

**Solving the Radial Schrödinger Equation  
at Energies Extremely Close to Dissociation:  
*Bound States and Scattering Lengths***

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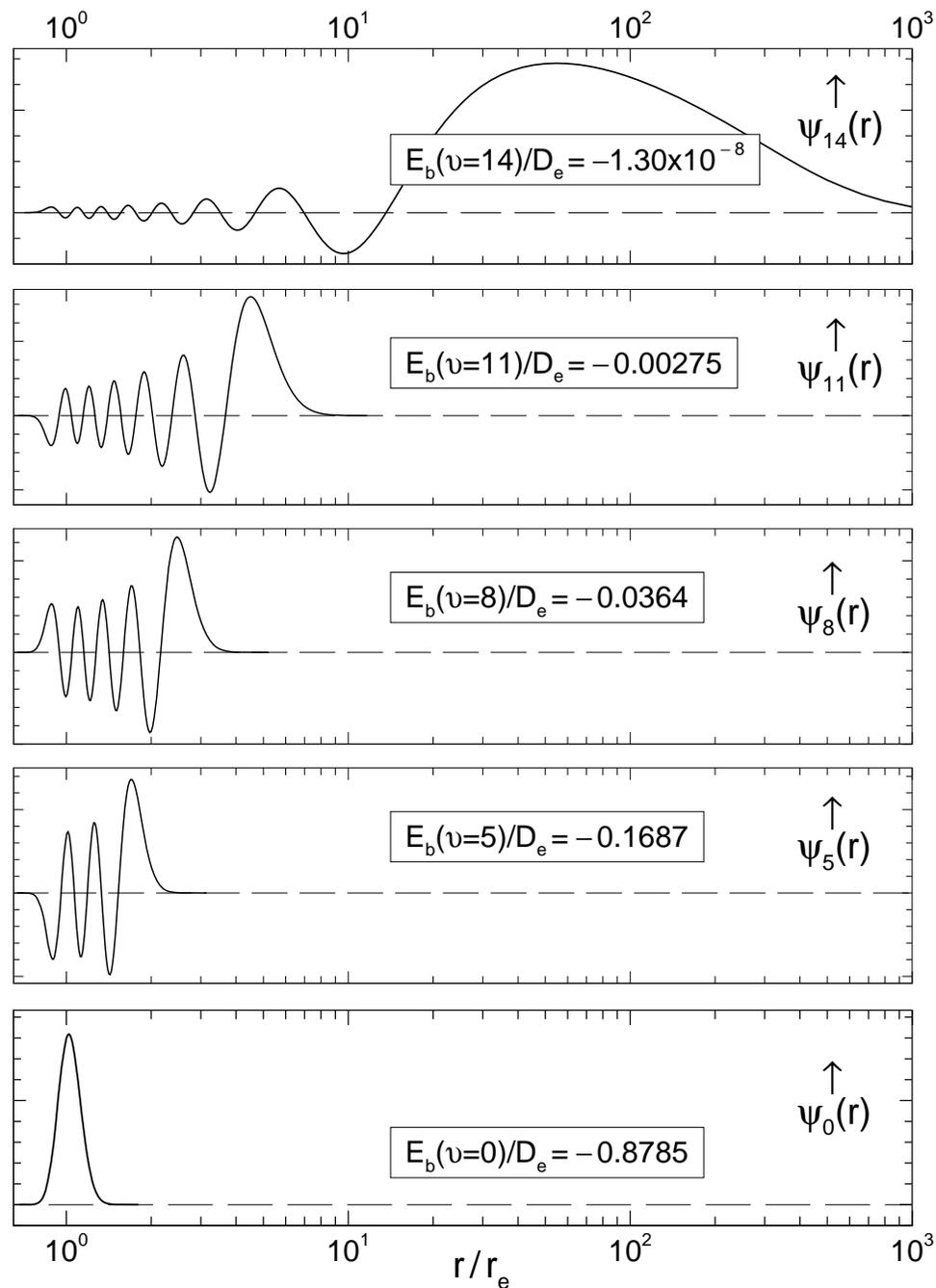
<sup>a</sup> Research supported by INTAS grant 06-1000014-5964 and by the Russian Foundation for Basic Research.

<sup>b</sup> Research supported by the Natural Sciences and Engineering Research Council of Canada.

# What is the Problem ?

For levels lying near dissociation:

- the wavefunctions extend across an immense and very asymmetric domain
- wavefunction amplitude changes very dramatically across that domain



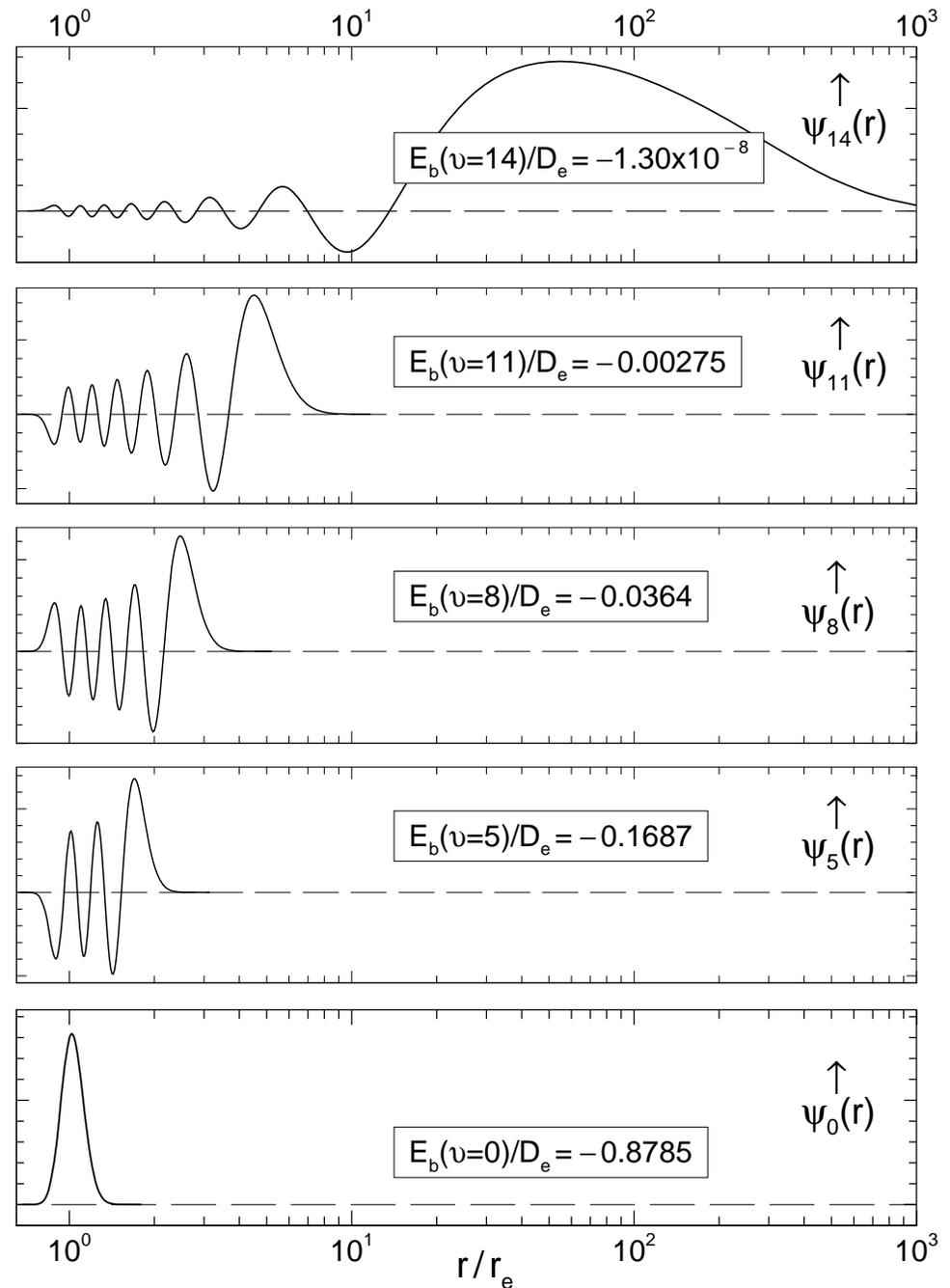
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As a result, when solving the radial Schrödinger equation for such levels:

