Ultracold molecules

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Plan

I *wanted* to give a broad overview of ultracold molecules,
how they are cooled (laser cooling, Feshbach association),
and their applications (precision measurement, quantum simulation, etc.)

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Instead we'll mostly discuss
Ultracold collisions

- Scattering length
- Resonances
  - Square well potential
  - Feshbach resonance
- Effective range
- Fermi pseudo potential
- Universality
- Quantum defect theory
- Collisional loss / Universal loss
- Applications to ultracold NaLi+Na collisions
- Applications of ultracold molecules

Collisions

Separate center of mass $\boldsymbol{R} = (\boldsymbol{r}_1 + \boldsymbol{r}_2)/2$ and relative $\boldsymbol{r} = \boldsymbol{r}_2 - \boldsymbol{r}_1$ motion.

$$\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)\right]\phi(\boldsymbol{r},\epsilon) = \epsilon\phi(\boldsymbol{r},\epsilon) \tag{1}$$

where $\mu = m_1 m_2/(m_1 + m_2)$.
Radial kinetic energy + centrifugal term

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}r + \frac{\hat{L}^2}{2\mu r^2} + V(r)\right]\phi(\boldsymbol{r},\epsilon) = \epsilon\phi(\boldsymbol{r},\epsilon) \tag{2}$$

and $\psi = r\phi$ satisfies

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{\hat{L}^2}{2\mu r^2} + V(r)\right]\psi(\boldsymbol{r},\epsilon) = \epsilon\psi(\boldsymbol{r},\epsilon). \tag{3}$$

If $V = V(r)$ the angular coordinates separate.
The angular solutions are spherical harmonics Y_{ℓ,m_ℓ}, and the radial problem can be solved per ℓ, m_ℓ

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2\mu r^2} + V(r)\right]\psi(r,\epsilon) = \epsilon\psi(r,\epsilon). \tag{4}$$

If $E \to 0$, centrifugal barriers cannot be overcome and only the lowest $\ell = 0$ contributes.

s-wave collisions at zero energy

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V(r)\right]\psi(\boldsymbol{r},\epsilon) = \epsilon\psi(\boldsymbol{r},\epsilon) \tag{5}$$

At $\epsilon = 0$, and for $r > r_0$ where $V(r) = 0$; ψ straight line!

$$\psi(\boldsymbol{r},0) \simeq a + br = c(r - a_0) \tag{6}$$

This defines the s-wave scattering length a_0

Hard-wall potential

$$a_0 = a \tag{7}$$

Square well potential

$$V = \begin{cases} \infty & R < a \\ -V_0 & a < R < b \\ 0 & R > b \end{cases} \tag{8}$$

$a < R < b$

$$\begin{aligned} \psi &= \sin\left(k_0\left[R - a\right]\right) \\ \psi' &= k_0 \cos\left(k_0\left[R - a\right]\right) \end{aligned} \tag{9}$$

$R > b$

$$\begin{aligned} \psi &= \sin\left(k\left[R - a_0\right]\right) \\ \psi' &= k \cos\left(k\left[R - a_0\right]\right) \end{aligned} \tag{10}$$

Equating the log-derivatives (ψ'/ψ) at $R = b$

$$\frac{k}{\tan\left(k\left[b - a_0\right]\right)} = \frac{k_0}{\tan\left(k_0\left[b - a\right]\right)} \tag{11}$$

For $k \to 0$

$$a_0 = b - \frac{\tan\left(k_0\left[b - a\right]\right)}{k_0} \tag{12}$$

Square well potential (continued)

For $k \to 0$

$$a_0 = b - \frac{\tan\left(k_0\left[b-a\right]\right)}{k_0} \tag{13}$$

When the square well is absent; $k_0 = k \to 0$

$$a_0 = b - \frac{k\left[b-a\right]}{k} = a \tag{14}$$

But if $k_0 \neq k$ huge modification if $k_0\left[b-a\right]/\pi = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$: Resonances
Divergence of scattering resonance = "*bound state*"

Shape resonances?

Feshbach resonance

$$V_1 = \begin{cases} \infty & R < a \\ 0 & R > a \end{cases} \tag{15}$$

A second "closed" channel

$$V_2 = \begin{cases} \infty & R < a \\ -V_0 & a < R < b \\ \infty & R > a \end{cases} \tag{16}$$

and constant coupling C for $a < R < b$. Here the potential becomes

$$\boldsymbol{V} = \begin{bmatrix} 0 & C \\ C & -V_0 \end{bmatrix} \tag{17}$$

Diagonalize $\boldsymbol{V}$ to find adiabatic potentials

$$\boldsymbol{V}\boldsymbol{U} = \boldsymbol{U} \begin{bmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{bmatrix} \tag{18}$$

$$\epsilon_1 = \frac{-V_0 + \sqrt{V_0^2 + (2C)^2}}{2}, \qquad \epsilon_2 = \frac{-V_0 - \sqrt{V_0^2 + (2C)^2}}{2} \tag{19}$$

$$\boldsymbol{U} = \begin{bmatrix} \cos\phi & -\sin\phi \\ \sin\phi & \cos\phi \end{bmatrix}, \qquad \tan\phi = \frac{V_0 - \sqrt{V_0^2 + (2C)^2}}{2C} \tag{20}$$

Feshbach resonance (continued)

For $a < R < b$ two independent solutions are

$$\psi_1 = \sin\left[k_1\left(R-a\right)\right] \tag{21}$$

living on the first adiabat, and

$$\psi_2 = \sin\left[k_2\left(R-a\right)\right] \tag{22}$$

living on the second ($k_1^2 = 2m\epsilon_1$, ...)
In the original channel basis a linear combination is

$$\phi(R) = \frac{1}{\cos\phi}\sin\left[k_1\left(R-a\right)\right]\begin{bmatrix}\cos\phi\\ \sin\phi\end{bmatrix} + \frac{C}{\cos\phi}\sin\left[k_2\left(R-a\right)\right]\begin{bmatrix}-\sin\phi\\ \cos\phi\end{bmatrix} \tag{23}$$

The second component of ϕ should vanish at $R = b$ which gives

$$C = -\tan\phi\frac{\sin\left[k_1\left(b-a\right)\right]}{\sin\left[k_2\left(b-a\right)\right]} \tag{24}$$

This gives the first component

$$\phi_1(R) = \sin\left[k_1\left(R-a\right)\right] + \tan^2\phi\frac{\sin\left[k_1\left(b-a\right)\right]}{\sin\left[k_2\left(b-a\right)\right]}\sin\left[k_2\left(R-a\right)\right] \tag{25}$$

The solution for $R > b$ is again $\sin[k(R-a_0)]$. We can again equate the log-derivatives and solve for a_0.

Feshbach resonance (continued 2)

$$\phi_1'(b) = k_1 \cos\left[k_1\left(b-a\right)\right] + k_2 \tan^2\phi \frac{\sin\left[k_1\left(b-a\right)\right]}{\sin\left[k_2\left(b-a\right)\right]} \cos\left[k_2\left(R-a\right)\right]$$
$$\phi_1(b) = \sin\left[k_1\left(b-a\right)\right]\left(1+\tan^2\phi\right) \tag{26}$$

equate log derivative to $k/\tan[k(b-a_0)]$.
Next we assume the initial state potential is unperturbed $k_1 = k$ yielding

$$\frac{k}{\tan\left(k\left[b-a_0\right]\right)} = \frac{k}{\tan\left(k\left[b-a\right]\right)\left(1+\tan^2\phi\right)} + \frac{\tan^2\phi}{1+\tan^2\phi}\frac{k_2}{\tan\left(k_2\left[b-a\right]\right)} \tag{27}$$

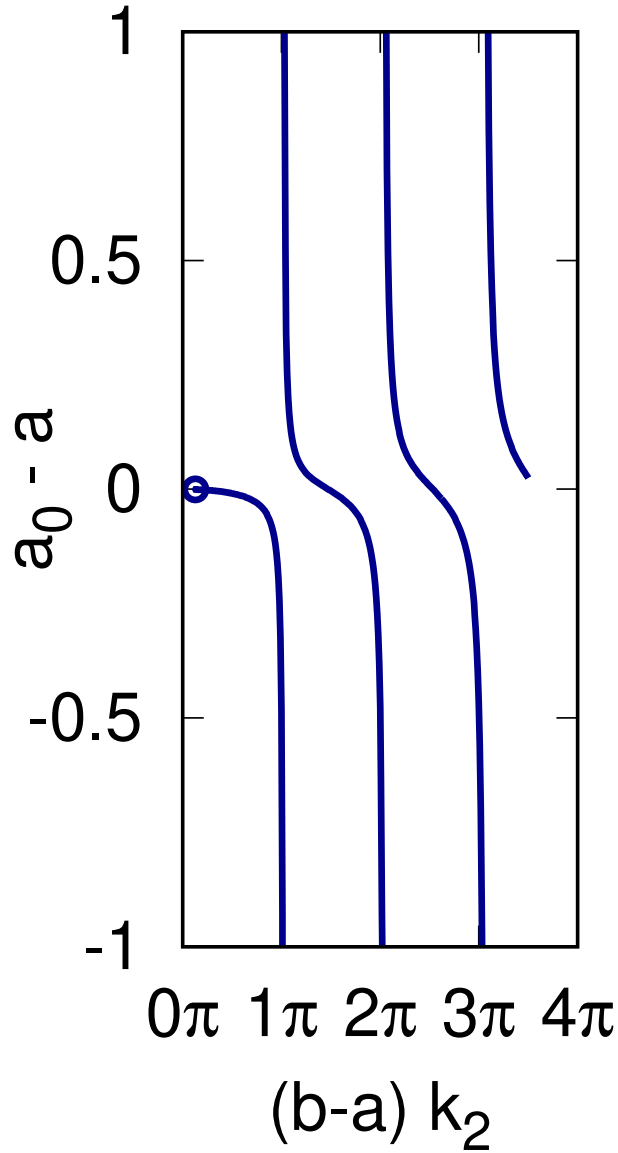
For small ϕ (sloppy)

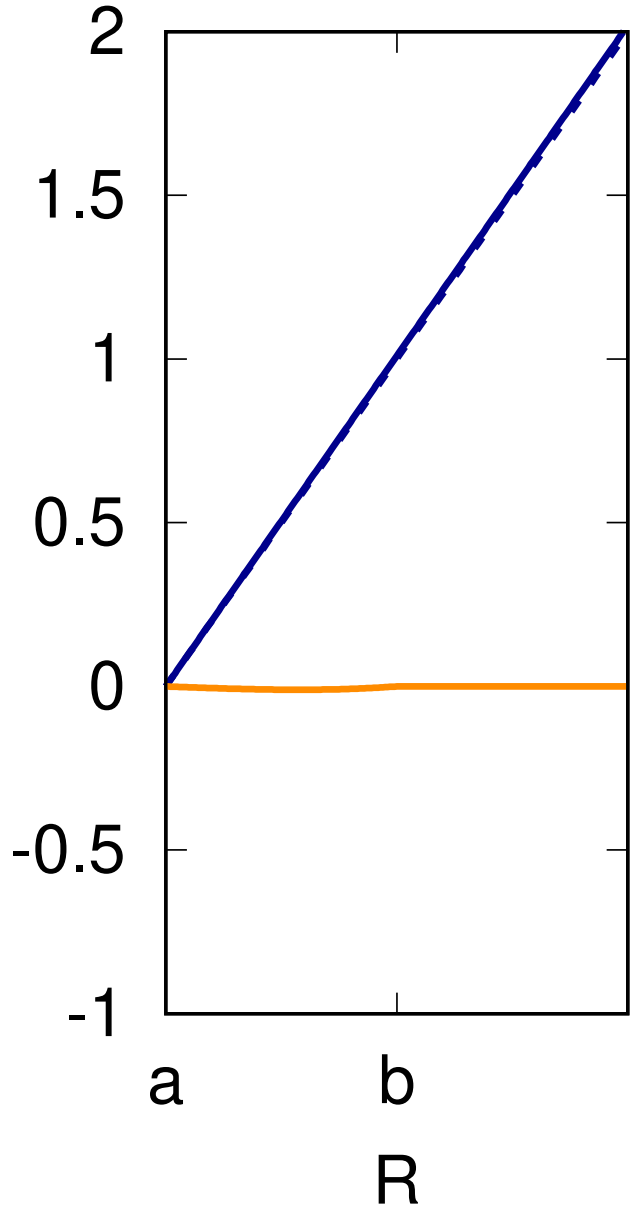
$$\frac{k}{\tan\left(k\left[b-a_0\right]\right)} = \frac{k}{\tan\left(k\left[b-a\right]\right)} + \tan^2\phi\frac{k_2}{\tan\left(k_2\left[b-a\right]\right)} \tag{28}$$

