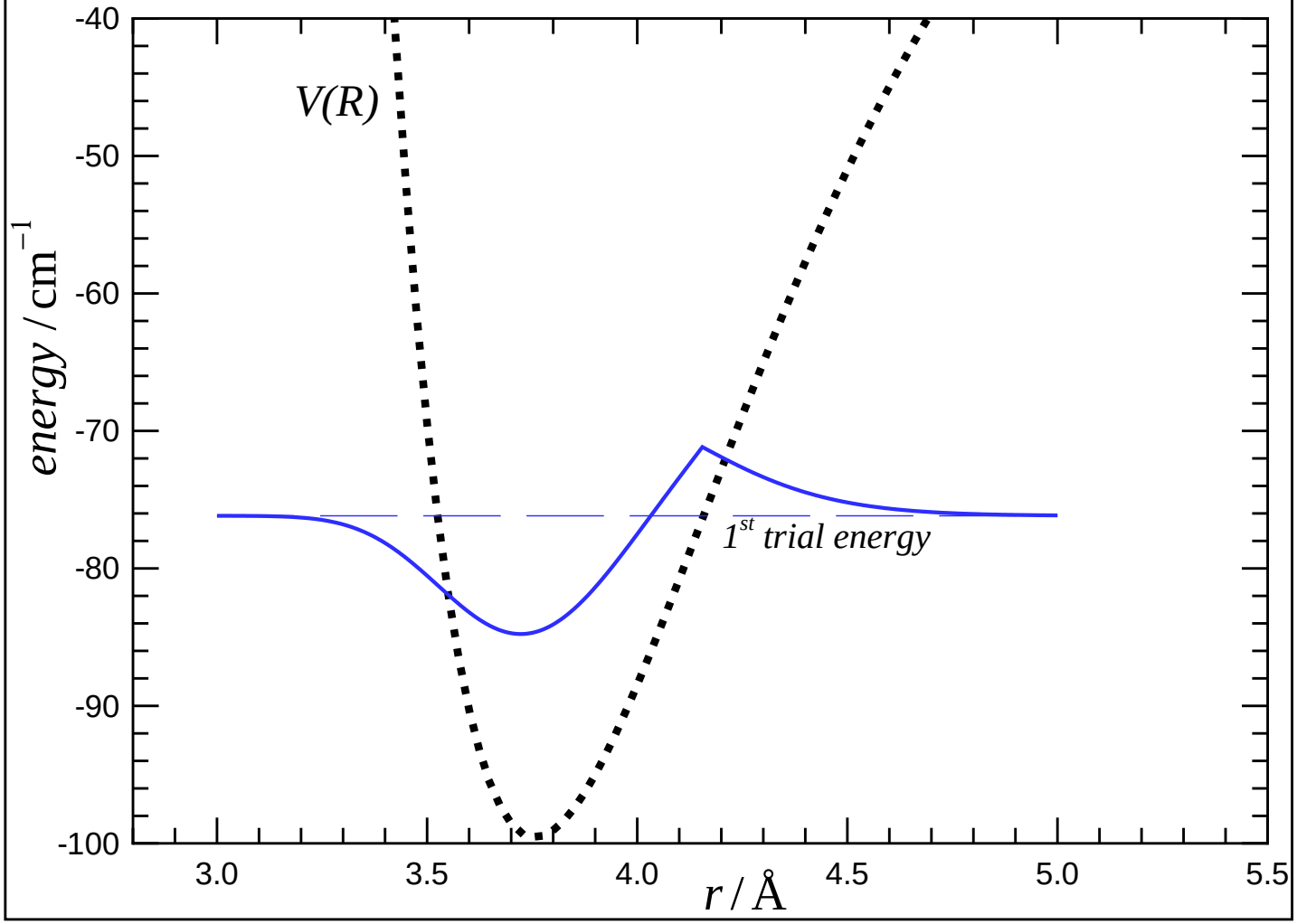
4. *repeat until node count shows a level was missed*



Recall how eigenvalue search procedure works:

♠ *match inward- and outward-propagating* $\psi(r)$ near a turning point