- No basis set method will work!
- Numerical integration with a mesh size suitable for small distances will require extremely large radial arrays!
- This very large number of integration mesh points makes calculations for such levels quite CPU intensive!



*Why does it matter ?*

## What is the Solution ?

Start from the conventional radial Schrödinger equation

$$\frac{d^2\psi(r)}{dr^2} = -Q(r)\psi(r) \quad \text{in which} \quad Q(r) = \frac{2\mu}{\hbar^2} [E - U(r)]$$

If we now map the radial coordinate  $r \in [0, \infty)$

- onto a new radial variable with a finite domain  $y = y(r) \in [a, b]$ , and
- make the substitution  $\psi(r) = \sqrt{g(y)} \phi(y)$  where  $g(y) \equiv \frac{dr(y)}{dy}$
- our differential equation becomes

$$\frac{d^2\phi(y)}{dy^2} = -\tilde{Q}(y)\phi(y) \quad \text{in which} \quad \tilde{Q}(y) = g(y)^2 Q(r(y)) + F(y)$$

and both  $g(y)$  and  $F(y) \equiv \frac{g''}{2g} - \frac{3}{4} \left(\frac{g'}{g}\right)^2$  depend only on the definition of the variable mapping.

Our new differential equation in  $y$  can readily be solved using *exactly the same array of techniques* used for treating the conventional equation in  $r$  !

## *How do we define the variable mapping ?*

There are many possibilities,<sup>†</sup> but a particularly convenient choice is

$$y(r) = \frac{r^\alpha - \bar{r}^\alpha}{r^\alpha + \bar{r}^\alpha}$$

where  $\alpha$  is a positive real number and  $\bar{r}$  a fixed reference distance.

With this choice. the domain  $[a, b] = [-1, +1]$  and

$$g(y) \equiv \frac{dr(y)}{dy} = \frac{2\bar{r}}{\alpha} \frac{(1+y)^{\frac{1}{\alpha}-1}}{(1-y)^{\frac{1}{\alpha}+1}} = \frac{(r^\alpha + \bar{r}^\alpha)^2}{2\alpha \bar{r}^\alpha r^{\alpha-1}}$$

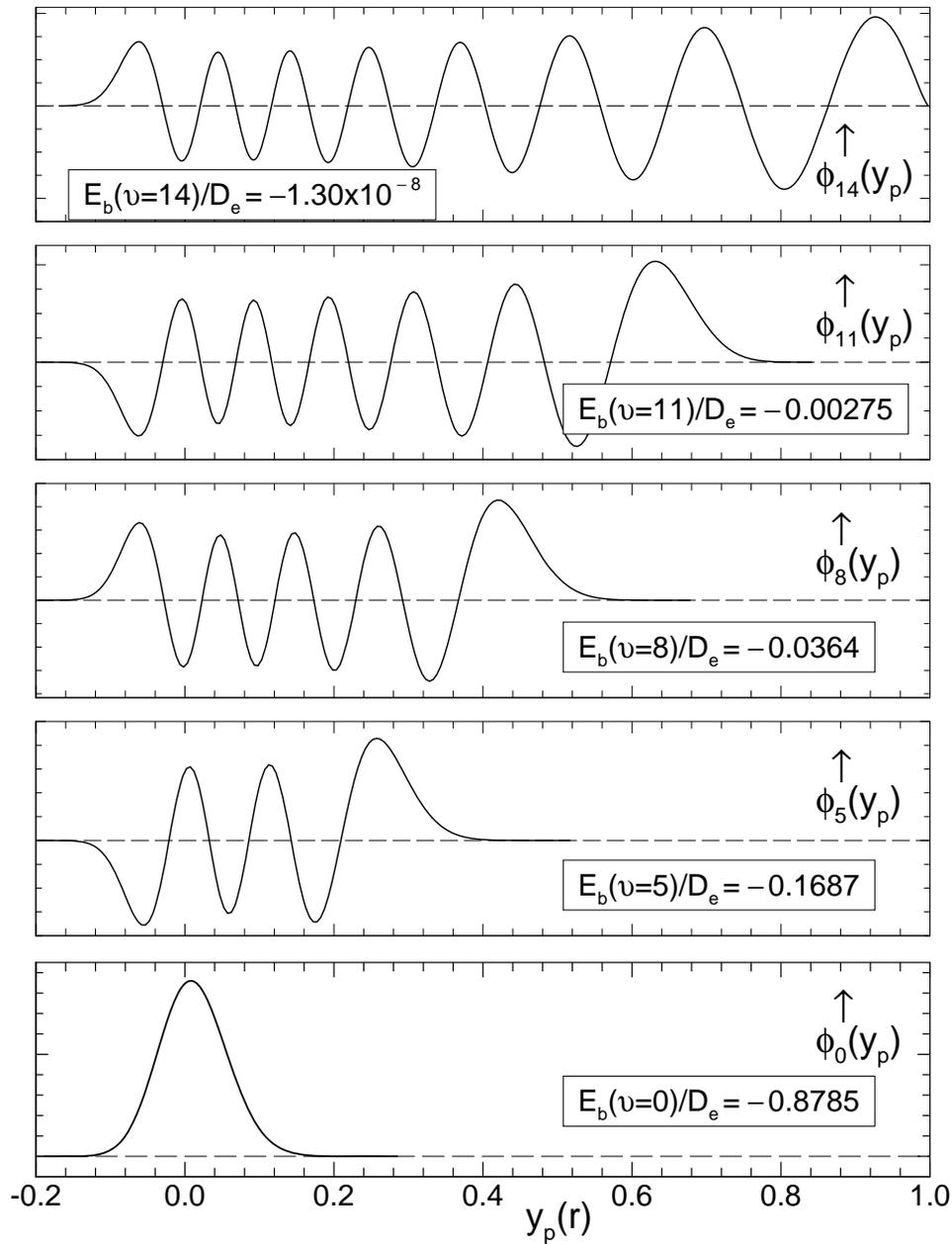
$$F(y) = \frac{1 - \frac{1}{\alpha^2}}{(1 - y^2)^2}$$