We have $a_0 = a$ plus a correction that is small in $\tan\phi$ <u>unless</u> $\tan\left(k_2\left[b-a\right]\right) \to 0$.
This is the condition that there exists a bound state in the closed channel.
For small k

$$a_0 = b - \frac{\left[b-a\right]\tan\left(k_2\left[b-a\right]\right)}{\tan\left(k_2\left[b-a\right]\right) + k_2\left[b-a\right]\tan^2\phi}. \tag{29}$$

Feshbach resonance





Effective range (1)

Solutions to Schrödinger at two energies

$$\left[\frac{d^2}{dR^2} - 2\mu V(R) + k_1^2\right]\psi_1(R) = 0 \tag{30}$$

$$\left[\frac{d^2}{dR^2} - 2\mu V(R) + k_2^2\right]\psi_2(R) = 0 \tag{31}$$

regular at $R = 0$, and asymptotically varying as $\sin(k_1 R + \delta_1)$ and $\sin(k_2 R + \delta_2)$. (The scattering length is the zero energy limit of $-\tan\delta/k$, and we can call $a_1 = -\tan\delta_1/k_1$ and $a_2 = -\tan\delta_2/k_2$ energy-dependent scattering lengths.)
Multiply Eq. (30) by ψ_2 and (31) by ψ_1, subtract, and integrate

$$\frac{d^2\psi_1}{dR^2}\psi_2 - \psi_1\frac{d^2\psi_2}{dR^2} = (k_2^2 - k_1^2)\psi_1\psi_2. \tag{32}$$

Integrate using

$$\frac{d^2\psi_1}{dR^2}\psi_2 - \psi_1\frac{d^2\psi_2}{dR^2} = \frac{d}{dR}\left[\frac{d\psi_1}{dR}\psi_2 - \psi_1\frac{d\psi_2}{dR}\right] \tag{33}$$

to obtain

$$\left.\frac{d\psi_1}{dR}\psi_2 - \psi_1\frac{d\psi_2}{dR}\right|_0^R = (k_2^2 - k_1^2)\int_0^R \psi_1\psi_2\ dR \tag{34}$$

Effective range (2)

For reference, solve Schrödinger Eq "asymptotically", for zero potential

$$\left[\frac{d^2}{dR^2} + k_1^2\right] u_1(R) = 0 \tag{35}$$

$$\left[\frac{d^2}{dR^2} + k_2^2\right] u_2(R) = 0 \tag{36}$$

where

$$u_1(R) = \sin(k_1 R + \delta_1)/\sin(\delta_1) \qquad u_2(R) = \sin(k_2 R + \delta_2)/\sin(\delta_2) \tag{37}$$

Normalization is such that $u_1(0) = u_2(0) = 1$, and asymptotically $\psi_1 \simeq u_1$ and $\psi_2 \simeq u_2$ with $a_1 = -\tan(\delta_1)/k_1$ and $a_2 = -\tan(\delta_2)/k_2$ are "energy dependent" scattering lengths (choose normalization of ψ_1 and ψ_2 such that this holds). Similarly derive

$$\frac{du_1}{dR} u_2 - u_1 \frac{du_2}{dR}\bigg|_0^R = (k_2^2 - k_1^2) \int_0^R u_1 u_2 \; dR \tag{38}$$

Subtract the previous result

$$\left[u_1' u_2 - u_1 u_2'\right]_0^R - \left[\psi_1' \psi_2 - \psi_1 \psi_2'\right]_0^R = (k_2^2 - k_1^2) \int_0^R u_1 u_2 - \psi_1 \psi_2 \; dR \tag{39}$$

Now because ψ_1 asymptotically approaches u_1, the upper limits cancel if $R \to \infty$. At lower limit $\psi_1(0) = \psi_2(0)$ so only u_1 and u_2 contribute.

Effective range (3)

$$u_1 = \sin(k_1 R + \delta_1)/\sin(\delta_1)$$
$$u_1' = k_1 \cos(k_1 R + \delta_1)/\sin(\delta_1) \tag{40}$$

So $u_1'(0) = -1/a_1$ and similarly $u_2'(0) = -1/a_2$. Hence we obtain

$$\frac{1}{a_1} - \frac{1}{a_2} = (k_2^2 - k_1^2) \int_0^R u_1 u_2 - \psi_1 \psi_2 \; dR \tag{41}$$

Now the integrand on the right-hand side is appreciable only where $V(R)$ is appreciable such that it causes a difference between $u_1(R)$ and $\psi_1(R)$. Here, $V(R)$ is also appreciable compared to E_1 and E_2 if these are sufficiently low, so we can neglect their energy dependence. So approximately we can use the zero-energy wavefunctions

$$\int_0^R u_1 u_2 - \psi_1 \psi_2 \; dR \approx \int_0^R u_0^2 - \psi_0^2 \; dR = \frac{1}{2} r_0 \tag{42}$$

which defines the "effective range" r_0.
This gives the energy-dependent scattering length a close to zero energy

$$\frac{1}{a} = \frac{1}{a_0} + \frac{1}{2} k^2 r_0 \tag{43}$$

Effective range (4)

Now we can take this a bit further and relate the scattering length to the position of the least-bound state at energy $-\frac{\hbar^2}{2m}\gamma^2$

$$\left[\frac{d^2}{dR^2} - 2\mu V(R) - \gamma^2\right]\psi_b(R) = 0, \qquad \left[\frac{d^2}{dR^2} - \gamma^2\right]u_b(R) \qquad = 0 \tag{44}$$

where the bound state asymptotically behaves as $u_b(R) = \exp(-\gamma R)$ (which is again normalized at the origin $u_b(0) = 1$, $u_b'(0) = -\gamma$).
Now we can repeat the derivation to obtain

$$\left[u_1' u_b - u_1 u_b'\right]_0^R - \left[\psi_1'\psi_b - \psi_1\psi_b'\right]_0^R = (-\gamma^2 - k_1^2)\int_0^R u_1 u_b - \psi_1\psi_b \; dR \tag{45}$$

(note $k_2^2 \to -\gamma^2$ on the right-hand side). This yields

$$\frac{1}{a_1} - \gamma = -(\gamma^2 + k_1^2)\int_0^R u_1 u_b - \psi_1\psi_b \; dR \tag{46}$$

This gives the relation between the energy-dependent scattering length, the effective range, and the energy of the least-bound state

$$\frac{1}{a} = \gamma - \frac{1}{2}(\gamma^2 + k^2)r_0. \tag{47}$$

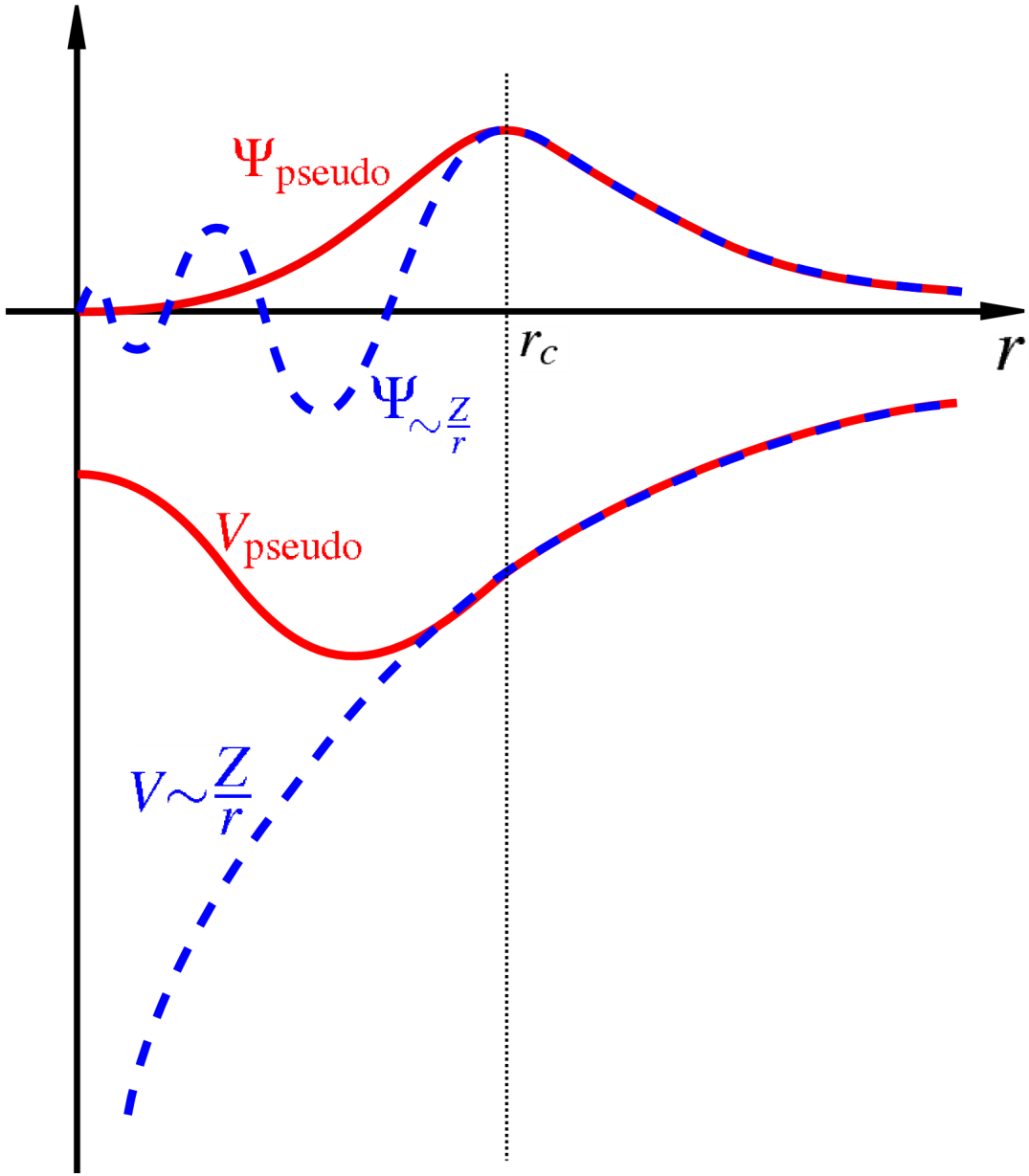
The energy of the least bound state is $E_b = -\frac{\hbar^2}{2\mu}\gamma^2$, which (neglecting the effective range correction) is related to the zero-energy scattering length as

$$E_b = -\frac{\hbar^2}{2\mu a_0^2}. \tag{48}$$

Dilute gas, typical interparticle spacing d
Short-range interactions $V(r > r_0) = 0$
$d \gg r_0$