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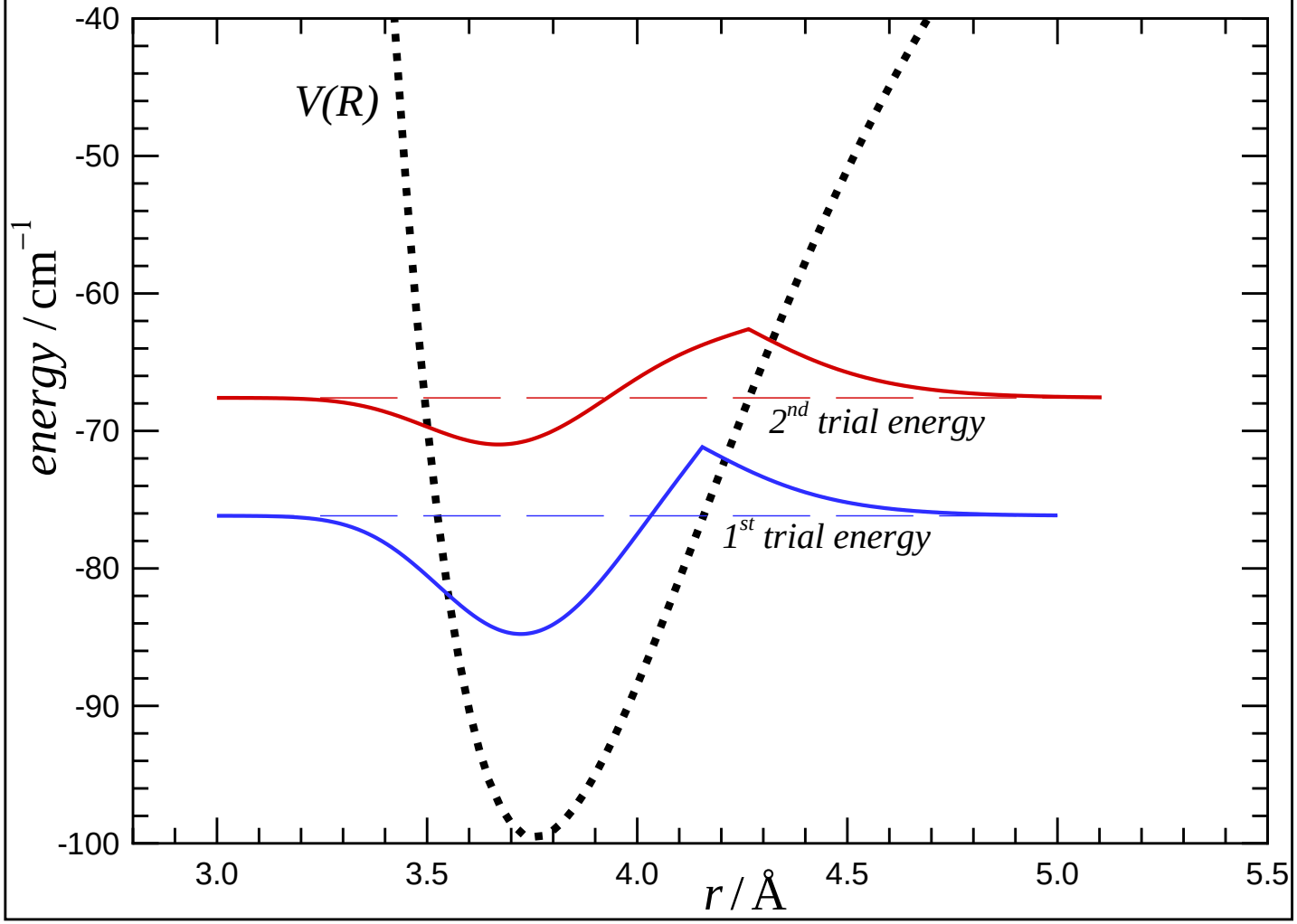

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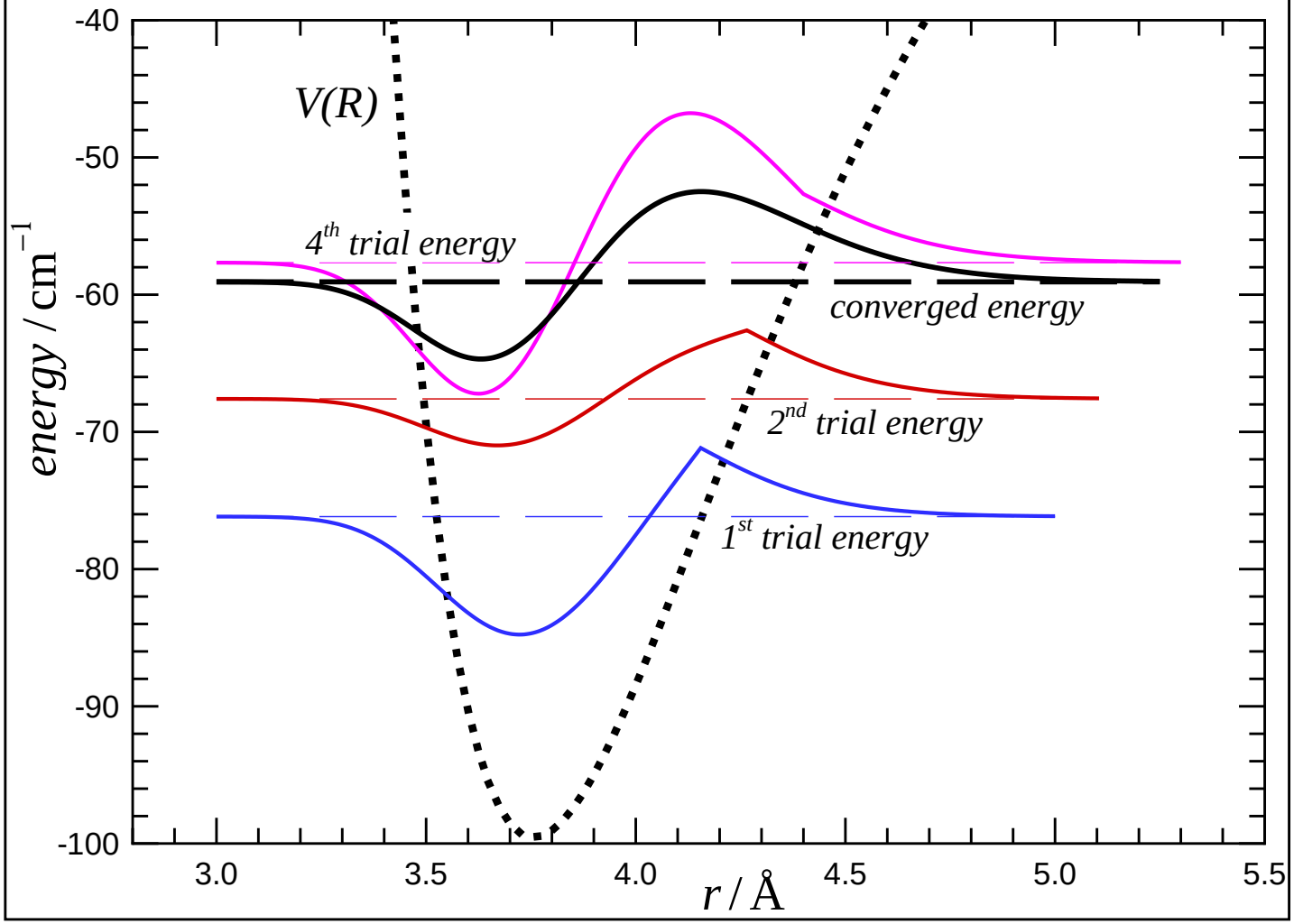