We test our new procedure by applications to a set of 15-level model LJ( $2n, n$ ) potential energy functions  $V_{\text{LJ}}(r) = \mathfrak{D}_e \left[ \left( \frac{r_e}{r} \right)^{2n} - 2 \left( \frac{r_e}{r} \right)^n \right]$  with parameters chosen so that the highest level is extremely weakly bound.

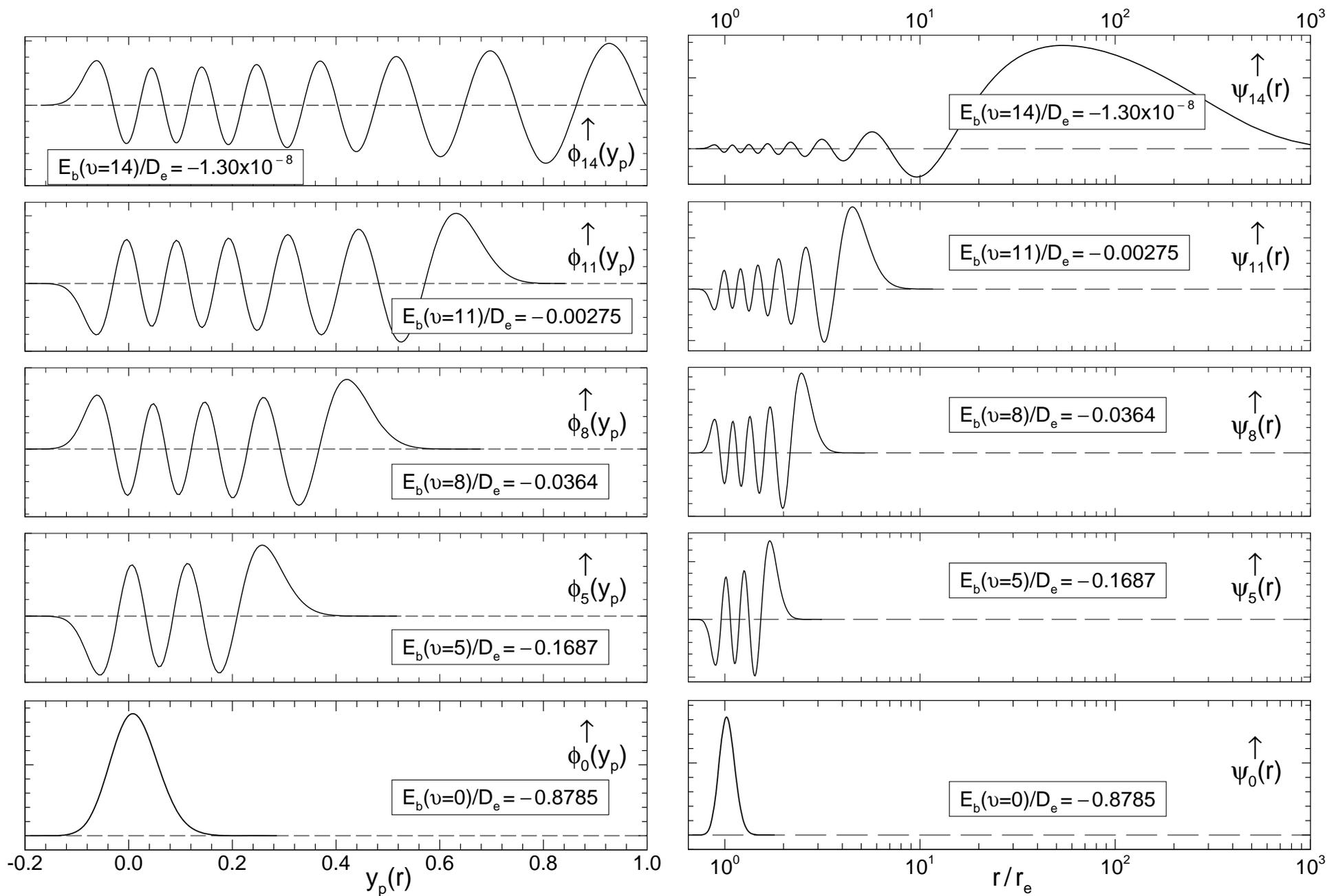
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<sup>†</sup> Three others are:  $y(r) = 1 - \exp(-\alpha r^\gamma)$ ,  $y(r) = \exp\{-\exp[\alpha(r - \bar{r})]\}$ , and  $y(r) = \arctan\{\alpha(r - \bar{r})\}$ .

For the same LJ(8,4) potential considered in slide #2, we find (with  $\alpha = 1$ ,  $\bar{r} = r_e$ )



