

# Theoretical determination of properties of helium for new temperature and pressure standards

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“metrology truly is the mother of science”

John Hall, 2011

## Motivation

- Temperature and pressure are widely measured in science, technology, and everyday life
- Because the small deviation from the ideal gas behavior, helium is used in primary:
  - gas thermometry
  - acoustic gas thermometry
  - dielectric-constant gas thermometry
  - refractive index gas thermometry
- Helium based primary manometers are being developed at NIST to replace the mercury based ones (Jay H. Hendricks's, Thermodynamic Metrology Group).
- The knowledge of the properties of helium are important or critical for the accuracy of these primary determinations (also for the “final” determination of the Boltzmann constant).

## Next Generation in Pressure, Temperature and Length Metrology

### Current Technology

$$P = \rho gh$$



Artifact-based standards



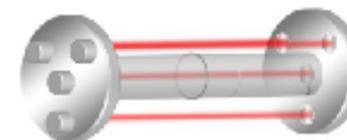
### Future Direction

$$PV = nRT$$

(n here is moles)



Quantum-based standards  
Helium refractive index  
quantum chemistry calculations



## Primary manometer based on the refractive index of helium

The idea is to combine the virial equation of state for the helium gas

$$p = \rho kT [1 + B\rho + C\rho^2 + \mathcal{O}(\rho^3)]$$

with optical measurements of the particle density  $\rho$ .

The density  $\rho$  is related to the refractive index  $n$  via ( $n-1 \approx 3.5 \times 10^{-5}$  at 1 bar)

$$n = 1 + 2\pi(\alpha + \chi)\rho + 2\pi\alpha(b_\epsilon + \frac{1}{3}\pi\alpha)\rho^2 + \mathcal{O}(\rho^3)$$

where

$\alpha$  is the dipole polarizability

$\chi$  is the magnetic susceptibility

$b_\epsilon$  is the dielectric virial coefficient.

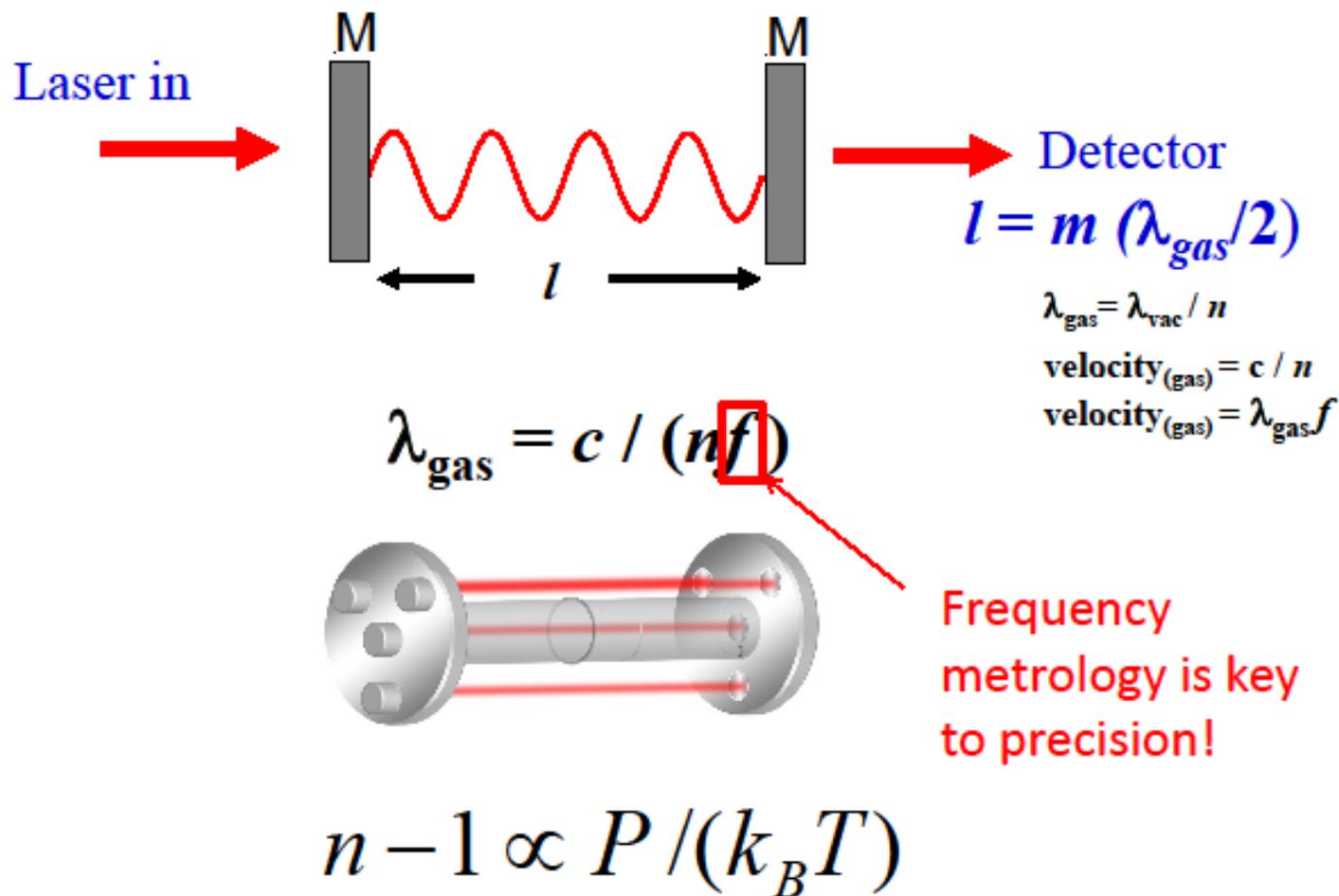
After eliminating the density  $\rho$  one finds