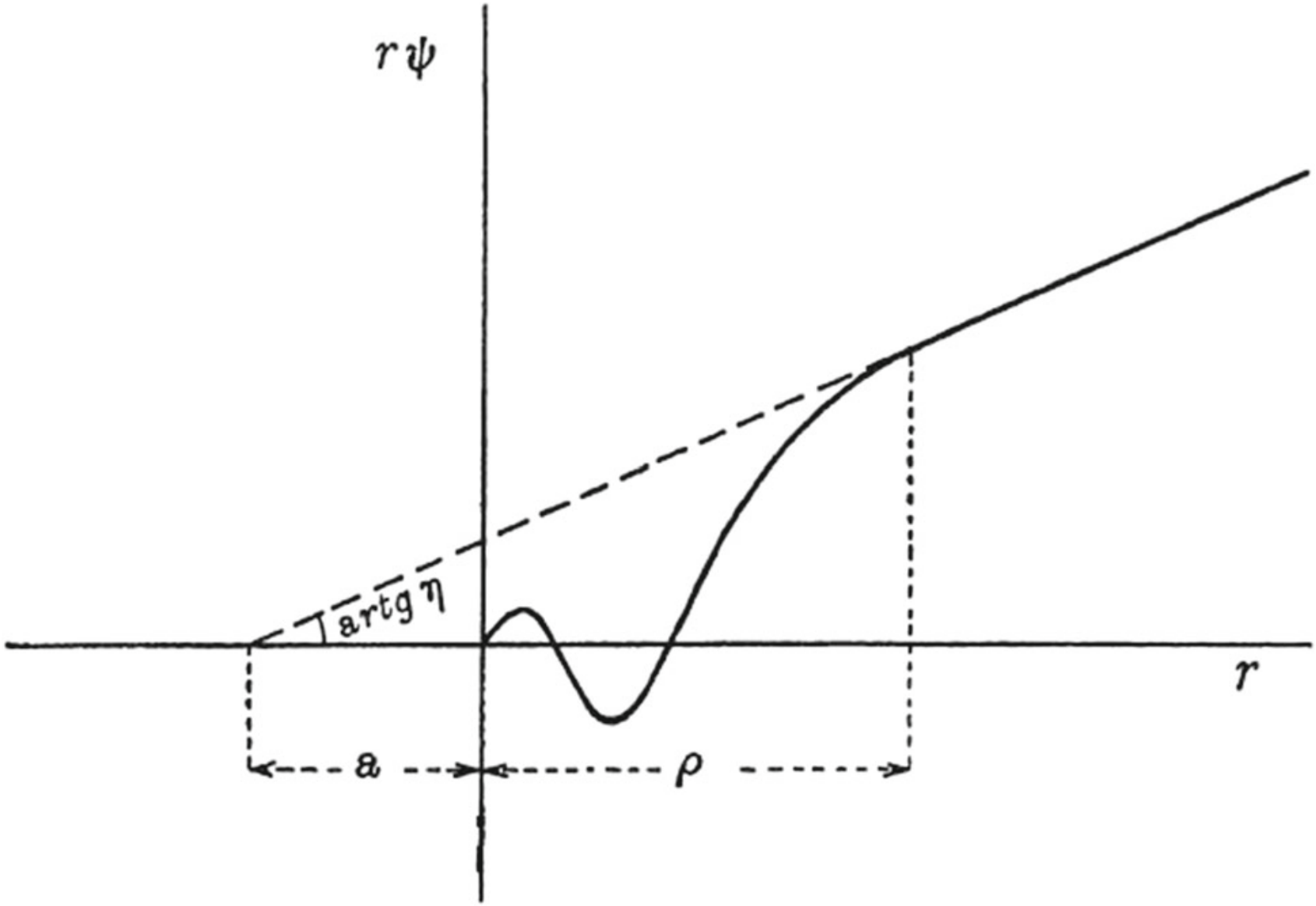
Pseudo potentials

Simpler (unphysical) potential that produces the same states for part of the spectrum
(Say, same energy and large-r wave function)



[wikipedia]

Pseudo potentials



[Fermi]

Hard-wall pseudopotential

$$V = \begin{cases} \infty & R < a_0 \\ 0 & R > a_0 \end{cases} \tag{49}$$

Fermi pseudopotential

$$\frac{4\pi\hbar^2}{2\mu} a_0 \delta(\boldsymbol{r}) \tag{50}$$

It's not the real potential

Counter examples

- ψ that vanishes for $r > 0$, so $\langle\psi|\delta(r)|\psi\rangle = 0$.
- Repulsive interactions for semi-infinite square well, for which $\langle\psi|V|\psi\rangle$ is always attractive

Loss by an absorbing potential

$$\int \psi^* \mathrm{Im}(V)\psi \; d\boldsymbol{r} = \frac{1}{2i}\left[\int \psi^* V \psi \; d\boldsymbol{r} - \int \psi V^* \psi^* \; d\boldsymbol{r}\right] \tag{51}$$

Now $\left(\hat{T} + \hat{V}\right)\psi = 0$ at zero energy

$$\begin{aligned}\int_0^R \psi^* \mathrm{Im}(V)\psi \; dr &= \frac{1}{2i}\frac{\hbar^2}{2\mu}\int_0^R \psi^* \frac{d^2}{dr^2}\psi \; dr - \int_0^R \psi \frac{d^2}{dr^2}\psi^* \; dr \\ &= \frac{1}{2i}\frac{\hbar^2}{2\mu}\left[\psi^* \frac{d}{dr}\psi - \psi \frac{d}{dr}\psi^*\right]_0^R \end{aligned} \tag{52}$$

Now if R is large enough, we can use the asymptotic form of $\psi = c(r - a_0)$ to evaluate the upper limit, and $\psi(0) = 0$ for the lower limit. This gives

$$\int \psi^* \mathrm{Im}(V)\psi \; dr = \frac{1}{2i}\frac{\hbar^2}{2\mu}\left[c^*(R - a_0^*)c - c(R - a_0)c^*\right] = \frac{\hbar^2}{2\mu}|c|^2 \mathrm{Im}(a_0) \tag{53}$$

Exact relation between integral over ψ where $V \neq 0$ and the asymptotic ψ where $V = 0$

$$\iiint \psi^* \mathrm{Im}(V)\psi \; d\boldsymbol{r} = 4\pi \frac{\hbar^2}{2\mu}\mathrm{Im}(a_0) \tag{54}$$

As we have seen, an analogous relation does not exist for $\mathrm{Re}(a_0)$!

($\mathrm{Re}(a_0)$ does set an effective interaction, $\frac{4\pi\hbar^2 \mathrm{Re}(a_0)}{2\mu}\delta(r)$, but it's not actually related to $\iiint \psi^* \mathrm{Re}(V)\psi \; d\boldsymbol{r}$)

But the pseudopotential does have meaning ...

Let us say we have two molecules in a harmonic potential.
The center of mass and relative motion separate, and we consider the latter.
The physical interaction might be

$$V(r) = V_{\mathrm{SR}}(R) + \frac{1}{2}\mu\omega^2 R^2 \tag{55}$$

where $V_{\mathrm{SR}}(R)$ could be a Lennard-Jones potential, for example.
Now the idea is that if $V_{\mathrm{SR}}(R)$ acts on short separation, and we're interested only in the wavefunction at larger R, we can just replace it by the Fermi pseudopotential

$$V_{\mathrm{SR}}(R) \to \frac{4\pi\hbar^2 a_0}{2\mu}\delta(\boldsymbol{r}) \tag{56}$$

Then if a_0 is small enough we might treat this perturbatively and compute the energy shift compared to a bare isotropic harmonic oscillator in 3D, which has energy $3/2\hbar\omega$ in the ground state and

$$\begin{aligned}\psi(\boldsymbol{r}) &= \psi_0(x)\psi_0(y)\psi_0(z)\\ \psi_0(x) &= \pi^{-1/4} a_{\mathrm{harm}}^{-1/2} \exp(-1/2 r^2/a_{\mathrm{harm}}^2)\end{aligned} \tag{57}$$

where $a_{\mathrm{harm}} = \sqrt{\hbar/\mu\omega}$ is the harmonic oscillator length.

But the pseudopotential does have meaning ... (2)

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where $a_{\mathrm{harm}} = \sqrt{\hbar/\mu\omega}$ is the harmonic oscillator length.

$$\begin{aligned}\langle\psi|\delta(\boldsymbol{r})|\psi\rangle &= \langle\psi_x|\delta(x)|\psi_x\rangle^3 \\ &= \left[\frac{1}{a_{\mathrm{harm}}\sqrt{\pi}}\right]^3\end{aligned} \tag{59}$$

and so

$$\langle\psi|\frac{4\pi\hbar^2 a_0}{2\mu}\delta(\boldsymbol{r})|\psi\rangle = \frac{2}{\sqrt{\pi}}\frac{\hbar^2}{\mu a_{\mathrm{harm}}^2}\frac{a_0}{a_{\mathrm{harm}}} = \hbar\omega\frac{2}{\sqrt{\pi}}\frac{a_0}{a_{\mathrm{harm}}}. \tag{60}$$

Two molecules in an isotropic harmonic trap

Without interactions, we solve a harmonic oscillator problem for the radial coordinate

$$\left[-\frac{\hbar}{2\mu}\frac{d^2}{dR^2}+\frac{1}{2}\mu\omega^2R^2\right]R\psi = ER\psi \tag{61}$$

which is the usual 1D harmonic oscillator SE for $R\psi$ (rather than ψ).
The solutions are

$$R\psi_n = \frac{1}{\sqrt{2^n n!}}\pi^{-1/4}a_{\rm harm}^{-1/2}\exp(-\frac{1}{2}R^2/a_{\rm harm}^2)H_n(R/a_{\rm harm})$$
$$E_n = \hbar\omega(n+\frac{1}{2}) \tag{62}$$

But now the boundary conditions are different. Normally you take x between $\pm\infty$ and require $\psi(\pm\infty)\to 0$. Now, R ranges from 0 to $+\infty$. If ψ_n is to remain finite at $R=0$, then $R\psi_n$ should vanish at $R=0$, and only the odd n work.

$$E/\hbar\omega = \frac{3}{2},\frac{7}{2},\ldots \tag{63}$$

are allowed (for s-wave states).

Two molecules in an isotropic harmonic trap (2)

Now, rather than including the physical $V_{\rm SR}(R)$ or the pseudopotential, we can just solve the harmonic oscillator with different boundary conditions

$$R\psi \to R - a_0 \tag{64}$$

rather than $R\psi \to 0$. This is solved for

$$R\psi_n = \frac{1}{\sqrt{2^n n!}} \pi^{-1/4} a_{\rm harm}^{-1/2} \exp(-\frac{1}{2} R^2/a_{\rm harm}^2) H_n(R/a_{\rm harm}) \tag{65}$$

for non-integer n. For large $x = R/a_{\rm harm}$ $H_n(x) \simeq x^n$. (The hermite function for non-integer n blows up for large negative x, but we don't worry about this as we impose the boundary condition at $R = 0$).
So we are left to solve for n such that $H_n(x) \approx x - \frac{a_0}{a_{\rm harm}}$ for small x.

$$H_n(x) \approx \frac{\sqrt{\pi} 2^n}{\Gamma(\frac{1-n}{2})} \left[1 + \frac{n\Gamma(\frac{1-n}{2})}{\Gamma(\frac{2-n}{2})} x \right] \tag{66}$$

For small a_0/a we expect n to be close to the undisturbed $n = 1, 3, 5, \ldots$. For the ground state expand around $n = 1$

$$H_n(x) \propto r - \frac{(n-1)\sqrt{\pi}}{2} a_{\rm harm} + (n-1)^2 \ldots \tag{67}$$

Equate to scattering length

$$a_0 = \frac{(n-1)\sqrt{\pi}}{2} a_{\rm harm} \tag{68}$$

or

$$n = 1 + \frac{2}{\sqrt{\pi}} \frac{a_0}{a_{\rm harm}} \tag{69}$$

Two molecules in an isotropic harmonic trap (3)

So we are left to solve for n such that $H_n(x) \approx x - \frac{a_0}{a_{\mathrm{harm}}}$ for small x.

$$H_n(x) \approx \frac{\sqrt{\pi}2^n}{\Gamma(\frac{1-n}{2})}\left[1 + \frac{n\Gamma(\frac{1-n}{2})}{\Gamma(\frac{2-n}{2})}x\right] \tag{70}$$

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or

$$n = 1 + \frac{2}{\sqrt{\pi}}\frac{a_0}{a_{\mathrm{harm}}} \tag{73}$$

Meaning the energy shifted by $\hbar\omega\frac{2}{\sqrt{\pi}}\frac{a_0}{a_{\mathrm{harm}}}$, which is identical to Fermi pseudopotential result.

Universality

Hydrogen atom

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{R}\right]\psi = E\psi \tag{74}$$

measure distance in

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2 m_e} \tag{75}$$

and energy in

$$E_h = \frac{\hbar^2}{m_e a_0^2} \tag{76}$$

to get

$$\left[-\frac{1}{2}\nabla^2 - \frac{1}{r}\right]\psi = \epsilon\psi \tag{77}$$

looks the same no matter the "electron" mass.

Universality

Harmonic oscillator

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+\frac{1}{2}\mu\omega^2 R^2\right]\psi = E\psi \tag{78}$$

measure distance in

$$a_{\mathrm{harm}} = \sqrt{\frac{\hbar}{\mu\omega^2}} \tag{79}$$

and energy in

$$\hbar\omega = \frac{\hbar^2}{\mu a_{\mathrm{harm}}^2} \tag{80}$$

to get

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{1}{2}r^2\right]\psi = \epsilon\psi \tag{81}$$

looks the same no matter the mass or spring constant.