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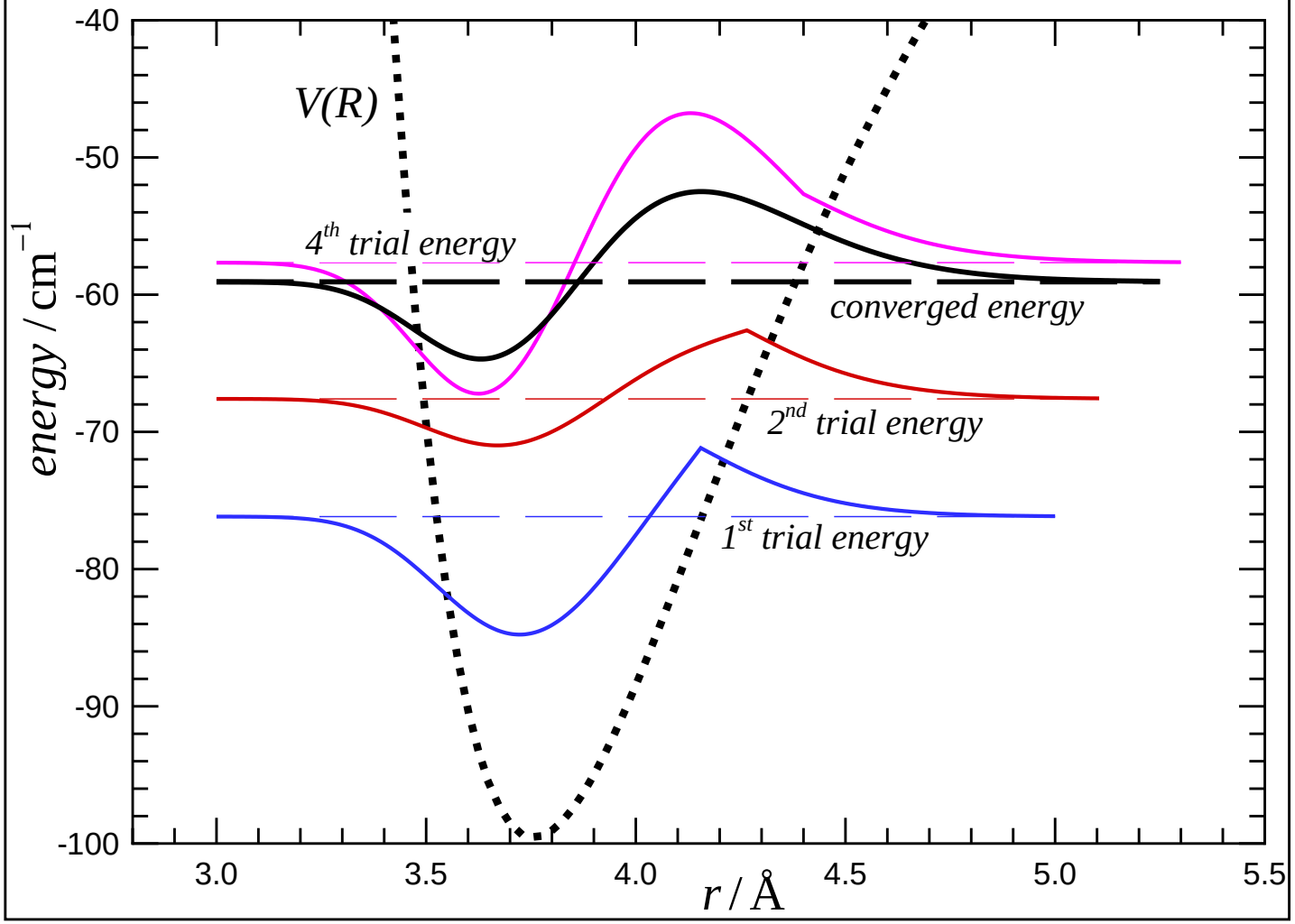
⇒ *for double-minimum potential, matching must occur over well with maximum wavefunction amplitude*