$$p = \frac{kT}{2\pi(\alpha + \chi)}(n - 1) + \frac{kT}{4\pi^2\alpha^2} \left( B - b_\epsilon - \frac{1}{3}\pi\alpha \right) (n - 1)^2 + \mathcal{O}((n - 1)^3)$$

When  $\alpha$ ,  $\chi$ ,  $B$ ,  $C$ , and  $b_\epsilon$  are known with sufficient accuracy, a measurement of  $n$  gives the pressure  $p$ . Accuracy better than 0.1 ppb for  $n$  and 1 ppm for  $p$  is feasible.

## Optical Based Primary Pressure Standard

### Basic Principal Fabry-Perot Interferometer



## Metrology relevant helium properties to be obtained from theory:

- dipole polarizability  $\alpha(\omega)$
- two-body interaction potential  $V(\mathbf{R})$
- collision induced polarizability  $\alpha(\omega, \mathbf{R})$
- leading density,  $B(T)$ , and dielectric,  $b_\epsilon(T)$ , virial coefficients
- diamagnetic susceptibility  $\chi$
- three-body interaction potential
- second-order density virial coefficient  $C(T)$
- three-body collision induced polarizability
- second-order dielectric virial coefficient  $c_\epsilon(T)$
- frequency dependent magnetizability  $\chi(\omega)$
- magnetic virial coefficient

Other applications of these data are possible, for example:

- to calibrate apparatus used to measure thermophysical properties
- in helium droplets spectroscopy and liquid helium simulations

## The predictive power of present-day quantum theory (QED)

### Magnetic moment of the electron in $\mu_B$

Predicted:  $-1.001\ 159\ 652\ 181\ 78\ (77)$  (Aaoama et al. 2012)

Measured:  $-1.001\ 159\ 652\ 180\ 73\ (28)$  (Gabrielse, 2014)

One part per trillion agreement

### Ionization energy of helium in MHz

Predicted:  $-5\ 945\ 204\ 174\ (36)$  (Pachucki 2006)

Measured:  $-5\ 945\ 204\ 212\ (6)$  (Kandula et al. 2010)

six parts per billion agreement

### $2^3P_1 - 2^3S_1$ excitation energy of helium in MHz

Predicted:  $-276\ 734\ 477.7\ (3.0)$  (Yerokhin and Pachucki 2010)