Universality

Van der Waals potential

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+\frac{\hbar^2\ell(\ell+1)}{2\mu R^2}-C_6R^{-6}\right]\psi=E\psi \tag{82}$$

measure distance in

$$a_6=\left(2\mu C_6/\hbar^2\right)^{1/4} \tag{83}$$

and energy in

$$E_6=\frac{\hbar^2}{\mu a_6^2} \tag{84}$$

to get

$$\left[-\frac{1}{2}\nabla^2+\frac{\ell(\ell+1)}{r^2}-\frac{1}{r^6}\right]\psi=\epsilon\psi \tag{85}$$

looks the same no matter the mass or C_6.

Universality

Inverse power-law potential

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+\frac{\hbar^2\ell(\ell+1)}{2\mu R^2}-C_nR^{-n}\right]\psi=E\psi \tag{86}$$

measure distance in

$$a_n=\left(2\mu C_n/\hbar^2\right)^{1/(n-2)} \tag{87}$$

and energy in

$$E_n=\frac{\hbar^2}{\mu a_n^2} \tag{88}$$

to get

$$\left[-\frac{1}{2}\nabla^2+\frac{\ell(\ell+1)}{r^2}-\frac{1}{r^n}\right]\psi=\epsilon\psi \tag{89}$$

looks the same no matter the mass or C_n.

Nonuniversality

Nonuniversality occurs only if there exists more than one length scale / energy scale.

For example the van der Waals + hard-sphere potential
a_6 versus $a_{\mathrm{hardsphere}}$.

For example the Lennard-Jones potential

$$V(R) = 4\epsilon \left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6} \right] \tag{90}$$

defines multiple length scales (say a_6 and also σ, or equivalently σ and $\sqrt{2\mu\epsilon}/\hbar$)

In such cases, things can depend on the ratio of length scales.
We saw this before for the harmonic oscillator with contact interactions, where in reduced units you still have a dependence on a_0/a_{harm}.
Scaling both length scales, however, affects results in a "universal way".
Also, for problems with two length scales, you can find universality in the limit where one of the length scales $\to 0$ or ∞.

Exact solutions for R^{-n} potentials

At zero energy

$$f(r) = \sqrt{r} J_{\frac{2l+1}{n-2}} \left(\frac{2}{n-2} r^{-\frac{n-2}{2}} \right) \tag{91}$$

$$g(r) = \sqrt{r} Y_{\frac{2l+1}{n-2}} \left(\frac{2}{n-2} r^{-\frac{n-2}{2}} \right) \tag{92}$$

$E \neq 0$ can also be solved analytically, but it's complicated ...
For small r, the argument of the Bessel function is large and we have

$$f(r) \simeq \sqrt{\frac{n-2}{\pi}} r^{n/4} \cos \left[\frac{2}{n-2} r^{-\frac{n-2}{2}} - \frac{4l+n}{n-2} \frac{\pi}{4} \right] \tag{93}$$

$$g(r) \simeq \sqrt{\frac{n-2}{\pi}} r^{n/4} \sin \left[\frac{2}{n-2} r^{-\frac{n-2}{2}} - \frac{4l+n}{n-2} \frac{\pi}{4} \right] \tag{94}$$

(You can get this from WKB)
Let the short range boundary condition determine the physical solution

$$\psi(r) = f(r) \sin \delta + g(r) \cos \delta \tag{95}$$

$$\psi(r) \simeq \sqrt{\frac{n-2}{\pi}} r^{n/4} \sin \left[\frac{2}{n-2} r^{-\frac{n-2}{2}} - \frac{4l+n}{n-2} \frac{\pi}{4} + \delta \right] \tag{96}$$

Asymptotic behavior and scattering length

$$f(r) = \sqrt{r} J_{\frac{2l+1}{n-2}} \left(\frac{2}{n-2} r^{-\frac{n-2}{2}} \right) \tag{97}$$

$$g(r) = \sqrt{r} Y_{\frac{2l+1}{n-2}} \left(\frac{2}{n-2} r^{-\frac{n-2}{2}} \right) \tag{98}$$

For large r the argument of the Bessel functions is small, and we can use small argument expansions. This gives

$$f(r) \simeq r^{-\ell}/c \tag{99}$$

$$g(r) \simeq r^{-\ell}/c \times \cot(\alpha\pi) - r^{\ell+1} \frac{c}{\pi\alpha} \tag{100}$$

where $c = (n-2)^{\alpha}\alpha!$ and $\alpha = \frac{2\ell+1}{n-2}$.
Scattering length is the root of the asymptotic wavefunction

$$r^{\ell}\psi/\cos\delta = \frac{\tan\delta + \cot(\alpha\pi)}{c_0} - r^{2\ell+1} \frac{c}{\alpha\pi} \tag{101}$$

$$\begin{aligned} (a_\ell/R_n)^{2\ell+1} &= \frac{\alpha\pi}{c^2} \left(\tan\delta + \cot(\alpha\pi)\right) \\ &= \frac{\alpha\pi}{c^2 \tan(\alpha\pi)} (1 + \tan(\alpha\pi)\tan\delta) \end{aligned} \tag{102}$$

For s-wave collisions on a van der Waals potential ($n = 6$)

$$a_0 = \bar{a}\,(1 + \tan\delta) \tag{103}$$

$$\bar{a} = \frac{2\pi}{\Gamma(1/4)^2} R_6 \approx 0.47 R_6 \tag{104}$$

QDT

Real potentials do not follow R^{-n}, except asymptotically.

You can find some $R = R^*$, the smallest R value where the potential can still reasonably be approximated as R^{-n}.

For $R > R^*$ we know *any* solution is a linear combination of the exact solutions we found, $f(R)\sin\delta + g(R)\cos\delta$. For $R < R^*$ we don't know what the wavefunction looks like. However, *whatever* it is, this only fixes the value of δ (i.e. a boundary condition at short range).

This becomes a real simplification when the unknown solution at $R < R^*$ can be assumed independent of some quantities

- δ L independent
- δ E independent

QDT

To illustrate, let's consider a potential thats $C_6 R^{-6}+$ hard sphere with radius A. Lets assume $a = A/R_6 \ll 1$ so we use the small r form of the exact solutions

$$f(r) = \sqrt{r} J_{\frac{2l+1}{n-2}} \left(\frac{2}{n-2} r^{-\frac{n-2}{2}} \right) \tag{105}$$

$$g(r) = \sqrt{r} Y_{\frac{2l+1}{n-2}} \left(\frac{2}{n-2} r^{-\frac{n-2}{2}} \right) \tag{106}$$

A linear combination

$$\psi(r) = f(r) \sin\delta + g(r) \cos\delta \tag{107}$$

$$\psi(r) \simeq \sqrt{\frac{n-2}{\pi}} r^{n/4} \sin\left[\frac{2}{n-2} r^{-\frac{n-2}{2}} - \frac{4l+n}{n-2} \frac{\pi}{4} + \delta \right] \tag{108}$$

So we might choose

$$\delta = \frac{4l+n}{n-2} \frac{\pi}{4} - \frac{2}{n-2} a^{-\frac{n-2}{2}}, \tag{109}$$

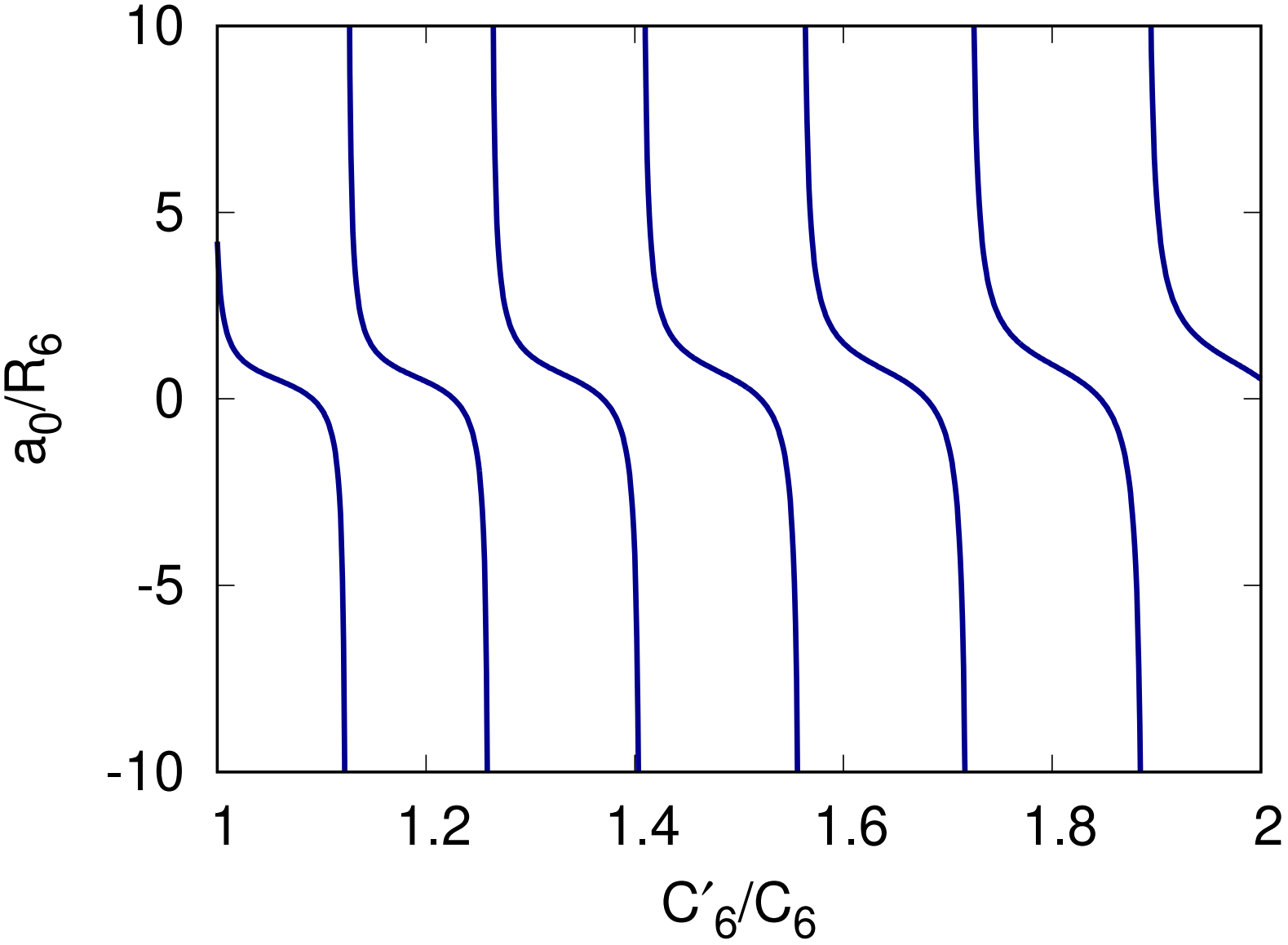
so that the wavefunction vanishes at $r = a$ (or $R = A$).
The scattering length is still given

$$a_0 = \bar{a}(1 + \tan\delta) \tag{110}$$

$$\bar{a} = \frac{2\pi}{\Gamma(1/4)^2} R_6 \approx 0.47 R_6 \tag{111}$$

Plugging in δ can give the scattering length, e.g. as a function of C_6 for fixed A, or as a function of A for fixed C_6, etc.