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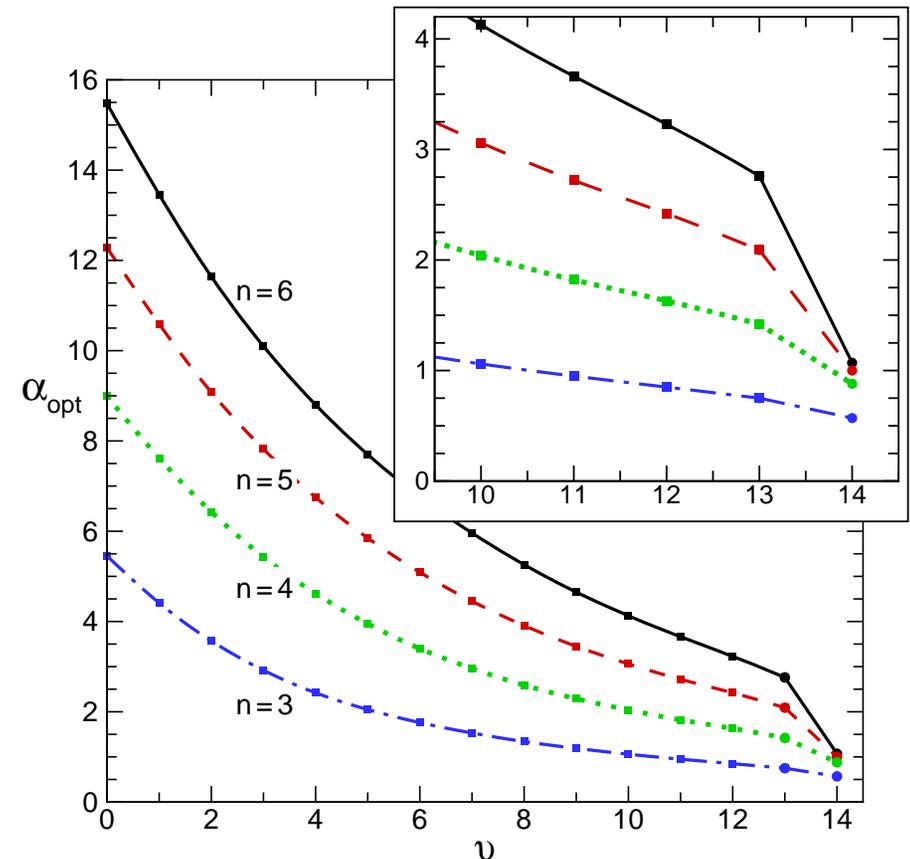
# How to select parameter mapping variables $\alpha$ and $\bar{r}$ ?

Tests show that  $\bar{r}$  has little effect, so focus on  $\alpha$  in the mapping:  $y = \frac{r^\alpha - r_e^\alpha}{r^\alpha + r_e^\alpha}$

For Numerov wavefunction propagation, with mesh size  $h$ , the eigenvalue error

$$\Delta E_{\text{Num}}(h) = \frac{\hbar^2}{2\mu} \left( \frac{h^4}{240} \right) \int_a^b \left[ \frac{d(\tilde{Q}\phi)}{dy} \right]^2 dy$$

For fixed  $h$ , vary  $\alpha$  to minimize error for each level of our model LJ( $2n, n$ ) potentials.



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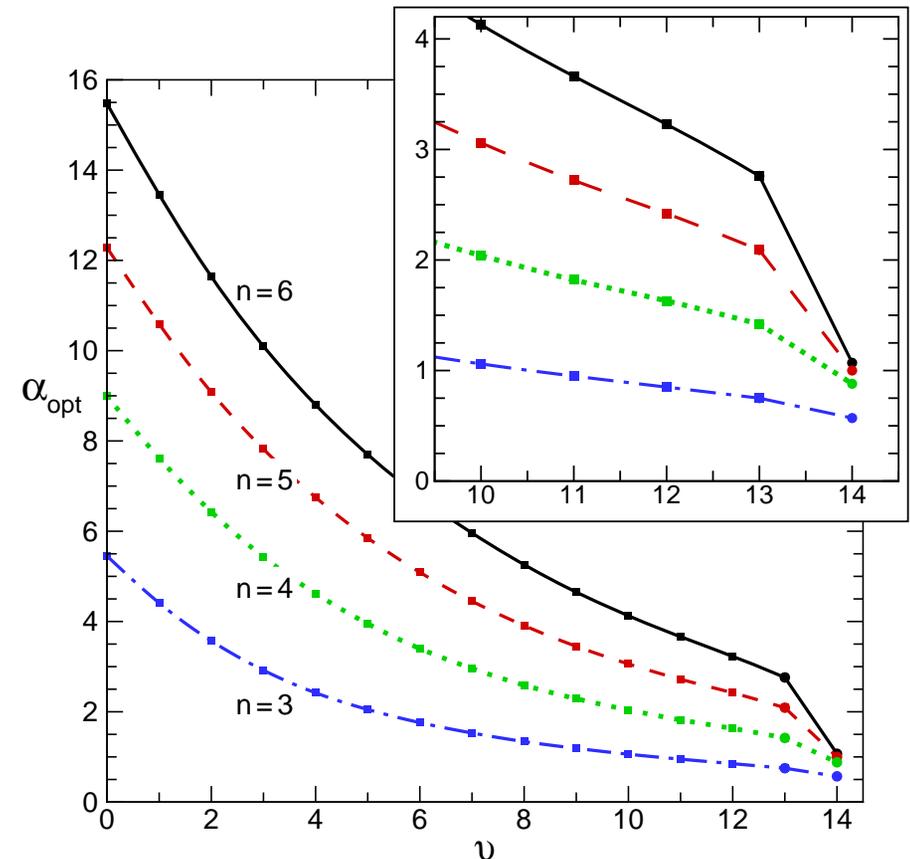
For Numerov wavefunction propagation, with mesh size  $h = dy$ , eigenvalue error

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For fixed  $h$ , vary  $\alpha$  to minimize error for each level of our model LJ( $2n, n$ ) potentials.

... but ...

- CPU intensive to optimize  $\alpha$  for each level
- matrix elements calculations require use of same mesh  $h$  and  $\alpha$  for all levels
- something funny happens for the very last level if  $n = 6, 5$  or  $4$ .