Measured:  $-276\ 734\ 477.724(2)$  (Pastor et al. 2004)

One part per billion agreement

## Expansion of the polarizability in powers of frequency $\omega$ and in inverse of powers of the velocity of light $c$

We use the expansion in powers of the angular frequency  $\omega$  (Cauchy expansion)

$$\alpha(\omega) = \alpha_0 + \alpha_2 \omega^2 + \alpha_4 \omega^4 + \dots ,$$

where  $\alpha_0$  is the static dipole polarizability and  $\alpha_n, n > 0$ , describes its dispersion.

Each  $\alpha_n$  is expanded in powers of  $c^{-1}$  in atomic units,  $c^{-1}=1/137.035999$

$$\alpha_n = \alpha_n^{(0)} + c^{-2} \alpha_n^{(2)} + c^{-3} \alpha_n^{(3)} + c^{-4} \alpha_n^{(4)} + \dots$$

$\alpha_n^{(2)}$  are the relativistic corrections while  $\alpha_n^{(3)}, \alpha_n^{(4)}, \dots$ , are QED corrections.

$\alpha_n^{(k)}, k \geq 2$ , must be expanded in powers of the mass ratio  $1/M$ ,  $M = m_\alpha/m_e$

$$\alpha_n^{(k)} = \alpha_n^{(k0)} + \frac{1}{M} \alpha_n^{(k1)} + \dots \quad \text{when } k \geq 2,$$

$\alpha_n^{(kl)}, l > 0$ , gives a correction of the order of  $M^{-l}c^{-k}$  (so called recoil correction)

## Nonrelativistic quantum electrodynamics (NRQED)

In NRQED the energy of a system in atomic units is expanded in powers of  $c^{-1}=1/137.036$

$$E = E^{(0)} + c^{-2}E^{(2)} + c^{-3}E^{(3)} + c^{-4}E^{(4)} + \dots$$

$E^{(0)}$  is the nonrelativistic energy, and  $E^{(n)}$  are expressed in terms of expectation values of certain operators with **nonrelativistic wave functions** and in terms of **Bethe logarithms**:

$$E^{(2)} = \langle H_{\text{BP}} \rangle = \langle H_{\text{kin}} \rangle + \langle H_{\text{D1}} \rangle + \langle H_{\text{D2}} \rangle + \langle H_{\text{OO}} \rangle + \langle H_{\text{SS}} \rangle$$

where  $H_{\text{BP}}$  is the Breit-Pauli Hamiltonian for electrons and nuclei, and

$$E^{(3)} = \frac{4}{3} \left( \frac{19}{30} - 2 \ln c^{-1} - \ln k_0 \right) \sum_i \langle \delta(r_i) \rangle \\ + \left( \frac{164}{15} + \frac{14}{3} \ln c^{-1} \right) \sum_{i < j} \langle \delta(r_{ij}) \rangle - \frac{7}{6\pi} \sum_{i < j} \langle P(r_{ij}^{-3}) \rangle$$

is the leading QED correction.  $\ln k_0$  is the Bethe logarithm and  $P(r_{12}^{-3})$  is the distribution

$$\langle \psi | P(r_{12}^{-3}) | \psi \rangle = \lim_{a \rightarrow 0} \langle \psi | \theta(r_{12} - a) r_{12}^{-3} + 4\pi (\gamma + \ln a) \delta(r_{12}) | \psi \rangle,$$

and

$$E^{(4)} \approx 4\pi \left( \frac{427}{96} - 2 \ln 2 \right) \langle \delta(r_{1a}) \rangle$$