$-C_6' R^{-6}$ + hard-sphere potential (radius $a = A/R_6 = 0.1$)

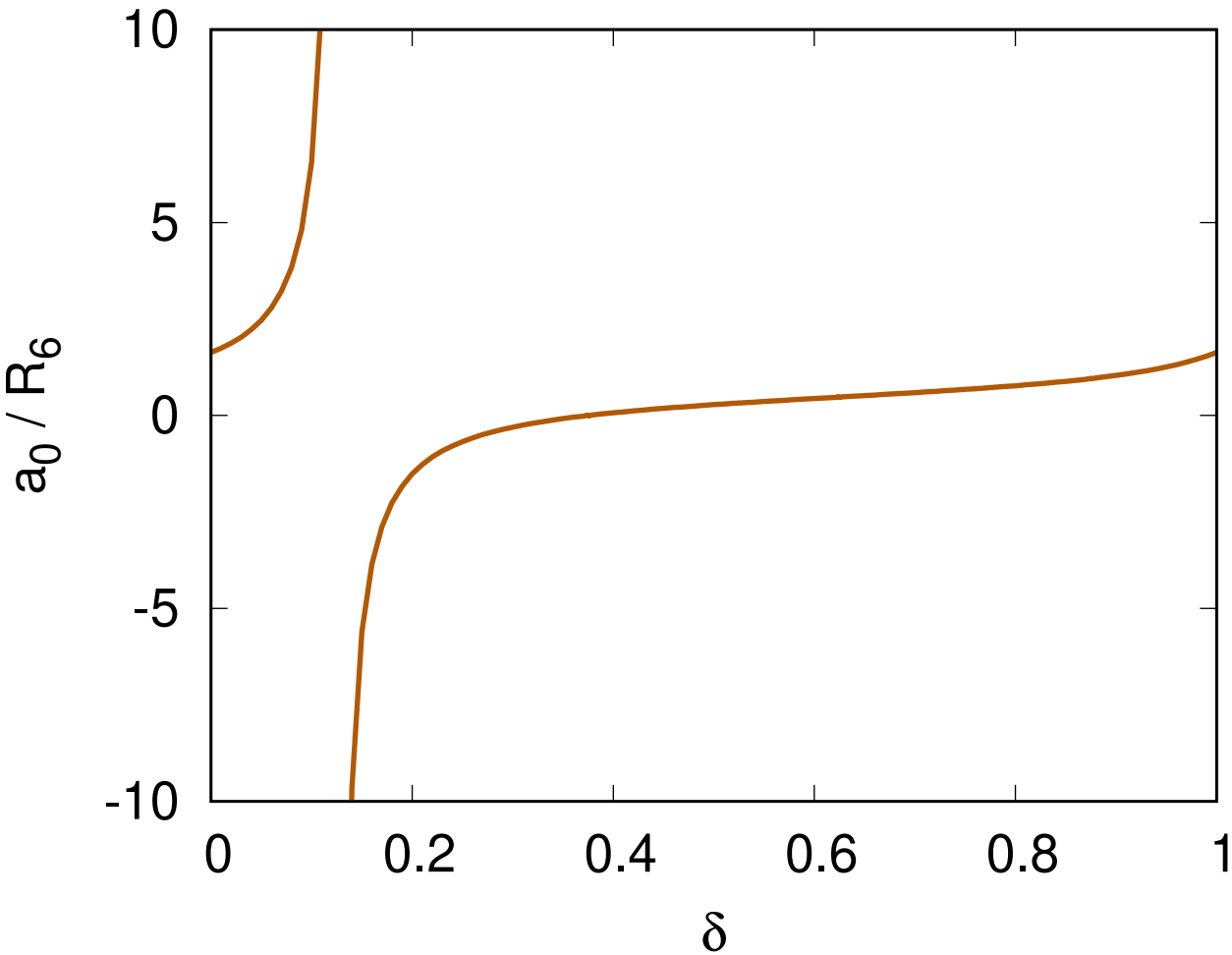


For s-wave collisions on a van der Waals potential ($n = 6$)

$$a_0 = \bar{a}\,(1 + \tan\delta) \tag{112}$$

$$\bar{a} = \frac{2\pi}{\Gamma(1/4)^2} R_6 \approx 0.47 R_6 \tag{113}$$

The scattering length can be anything between $\pm\infty$, but has a well-defined mean, and is positive for $3/4$ of the possible δ, and negative for $1/4$.



L dependence

Assume short-range solutions are L independent

The boundary conditions becomes

$$\psi(r) = f(r)\sin\delta' + g(r)\cos\delta' \tag{114}$$

$$\psi(r) \simeq \sqrt{\frac{n-2}{\pi}}\, r^{n/4} \sin\left[\frac{2}{n-2} r^{-\frac{n-2}{2}} - \frac{4l+n}{n-2}\frac{\pi}{4} + \delta'\right] \tag{115}$$

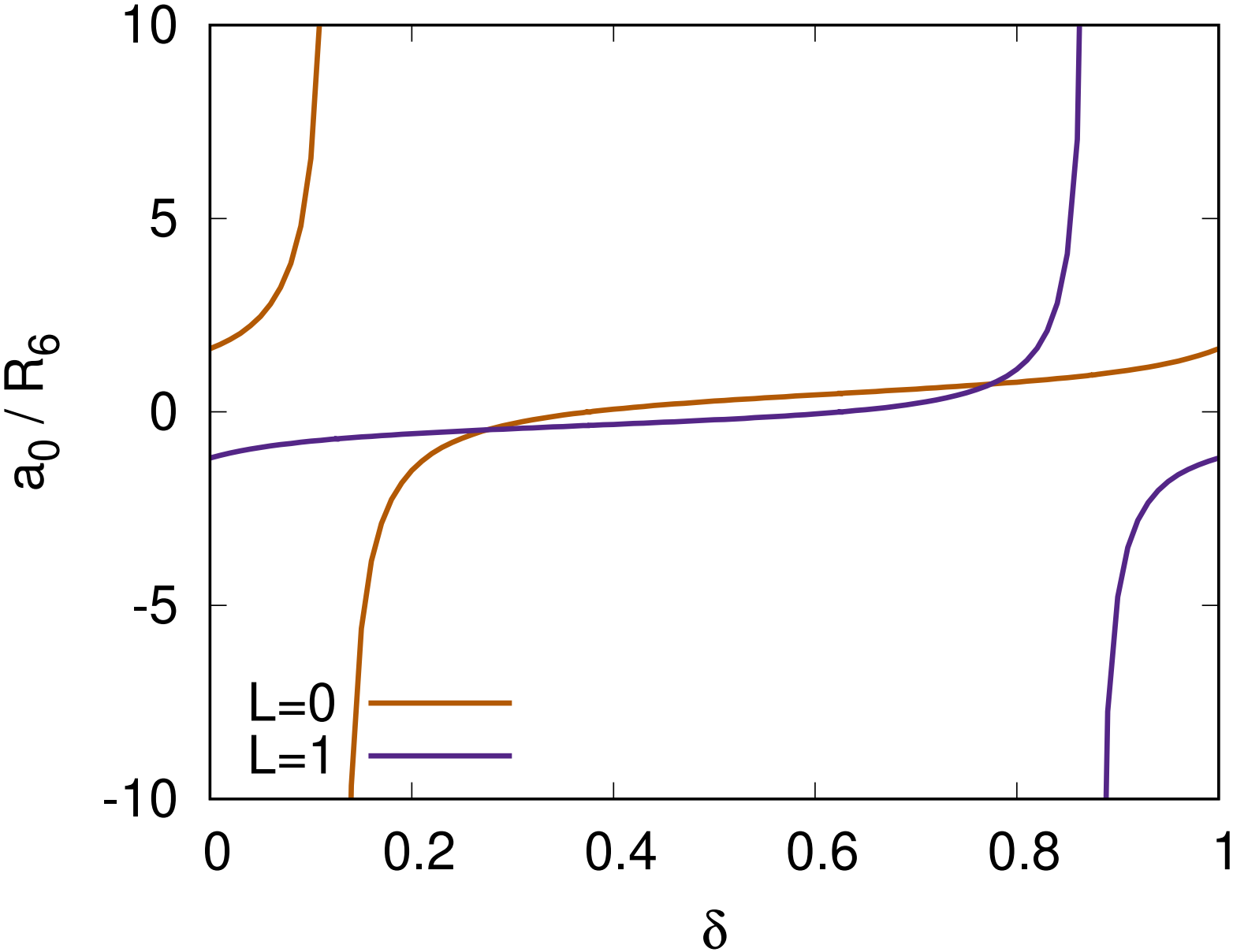
So we might choose

$$\delta' = \delta + \frac{4l+n}{n-2}\frac{\pi}{4} \tag{116}$$

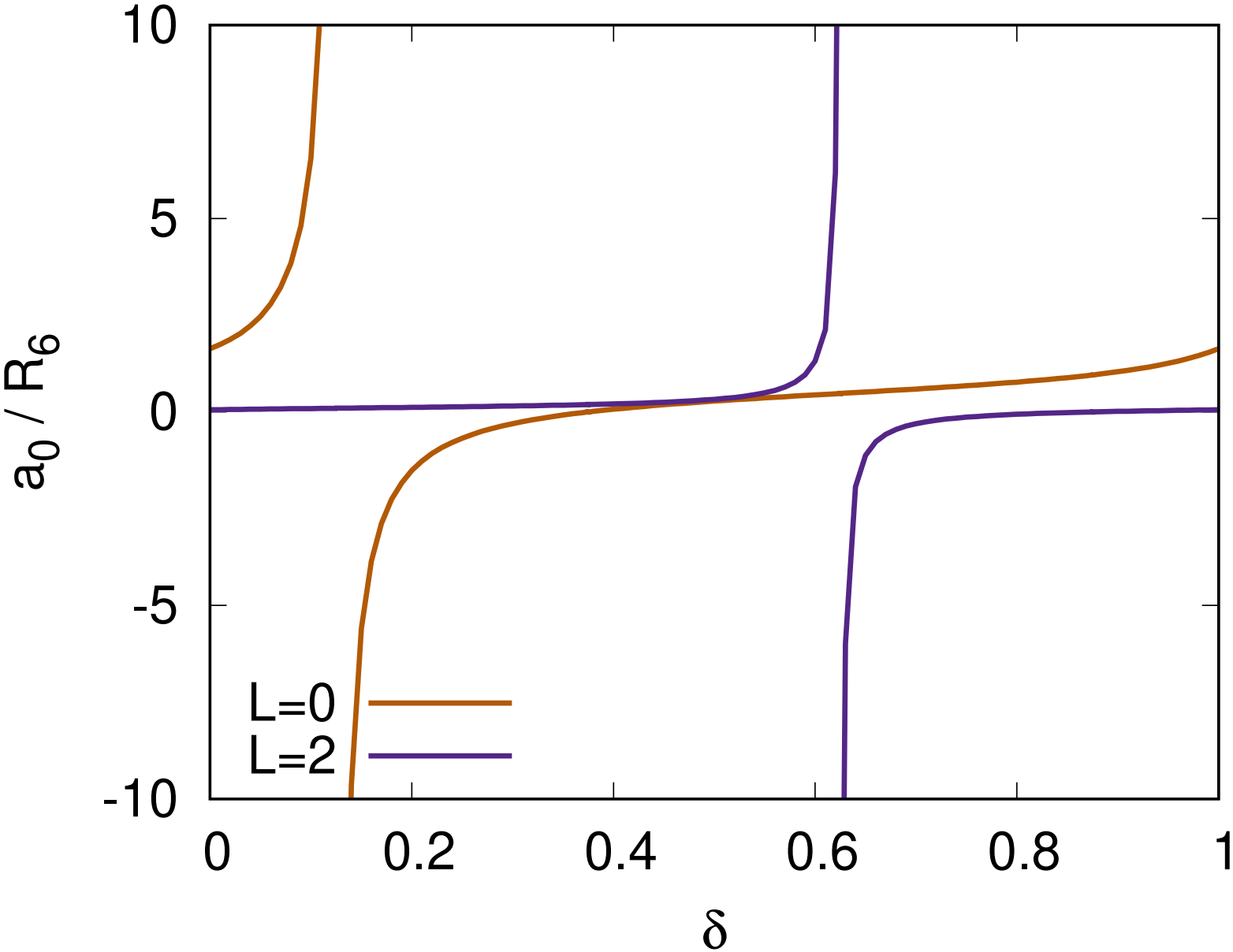
So that the wavefunction becomes L independent at short range

$$\psi(r) \simeq \sqrt{\frac{n-2}{\pi}}\, r^{n/4} \sin\left[\frac{2}{n-2} r^{-\frac{n-2}{2}} + \delta\right] \tag{117}$$

$L > 0$ collisions on a van der Waals potential ($n = 6$)



$L > 0$ collisions on a van der Waals potential ($n = 6$)