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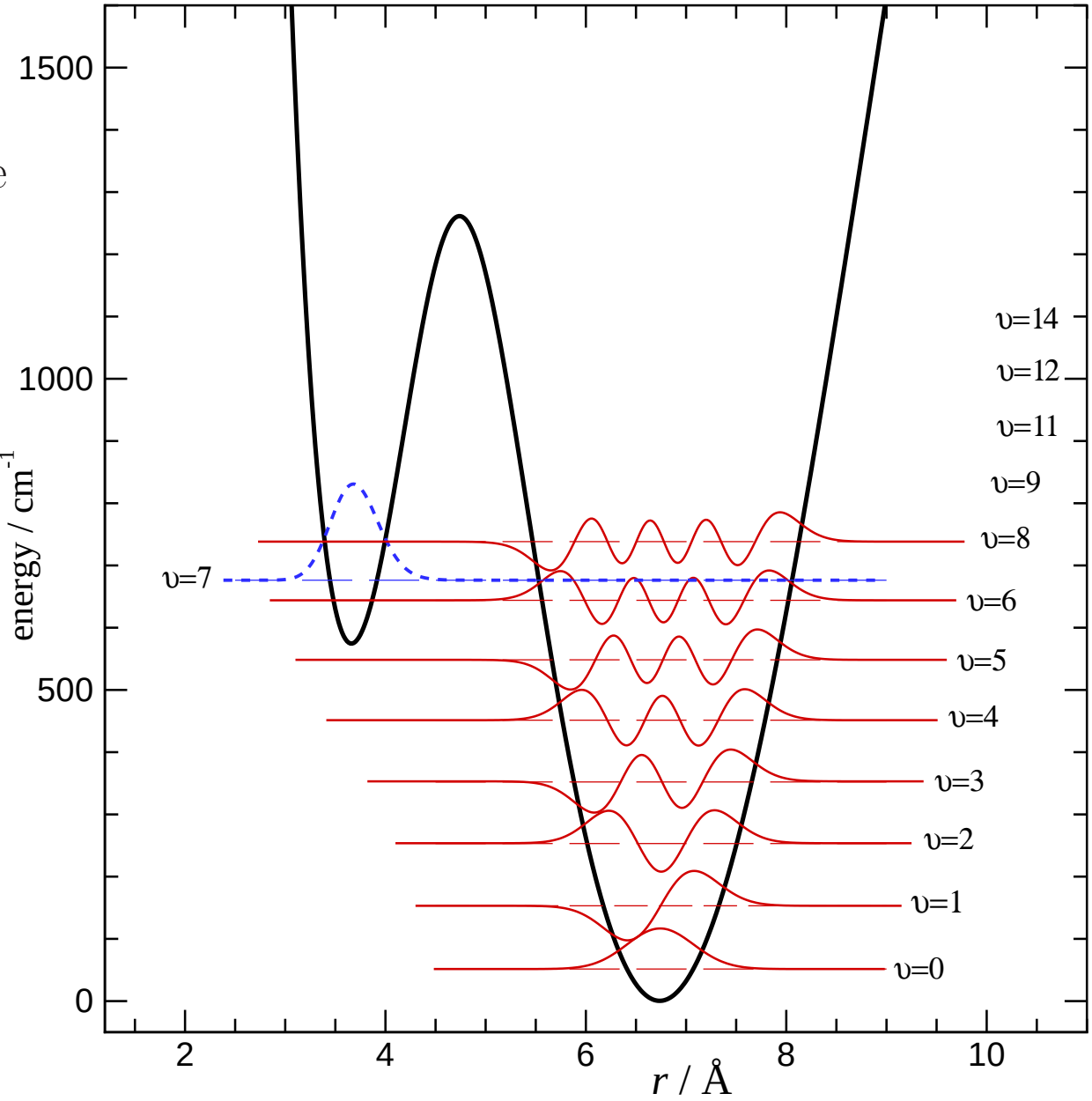

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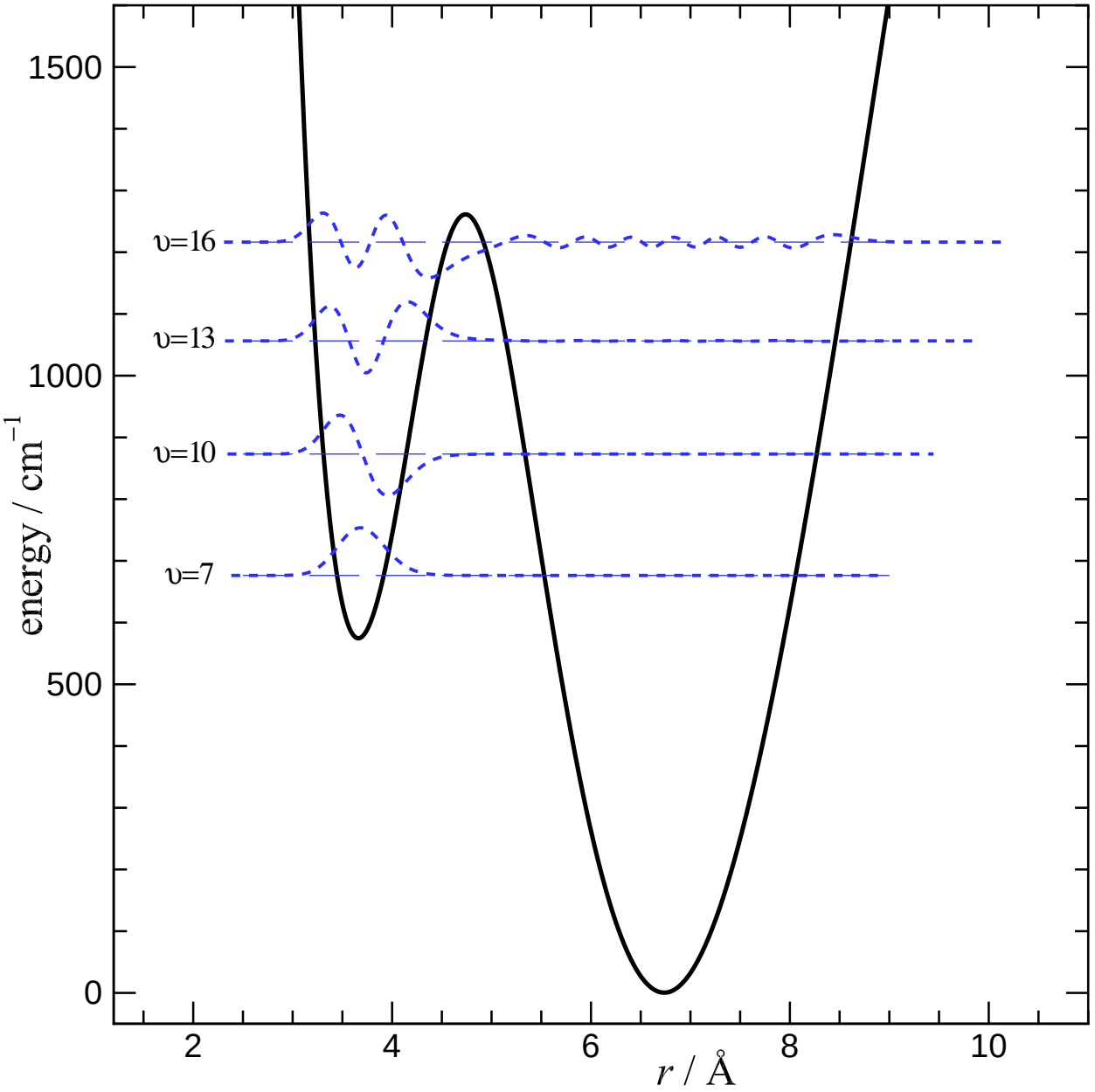