**Hence, need a general rule for all levels of all systems!**

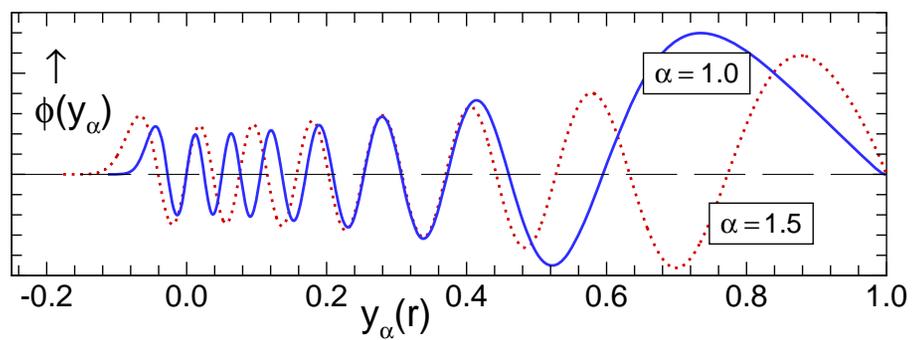
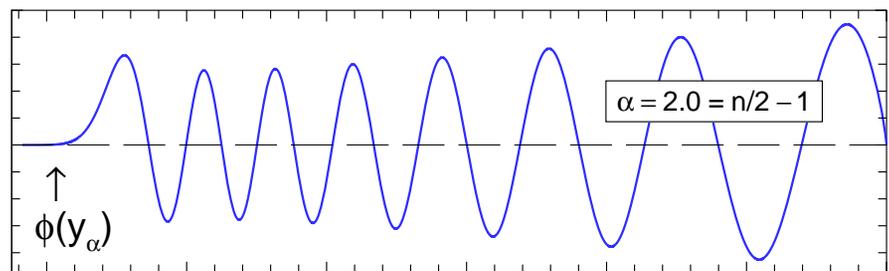
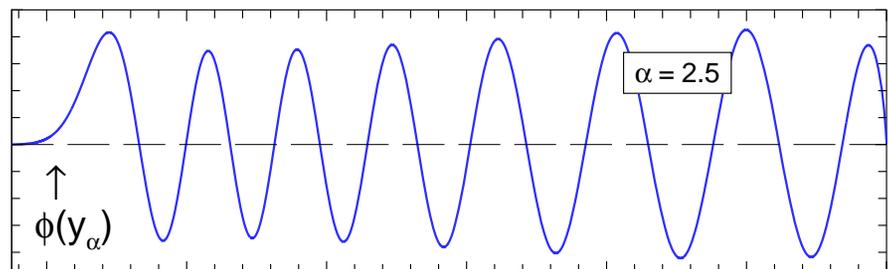
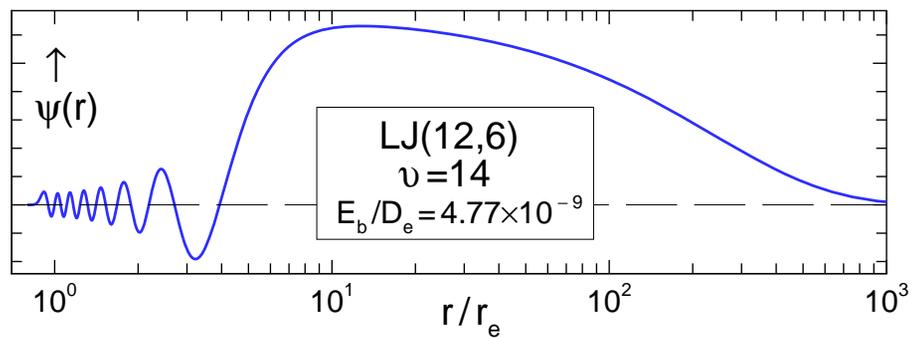
*Recall:* all intermolecular potentials have the limiting long-range form

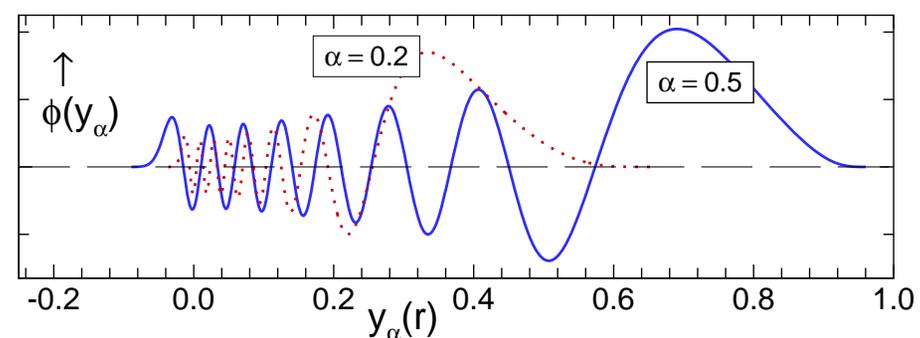
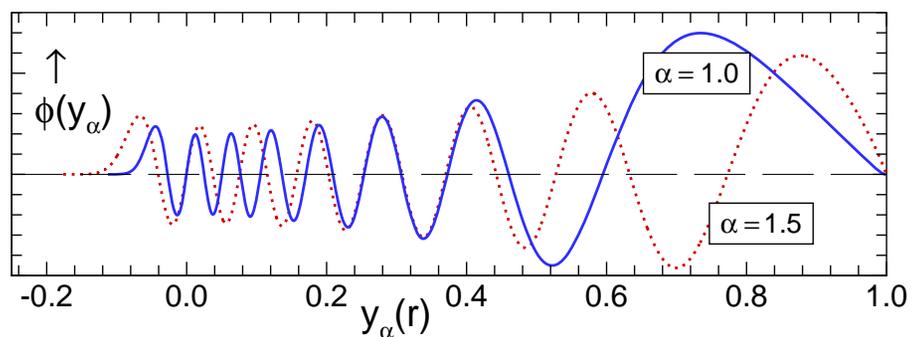
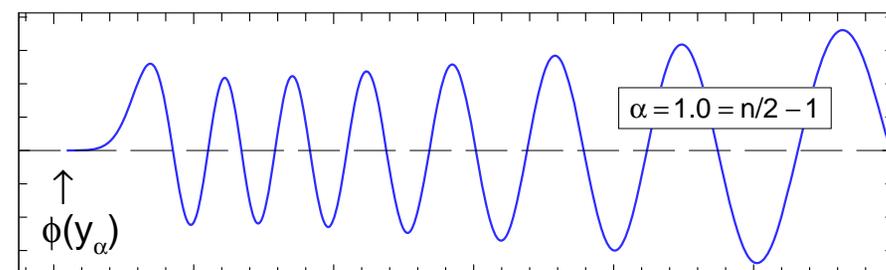
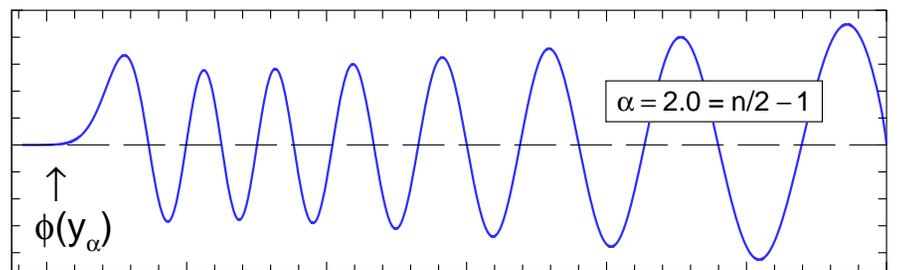
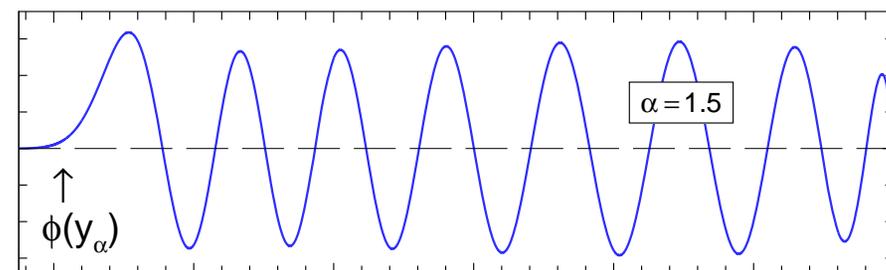
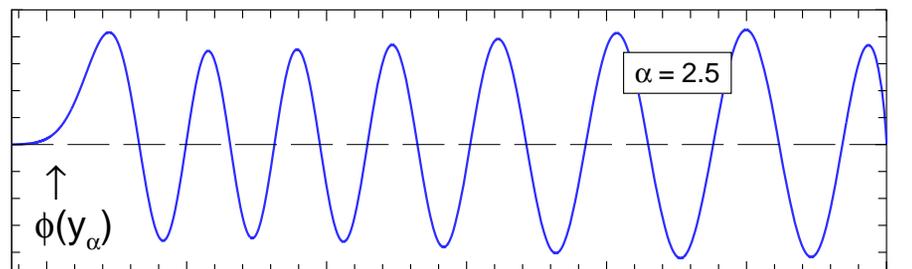
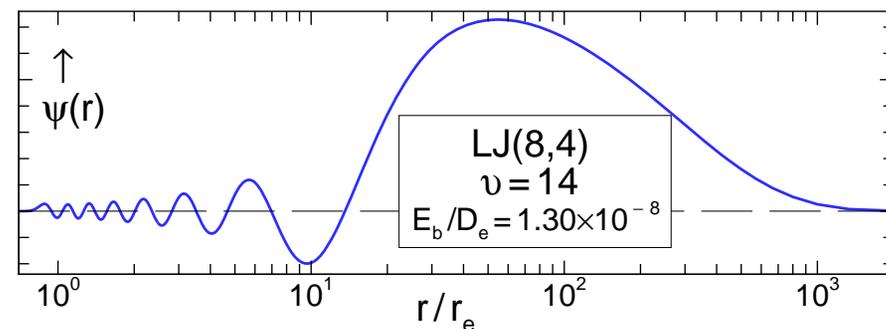
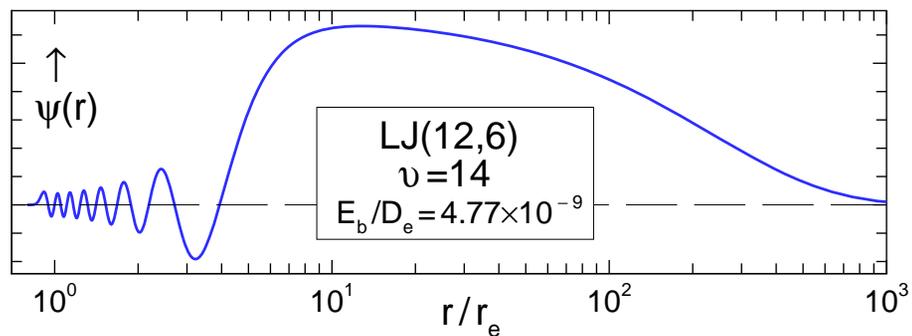
$$U(r) \simeq \mathfrak{D} - C_n/r^n \quad \text{with (except for ion-pair states) } n = 6, 5, 4 \text{ or } 3.$$