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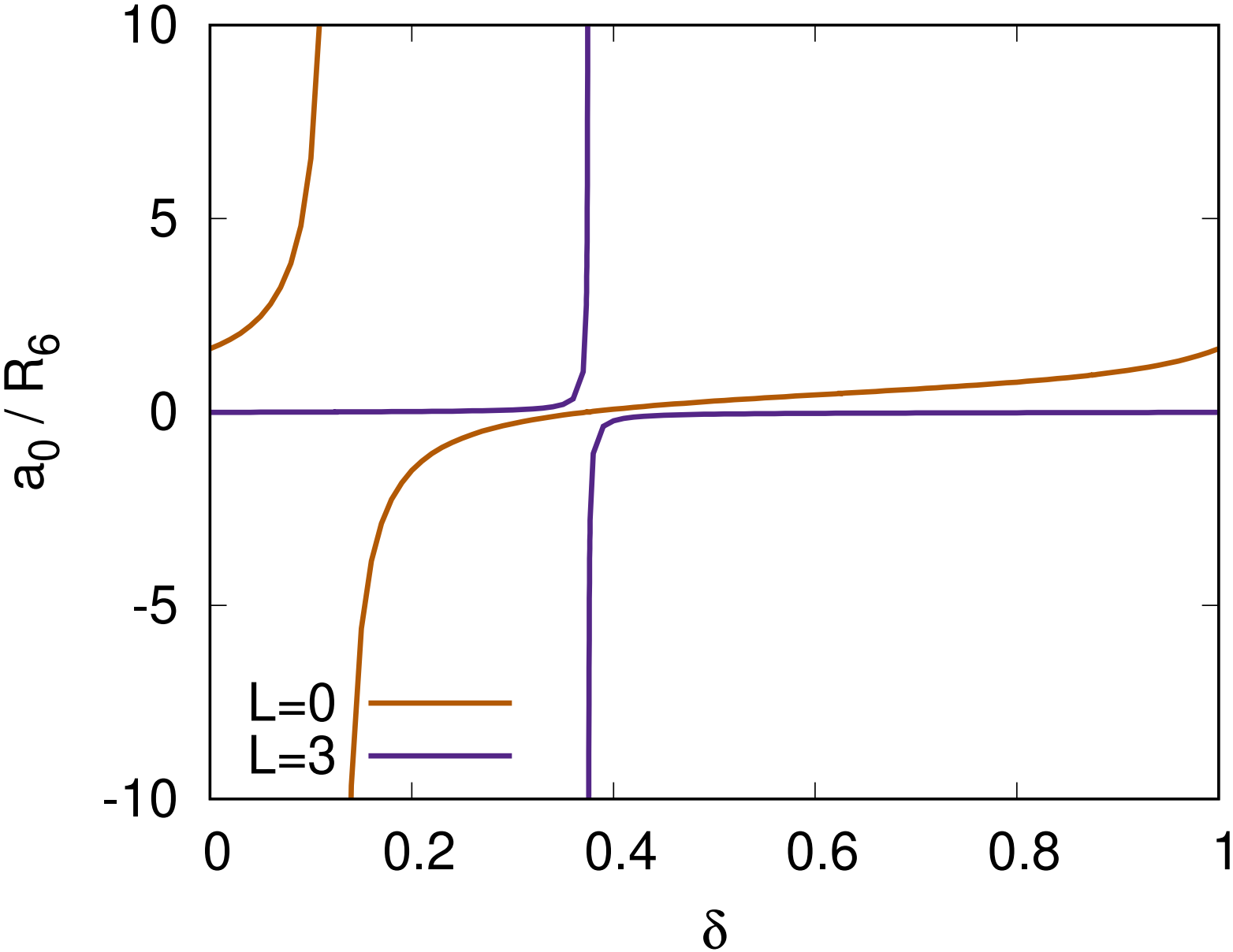
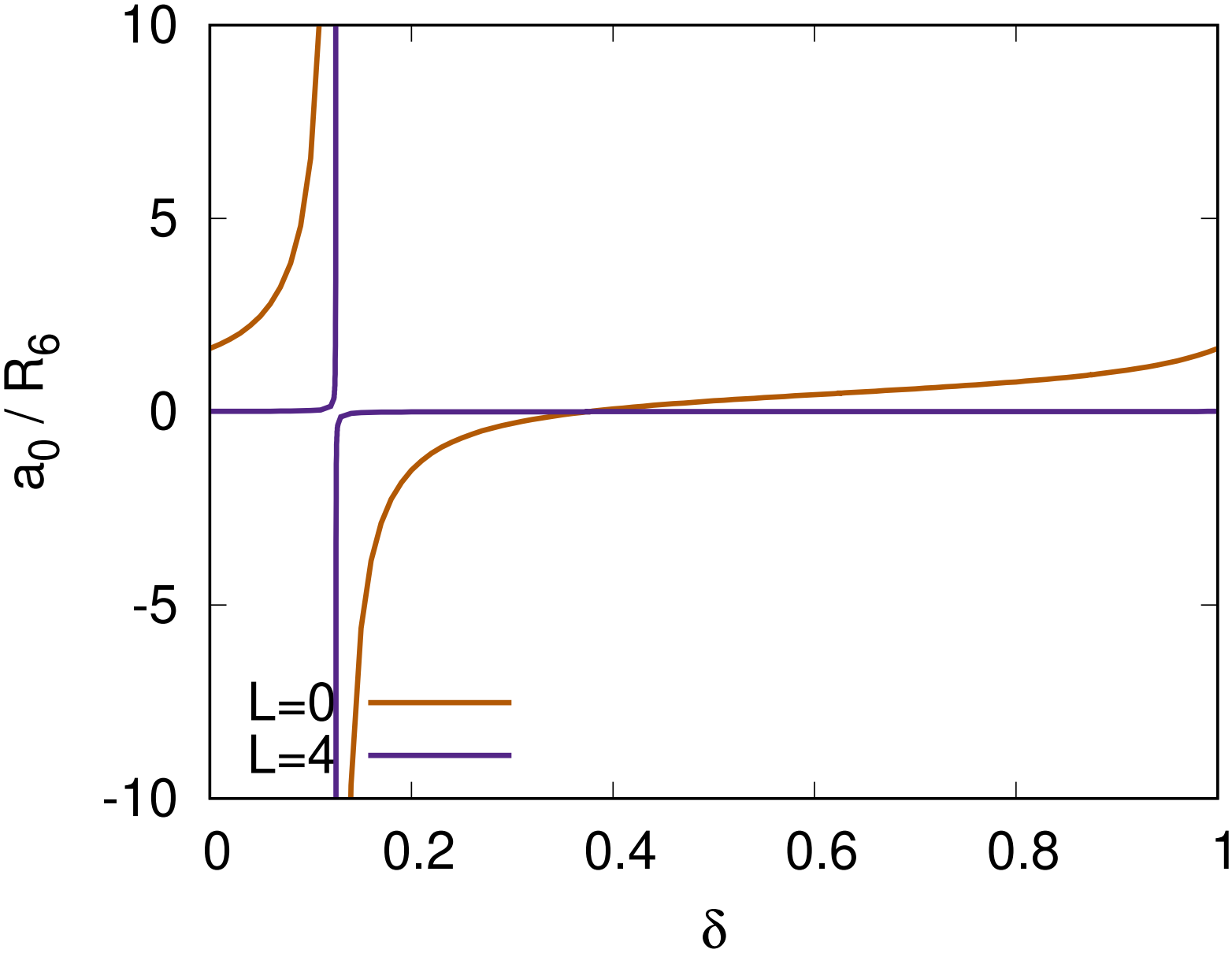
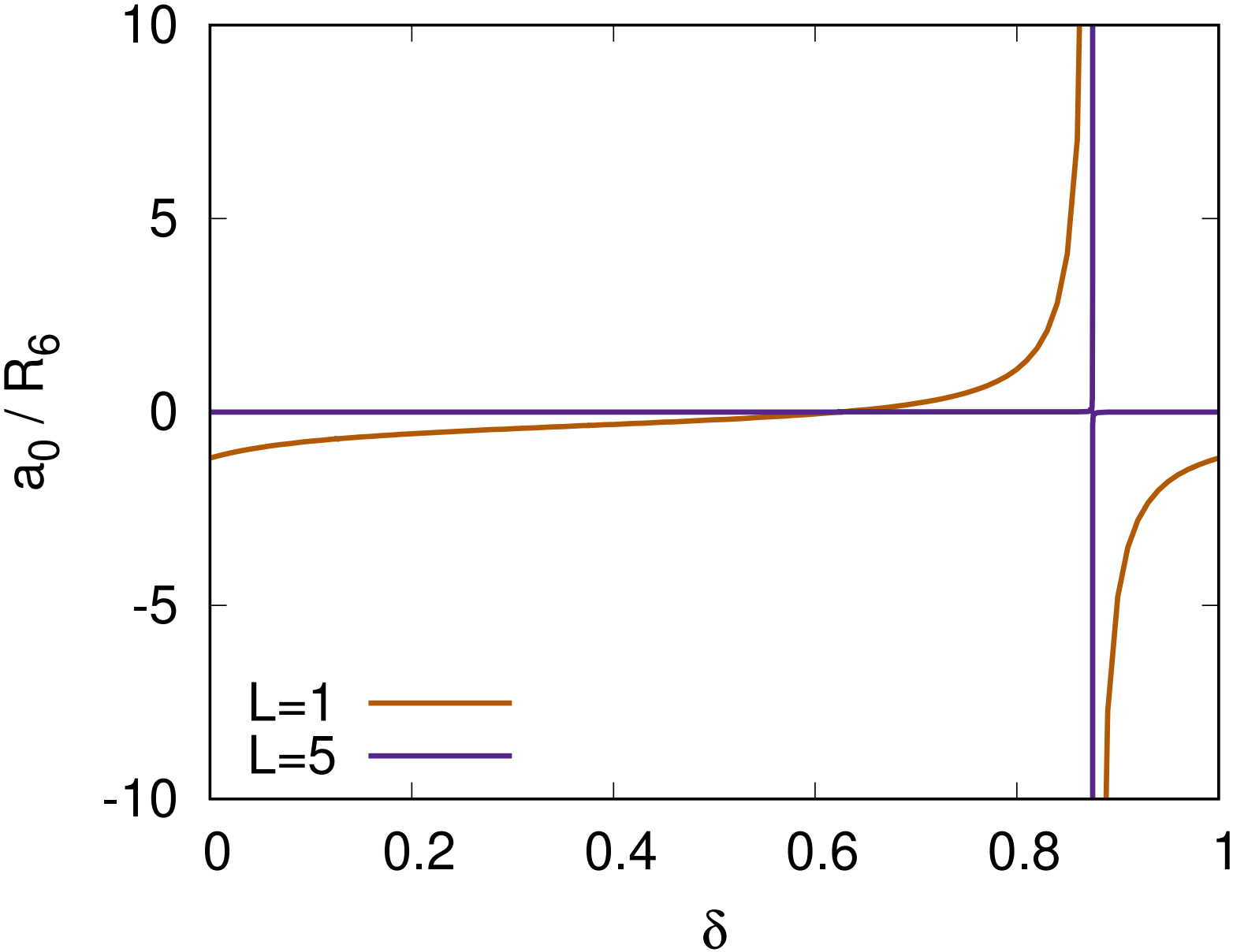


$L > 0$ collisions on a van der Waals potential ($n = 6$)



$L > 0$ collisions on a van der Waals potential ($n = 6$)