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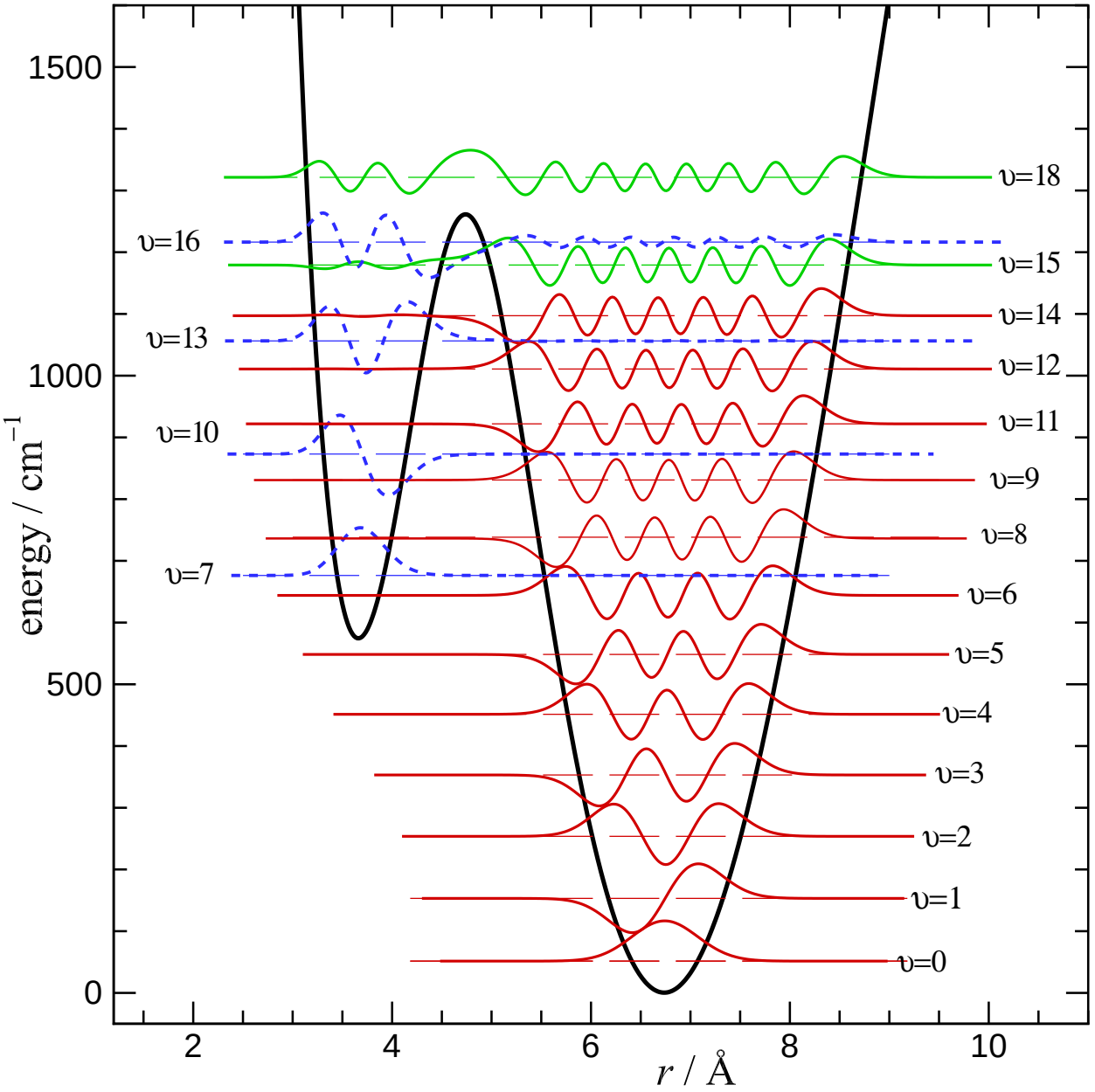

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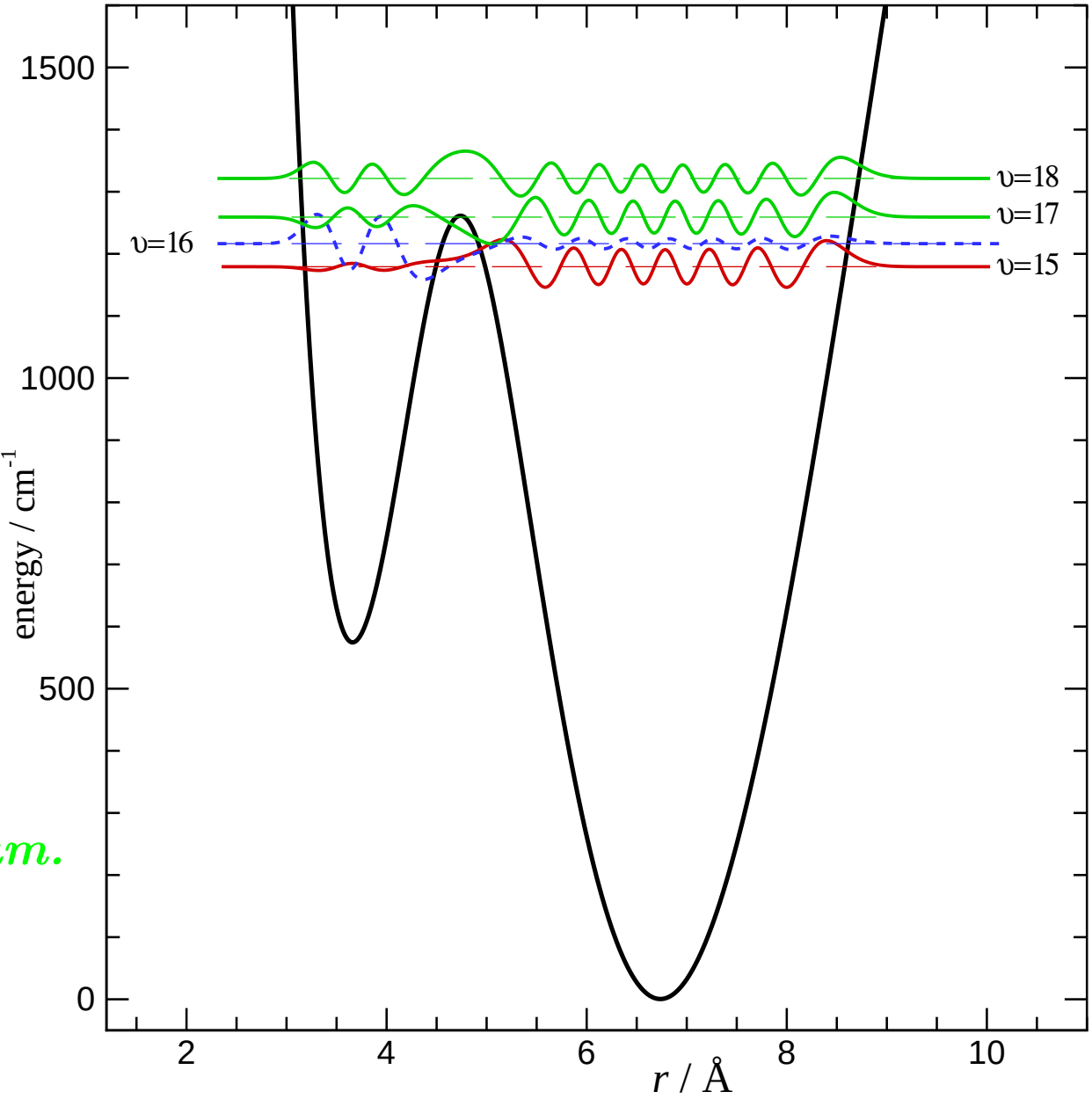

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