## Bethe logarithm

Definition:

$$\ln k_0 = \mathcal{N} / \mathcal{D}$$

where

$$\mathcal{N} = \langle \psi | \mathbf{p} (H - E_0) \ln[(H - E_0) / \mathbf{Ry}] \mathbf{p} | \psi \rangle$$

$$\mathcal{D} = \langle \psi | \mathbf{p} (H - E_0) \mathbf{p} | \psi \rangle$$

Method I - direct summation (Goldman and Drake):

$$\ln k_0 = \frac{\sum_n (E_n - E_0) \ln[2(E_n - E_0)] |\langle \psi | \mathbf{p} | \psi_n \rangle|^2}{\sum_n (E_n - E_0) |\langle \psi | \mathbf{p} | \psi_n \rangle|^2}$$

1 ppm error  $\rightarrow E_n \approx 10^6 mc^2$

Method II frequency integration (C. Schwartz):

$$\ln k_0 = \lim_{\Lambda \rightarrow \infty} \left[ -\mathcal{D}^{-1} \langle \psi | \mathbf{p}^2 \psi \rangle \Lambda + \ln(2\Lambda) + \mathcal{D}^{-1} \int_0^\Lambda \omega J(\omega) d\omega \right],$$

where

$$J(\omega) = \langle \psi | \mathbf{p} (H - E + \omega)^{-1} \mathbf{p} | \psi \rangle$$

$$J(\omega) = \frac{\langle \psi_0 | \mathbf{p}^2 \psi_0 \rangle}{\omega} - \mathcal{D} \left[ \frac{1}{\omega^2} - \frac{2Z\sqrt{2}}{\omega^{5/2}} + \frac{2Z^2 \ln \omega}{\omega^3} - \frac{2ZC_3}{\omega^3} \right] + \mathcal{O}\left(\frac{1}{\omega^{7/2}}\right)$$

## Second electric-field derivative of Bethe logarithm

$$\partial_{\mathcal{E}}^2 \ln k_0 = [ \partial_{\mathcal{E}}^2 \mathcal{N} - \ln k_0 \partial_{\mathcal{E}}^2 \mathcal{D} ] / \mathcal{D},$$

where

$$\partial_{\mathcal{E}}^2 \mathcal{N} = \lim_{\Lambda \rightarrow \infty} \left[ - \partial_{\mathcal{E}}^2 \langle \psi | \mathbf{p}^2 \psi \rangle \Lambda + \ln(2\Lambda) \partial_{\mathcal{E}}^2 \mathcal{D} + \int_0^{\Lambda} \omega \partial_{\mathcal{E}}^2 J(\omega) d\omega \right],$$

$$\text{and } J(\omega) = \langle \psi | \mathbf{p} (H_0 + \mathcal{E}z - E + \omega)^{-1} \mathbf{p} | \psi \rangle$$

The second electric-field derivative of  $J(\omega)$  is:

$$\begin{aligned} \partial_{\mathcal{E}}^2 J(\omega) = & \frac{2}{3} [ 2 \langle \psi_0 | r^i \mathcal{R}_0 r^i \mathcal{R}_0 p^j \mathcal{R}_0(\omega) p^j | \psi_0 \rangle \\ & + 2 \langle \psi_0 | r^i \mathcal{R}_0 p^j \mathcal{R}_0(\omega) r^i \mathcal{R}_0(\omega) p^j | \psi_0 \rangle \\ & + \langle \psi_0 | r^i \mathcal{R}_0 p^j \mathcal{R}_0(\omega) p^j \mathcal{R}_0 r^i | \psi_0 \rangle \\ & - \langle \psi_0 | p^j \mathcal{R}_0(\omega) p^j | \psi \rangle \langle \psi | r^i \mathcal{R}_0^2 r^i | \psi_0 \rangle \\ & + \langle \psi_0 | p^j \mathcal{R}_0(\omega) r^i \mathcal{R}_0(\omega) r^i \mathcal{R}_0(\omega) p^j | \psi_0 \rangle \\ & - \langle \psi_0 | r^i \mathcal{R}_0 r^i | \psi \rangle \langle \psi_0 | p^j \mathcal{R}_0(\omega)^2 p^j | \psi_0 \rangle ], \end{aligned}$$

where  $\mathcal{R}_0(\omega) = (H_0 - E_0 + \omega)^{-1}$  and  $\mathcal{R}_0 = \mathcal{R}_0(0)$ . Evaluating  $\partial_{\mathcal{E}}^2 J(\omega)$  and performing the divergent  $\omega$  integration numerically we found that

$$\partial_{\mathcal{E}}^2 \ln k_0 = 0.0512(4) \quad (\text{G. Łach, Ph.D. Thesis})$$