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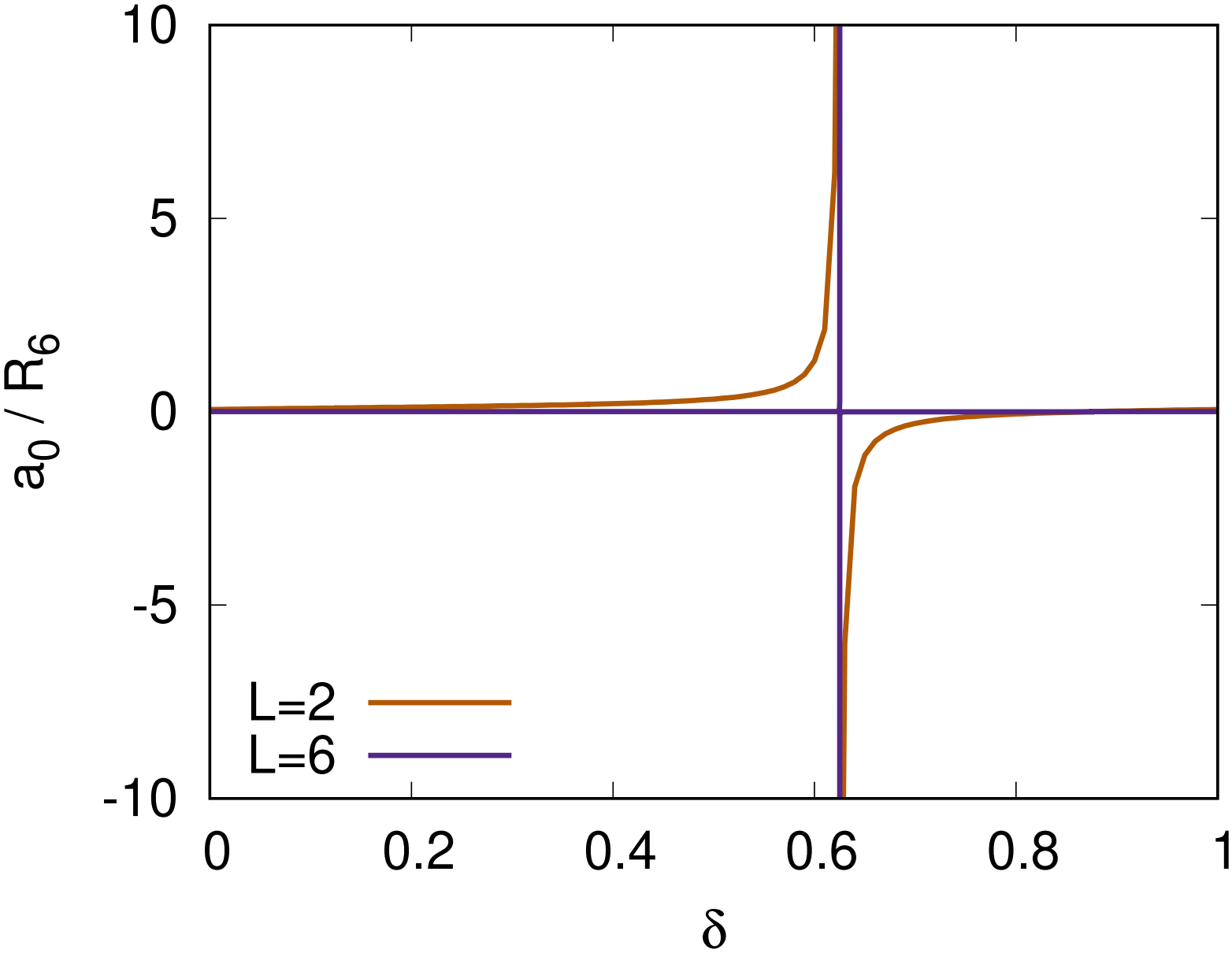
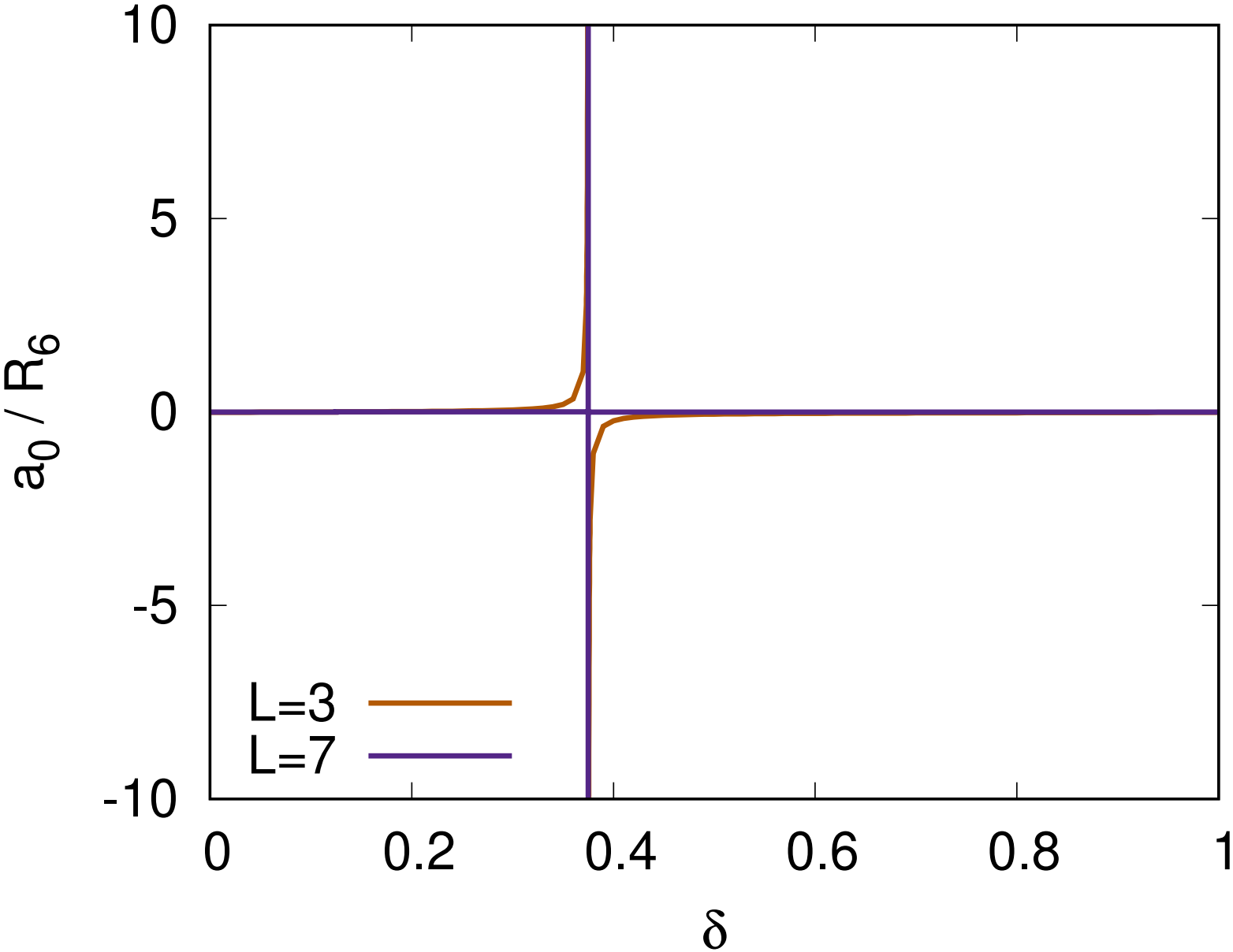
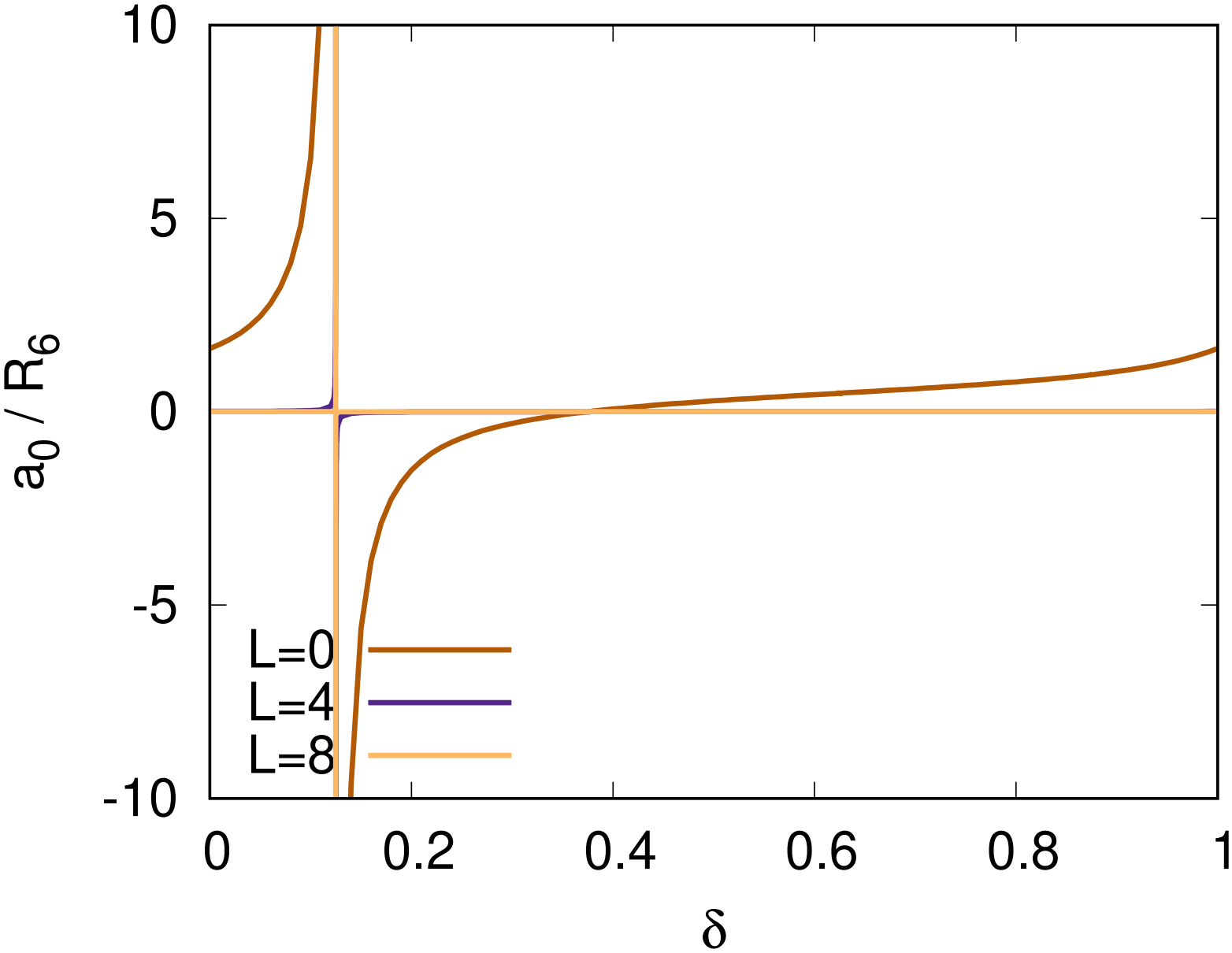


$L > 0$ collisions on a van der Waals potential ($n = 6$)



$L > 0$ collisions on a van der Waals potential ($n = 6$)



E-dependence from QDT

The typical application of QDT is to assume an energy-independent short-range boundary condition, so that the full energy dependences comes from the E-dependence of the exact solutions.