Semiclassical arguments show that for levels lying very near dissociation, over most of the classically allowed region between the turning points

$$\tilde{Q}(y) \approx \{\text{constant}\} \quad \text{if} \quad \alpha = \frac{n}{2} - 1$$

With this choice of  $\alpha$  the nodes of those wavefunctions  $\phi_v(y)$  should be approximately equally spaced – the *optimum* situation for efficient calculation.



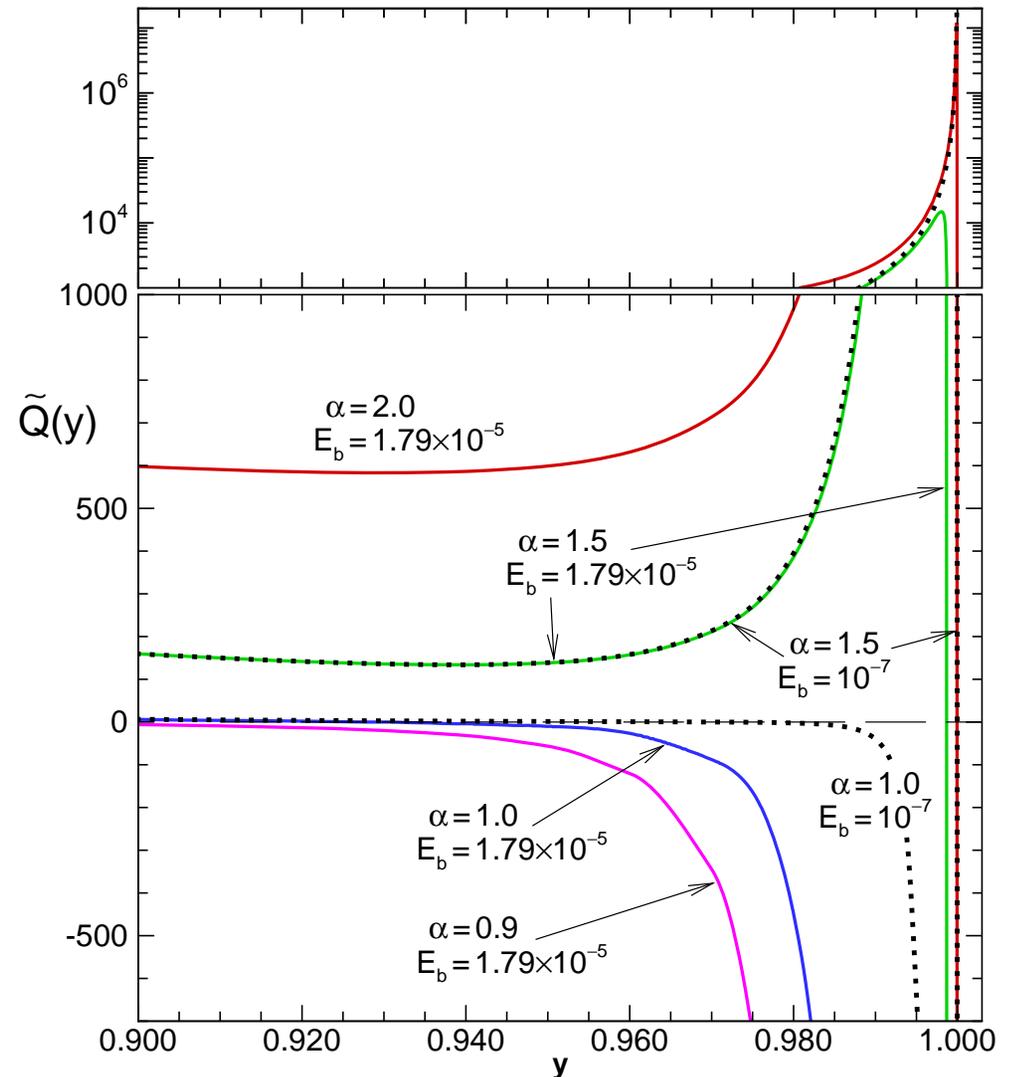


But what about the funny behaviour of  $\alpha^{\text{opt}}$  for the very last level?