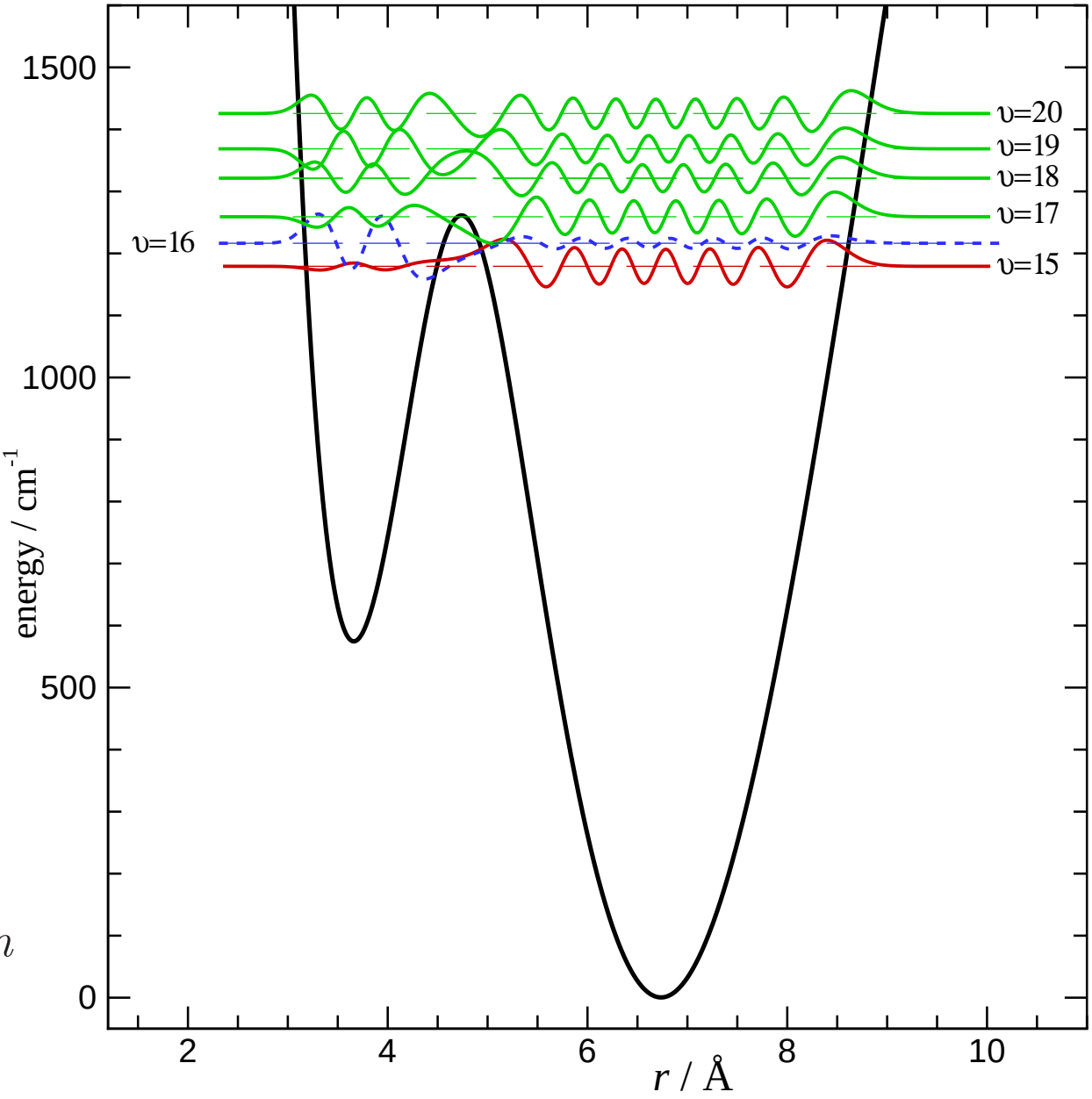

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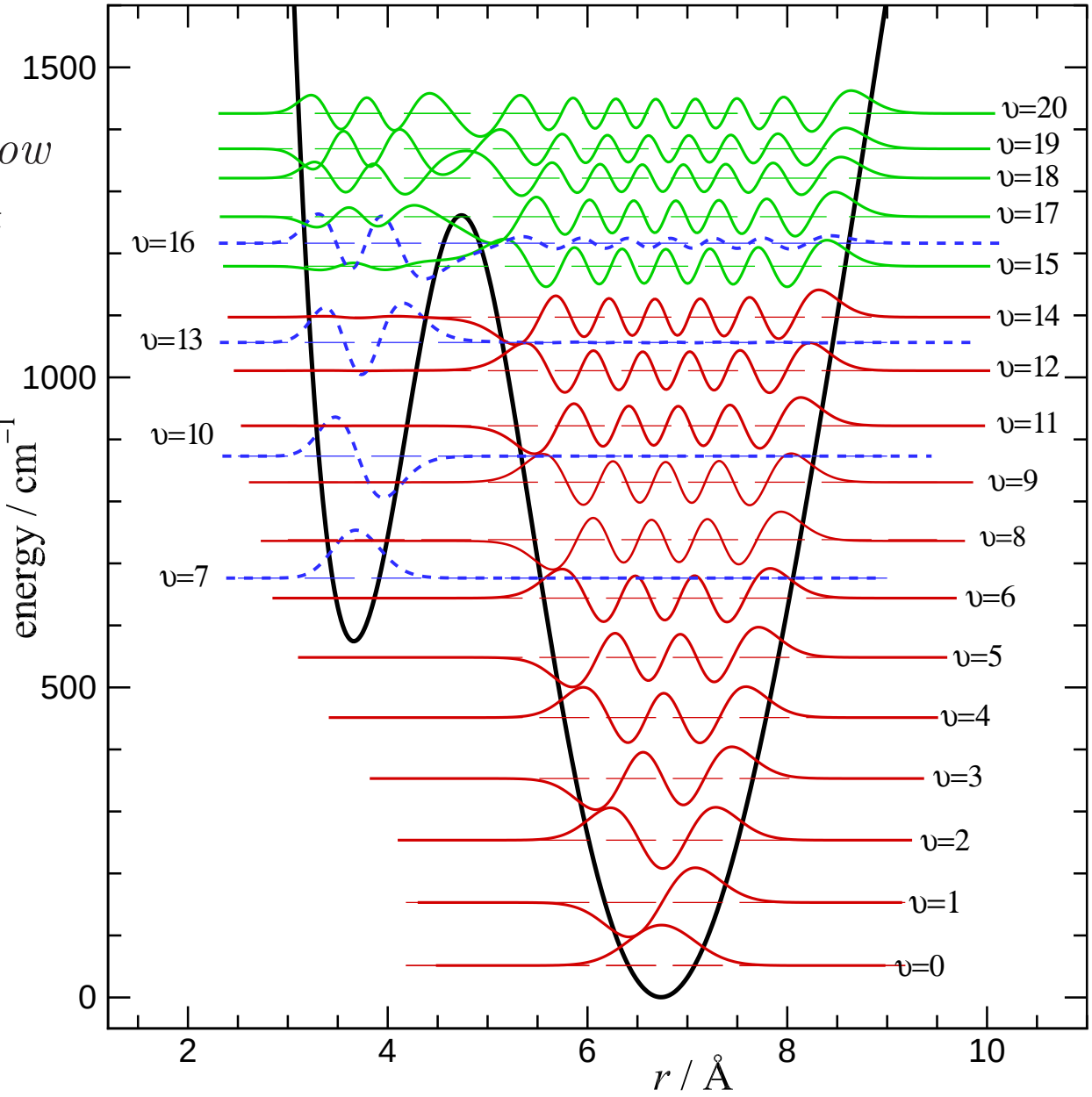
10. Conclude: *for any specified (v, J) level