(Conceptually the same as assuming L-independent SR boundary condition, so that the full L dependence comes from the L-dependence of the exact solutions)

We don't do this here because we only solved the Schrödinger Eq for $E = 0$. (for "simplicity")

Universal loss

$$f(r) = \sqrt{r} J_{\frac{2l+1}{n-2}} \left(\frac{2}{n-2} r^{-\frac{n-2}{2}} \right), \qquad g(r) = \sqrt{r} Y_{\frac{2l+1}{n-2}} \left(\frac{2}{n-2} r^{-\frac{n-2}{2}} \right) \tag{118}$$

For small r, the argument of the Bessel function is large and we have

$$f(r) \simeq \sqrt{\frac{n-2}{\pi}} r^{n/4} \cos \left[\frac{2}{n-2} r^{-\frac{n-2}{2}} - \frac{4l+n}{n-2} \frac{\pi}{4} \right] \tag{119}$$

$$g(r) \simeq \sqrt{\frac{n-2}{\pi}} r^{n/4} \sin \left[\frac{2}{n-2} r^{-\frac{n-2}{2}} - \frac{4l+n}{n-2} \frac{\pi}{4} \right] \tag{120}$$

(You can get this from WKB)
Lets take instead linear combinations such that

$$a(r) \simeq \sqrt{\frac{n-2}{\pi}} r^{n/4} \exp \left[+i \frac{2}{n-2} r^{-\frac{n-2}{2}} \right] \tag{121}$$

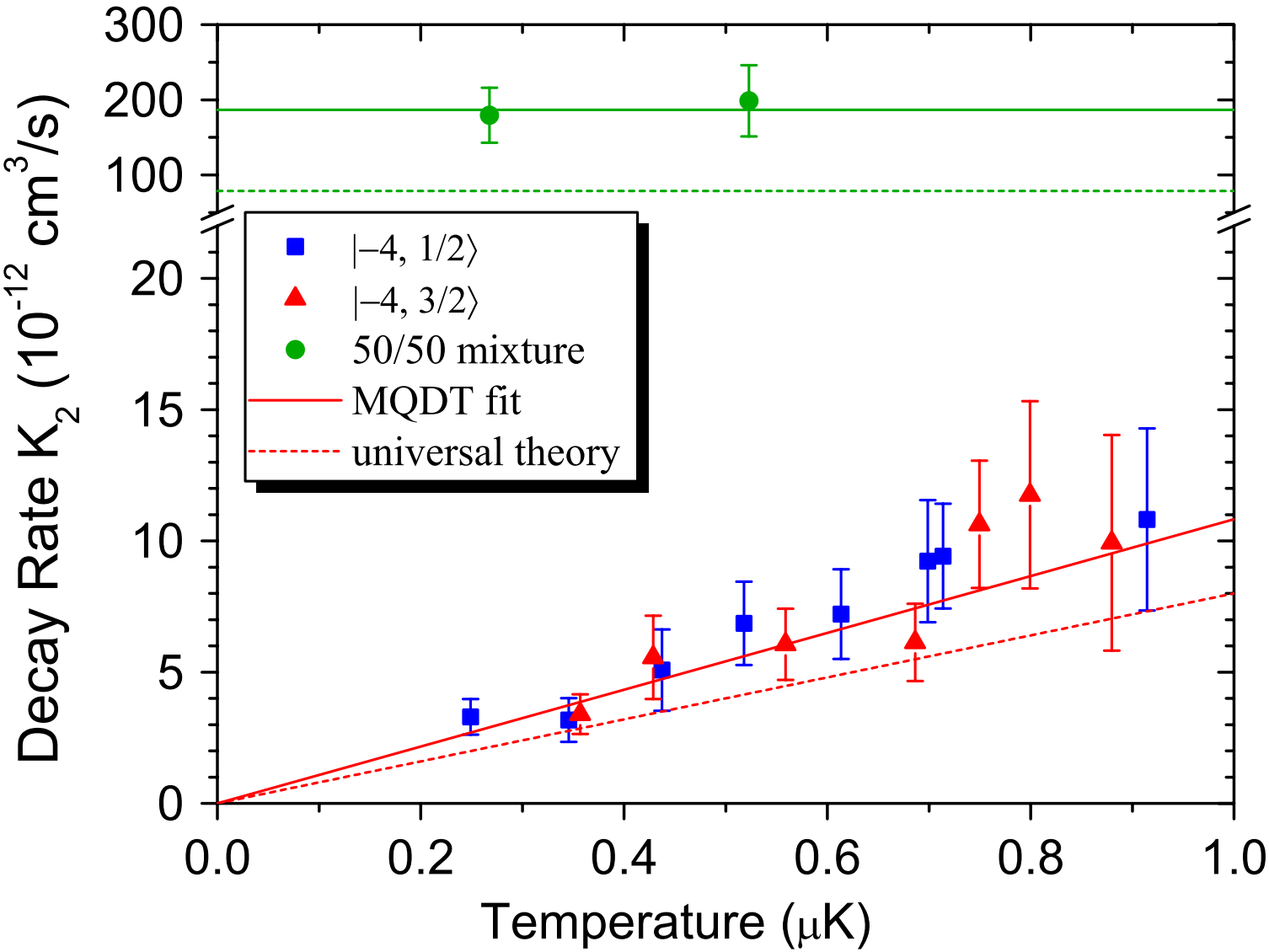
$$b(r) \simeq \sqrt{\frac{n-2}{\pi}} r^{n/4} \exp \left[-i \frac{2}{n-2} r^{-\frac{n-2}{2}} \right] \tag{122}$$

then we might write

$$\psi(r) = a(r) + \left(\frac{1-y}{1+y} \right) b(r) \exp(i\delta) \tag{123}$$

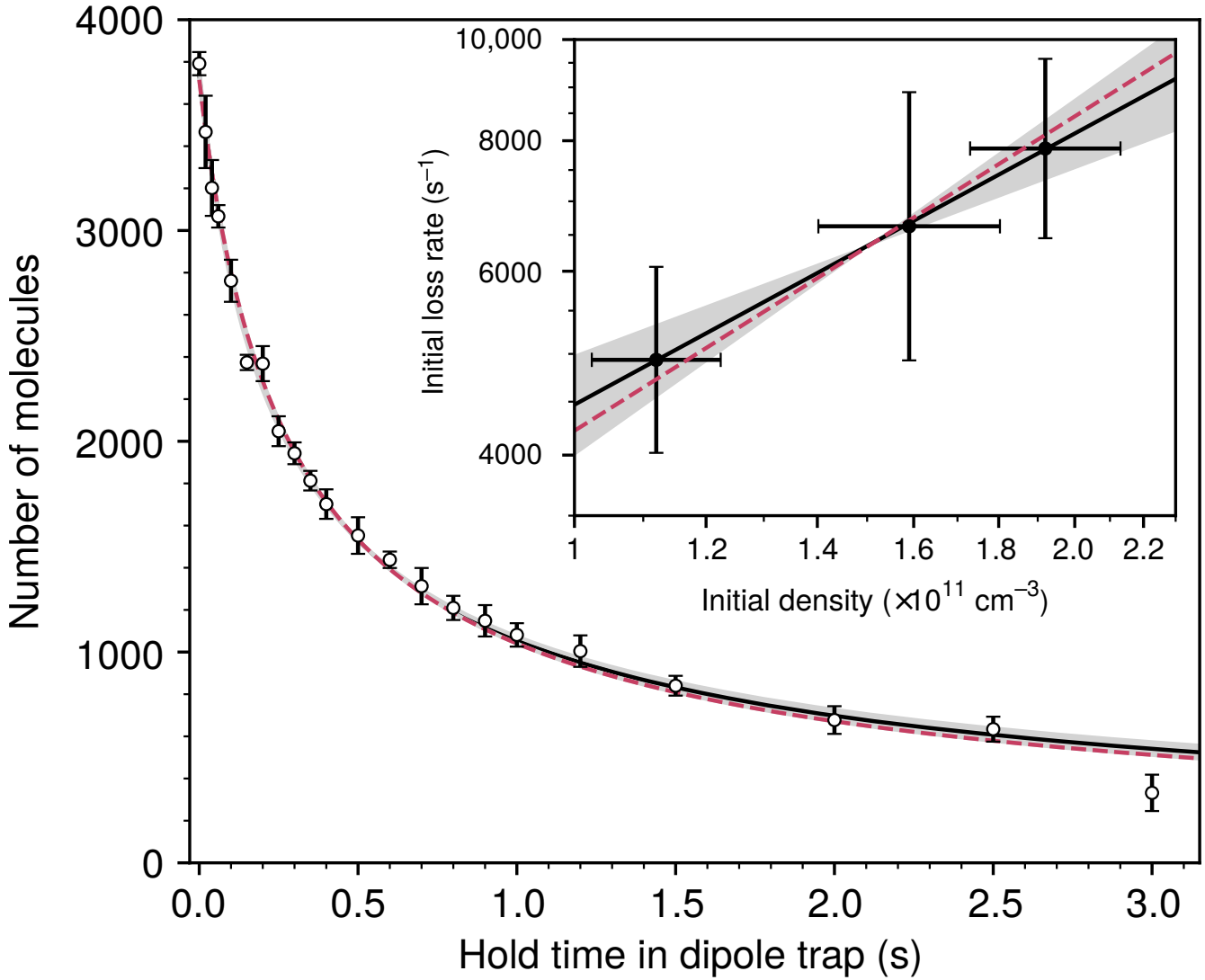
the reflected wave is phase shifted, and it's amplitude is diminished if $y \neq 0$.
For $y = 0$, this is identical to before.
For $y = 1$, there is complete loss at short range (no reflection) and $a_0 = \bar{a}[1 - i]$ is *universal*.

Universal loss: KRb+KRb → K_2+Rb_2



[Ospelkaus *et al.* Science, **327**, 853-857 (2010)]

Universal loss: RbCs+RbCs $\nrightarrow$ Rb_2 + Cs_2



[Gregory . . . Cornish *Nature Commun.* **10**, 3104 (2019)]

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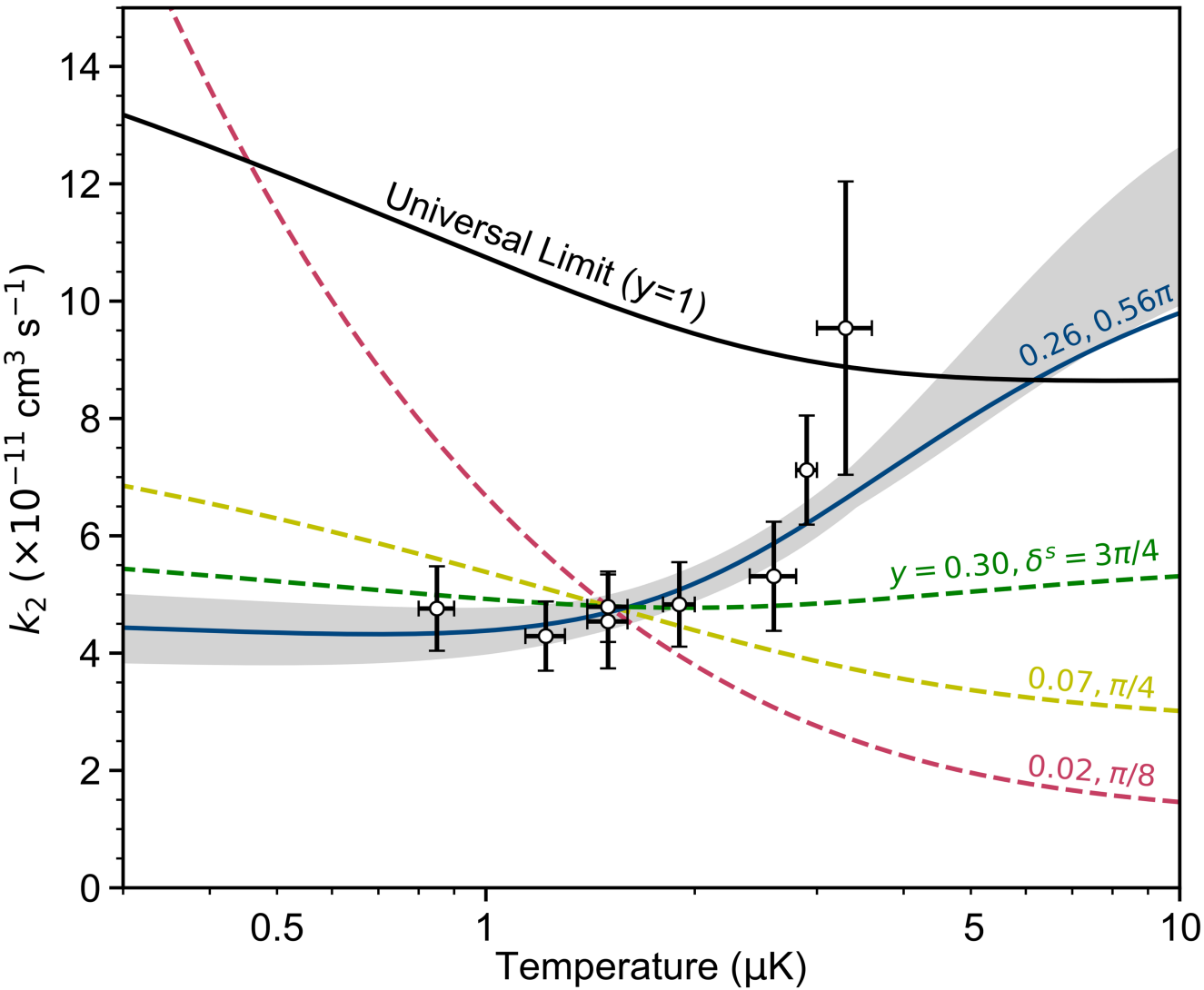

[Gregory . . . Cornish *Nature Commun.* **10**, 3104 (2019)]