The behaviour of the ‘curvature factor’  $\tilde{Q}(y)$  as  $y \rightarrow 1$  explains the abrupt drop-off of  $\alpha^{\text{opt}}$  for the very last level (for  $n = 4 - 6$ ). In that larger- $y$  region

$$\tilde{Q}(y) = - \left\{ \frac{2\mu}{\hbar^2} \left( \frac{2\bar{r}}{\alpha} \right)^2 [\mathcal{D} - E] \right\} \frac{(1+y)^{\frac{2}{\alpha}-2}}{(1-y)^{\frac{2}{\alpha}+2}} + \frac{1 - \frac{1}{\alpha^2}}{(1-y^2)^2}$$

For the very last level ( $v = 14$ ) of our model LJ(12,6) potential:

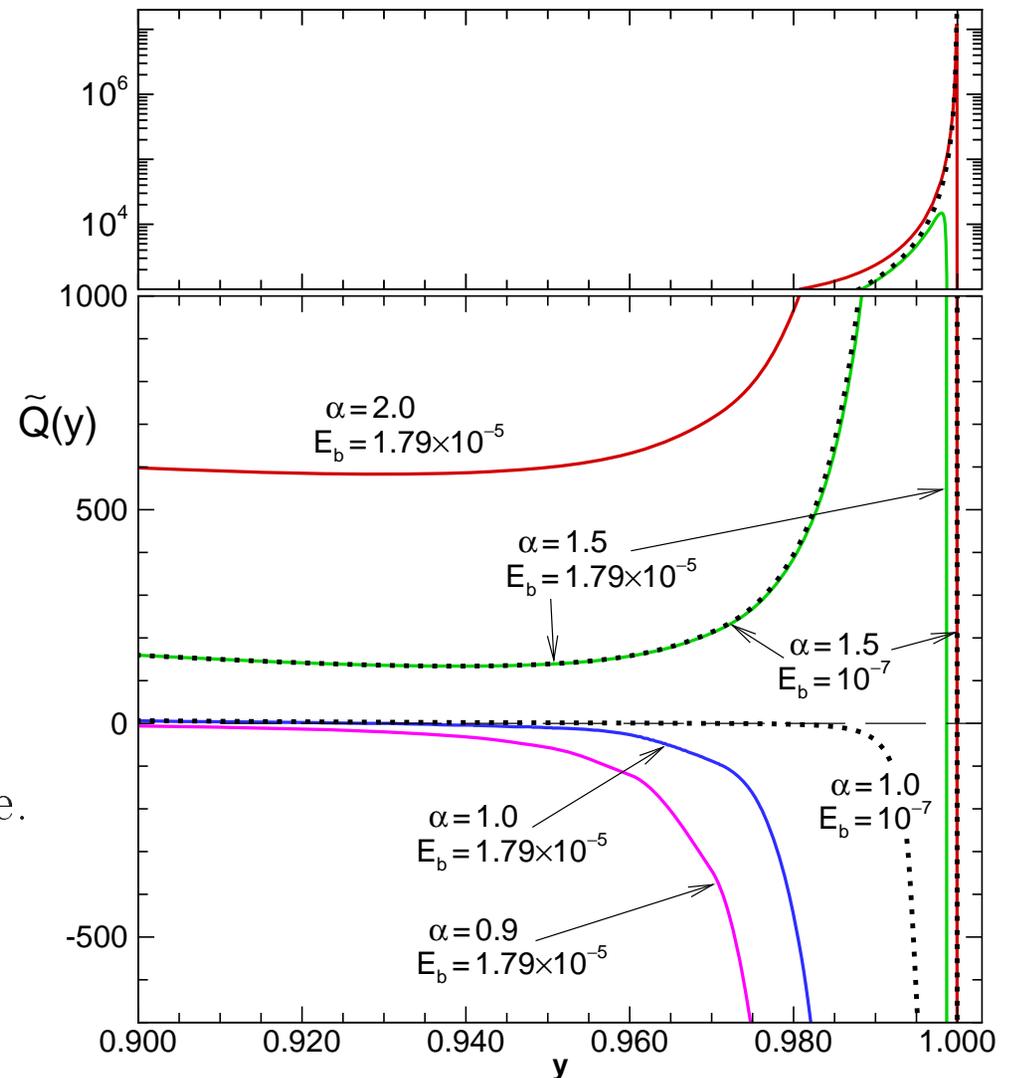


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For the very last level ( $v = 14$ ) of our model LJ(12,6) potential:

- if  $\alpha > 1$  the positive singularity of last term delays onset of exponential wavefunction die-off until too late.
- if  $\alpha = 1$  that term disappears, but for a level sufficiently close to  $\mathfrak{D}$  (dotted curve), exponential wavefunction die off still starts too late.
- setting  $\alpha < 1$  (say  $\alpha = 0.9$ ) forces early positive (exponential) curvature and accelerates wavefunction die off.



## *Conclusions for Bound State Calculations*

- The present method makes it very straightforward to treat levels lying *extremely* close to dissociation, which would have been virtually impossible to treat otherwise.

[ e.g., the last level of a 301-level LJ(6,3) potential with outer turning point at  $r/r_e = 1\,107\,853$  and binding energy  $E_b/\mathcal{D}_e = 1.5 \times 10^{-18}$  . ]

- The compact range and modest array sizes required make this method much more economical than conventional procedures, w.r.t. both array storage and CPU time.
- All ‘tricks’ associated with existing methods – such as inclusion of a centrifugal potential and locating and determining widths for tunneling predissociation level are readily implemented.
- As a default, set  $\alpha = \frac{n}{2} - 1$  .

If need higher accuracy for very last level of a potential

with a  $-C_n/r^n$  long-range tail for  $n = 4 - 6$  , use  $\alpha = 0.9$  .