can now 'routinely' and robustly get the energy and the wavefx. $\psi_{v,J}(r)$ required for calculating the partial derivatives needed in the fitting procedure !*



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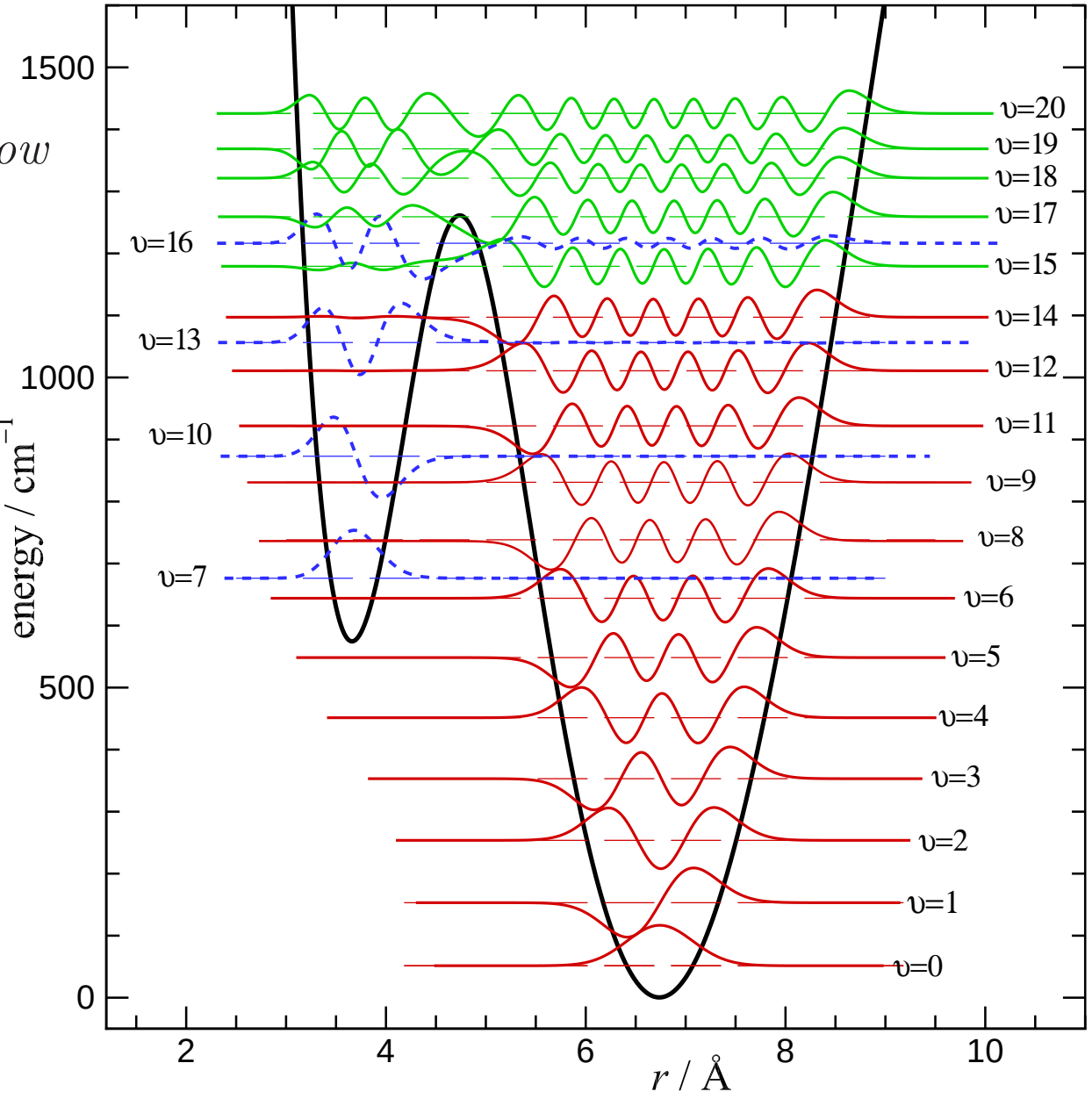

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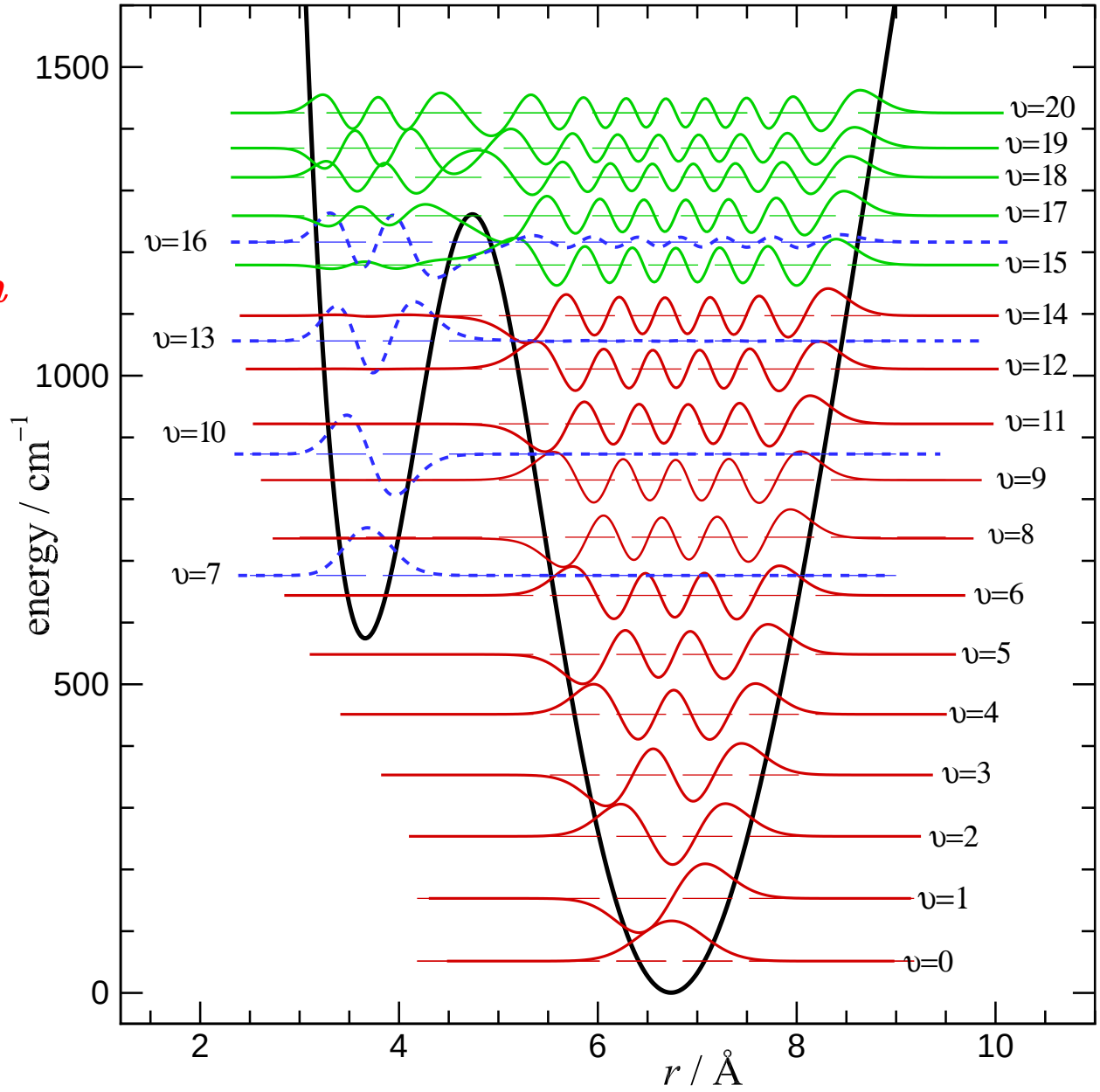

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