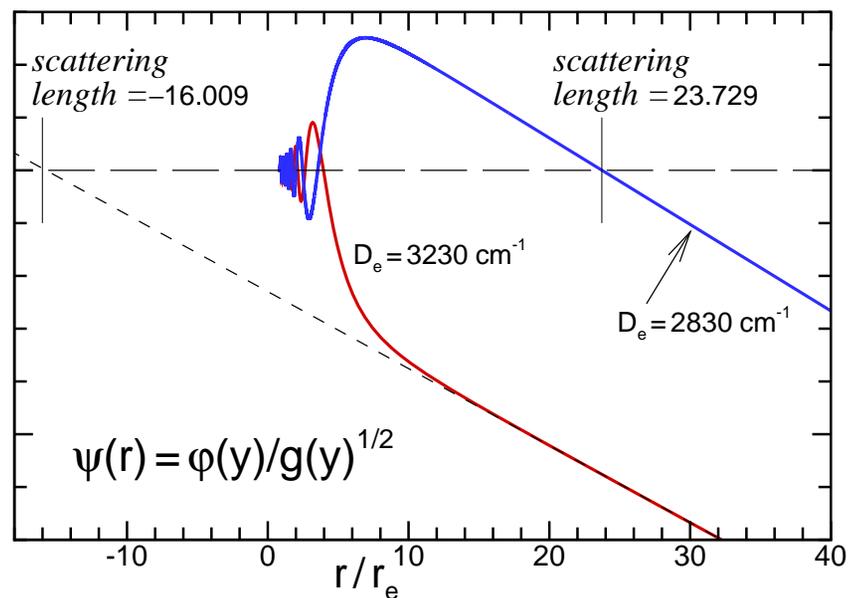
# Zero Energy Collision Properties: Scattering Lengths

The *scattering length* of a given potential is the distance  $a$  defined by the asymptotic form of the radial wavefunction at *zero collision energy*:

$$\psi(r) \simeq A(r - a)$$

A conventional calculation integrates  $\psi(r)$  to very large distances (e.g.,  $r \sim 100 - 1000$ ) and then fits it to this expression.

{ *very tedious; accumulates truncation error* }



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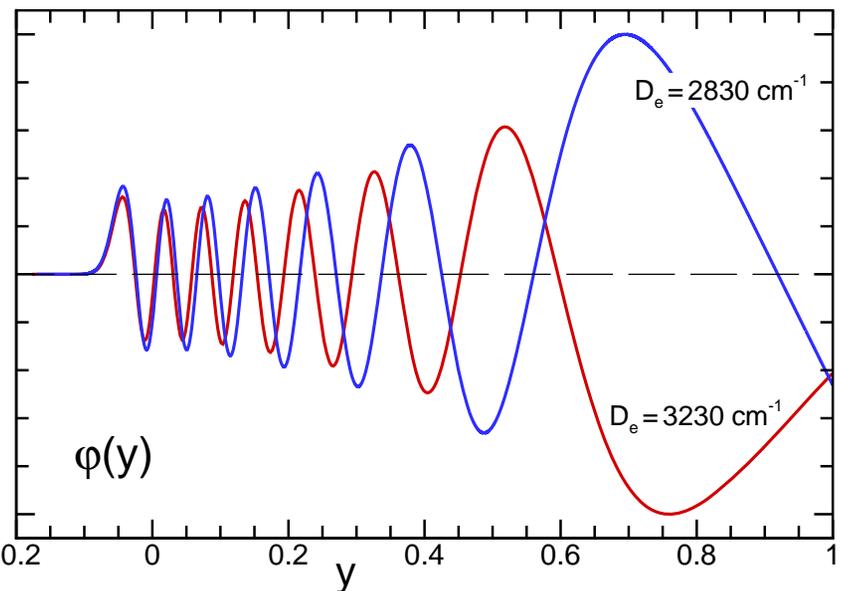
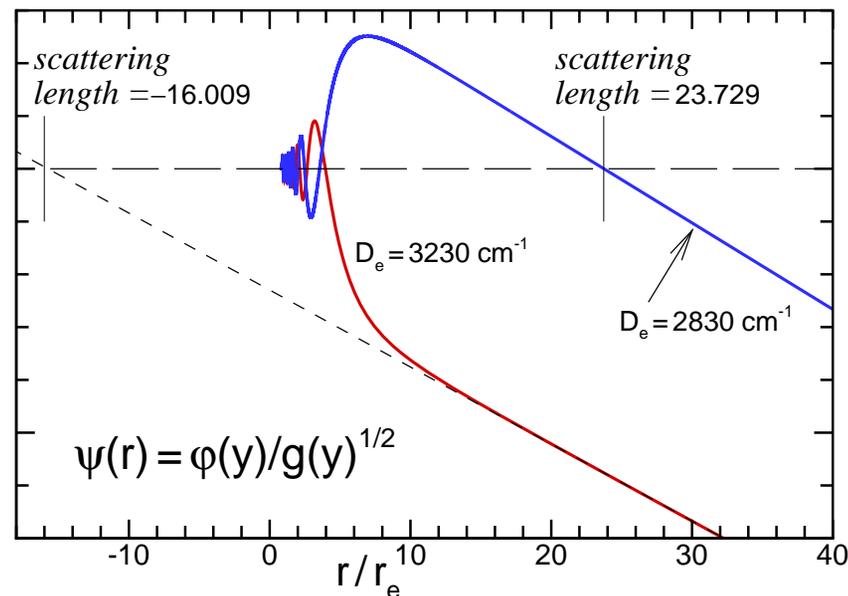
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In our method we merely

- propagate  $\phi(y)$  to  $y = 1$
- transforms  $\phi(y_i)$  at the preceding two mesh points to  $\psi(r(y_i))$
- fits those  $\psi(r(y_i))$  values to the limiting expression
- ***always use  $\alpha = 1$  for calculating properties at zero collision energy!***



Lennard-Jones(12, 6) potential with De= 3761.000(cm-1) Re = 1.000000(A)

=====  
y mesh: h= 0.00025

Calculate	SL= 2.42482642D+02	from wavefx at	R= 7997.500	3998.250
			y= 0.999750	0.999500
Calculate	SL= 2.42482642D+02	from wavefx at	R= 15996.000	7997.500
			y= 0.999875	0.999750
Calculate	SL= 2.42482642D+02	from wavefx at	R= 31993.000	15996.000
			y= 0.999932	0.999875

y mesh: h= 0.00005

Calculate	SL= 2.42483081D+02	from wavefx at	R= 39998.300	19998.650
			y= 0.999950	0.999900
Calculate	SL= 2.42483081D+02	from wavefx at	R= 79997.600	39998.300
			y= 0.999975	0.999950
Calculate	SL= 2.42483081D+02	from wavefx at	R= 159996.200	79997.600
			y= 0.999987	0.999975

=====