## Second derivative of Bethe logarithm – direct summation with a cutoff $L$

$$\partial_{\varepsilon}^2 \mathcal{N} = \mathcal{N}_L'' + \ln(2L + 2) \partial_{\varepsilon}^2 \mathcal{D} + \int_L^{\infty} \partial_{\varepsilon}^2 f(\omega) d\omega$$

where  $\mathcal{N}_L''$  is given by

$$\begin{aligned} & - \sum_n g(\omega_n) [4 \langle \psi_0 | z \mathcal{R}_0 z \mathcal{R}_0 p \psi_n \rangle \langle \psi_n | p \psi_0 \rangle + 2 \langle \psi_0 | z \mathcal{R}_0 p \psi_n \rangle \langle \psi_n | p \mathcal{R}_0 z \psi_0 \rangle] \\ & + 2 \langle \psi_0 | z \mathcal{R}_0^2 z \psi_0 \rangle \sum_n g(\omega_n) |\langle \psi_0 | p \psi_n \rangle|^2 - 2 \langle \psi_0 | z \mathcal{R}_0 z \psi_0 \rangle \sum_n h(\omega_n) |\langle \psi_0 | p \psi_n \rangle|^2 \\ & + 4 \sum_k \sum_n G(\omega_k, \omega_n) \langle \psi_0 | z \mathcal{R}_0 p \psi_k \rangle \langle \psi_k | z \psi_n \rangle \langle \psi_n | p \psi_0 \rangle \\ & + 2 \sum_l \sum_k \sum_n F(\omega_l, \omega_k, \omega_n) \langle \psi_0 | p \psi_l \rangle \langle \psi_l | z \psi_k \rangle \langle \psi_k | z \psi_n \rangle \langle \psi_n | p \psi_0 \rangle \end{aligned}$$

with

$$g(\omega_n) = \omega_n \ln \left( 1 + \frac{L}{\omega_n} \right), \quad h(\omega_n) = g'(\omega_n), \quad G(\omega_k, \omega_n) = \frac{g(\omega_k) - g(\omega_n)}{\omega_k - \omega_n}$$

$$F(\omega_l, \omega_k, \omega_n) = \frac{g(\omega_l)}{(\omega_l - \omega_k)(\omega_n - \omega_l)} + \frac{g(\omega_k)}{(\omega_k - \omega_n)(\omega_l - \omega_k)} + \frac{g(\omega_n)}{(\omega_n - \omega_l)(\omega_k - \omega_l)}$$

## Numerical results for $\partial_{\xi}^2 \ln k_0$

The excited pseudostates  $\psi_n$  were expanded in the so-called Slater geminals

$$\chi_i(\mathbf{r}_1, \mathbf{r}_2) = \mathcal{Y}(\mathbf{r}_1, \mathbf{r}_2) \exp(-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12}),$$

where  $\mathcal{Y}(\mathbf{r}_1, \mathbf{r}_2)$  appropriate angular factors for scalar, vector, pseudovector, and tensor pseudostates, respectively.

A stochastic optimization was used to obtain exponents from the Hylleraas functionals

$$\mathcal{F}[\tilde{\psi}] = \langle \tilde{\psi} | H_0 - E_0 + L | \tilde{\psi} \rangle + 2 \langle \tilde{\psi} | \mathcal{Y} \psi_0 \rangle$$

Goldman Drake method, 2015

$$\partial_{\xi}^2 \ln k_0 = 0.0487(3)$$

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Schwartz,  $t$ -integration, 2016

$$\partial_{\xi}^2 \ln k_0 = 0.04856(2) \quad t = (1 + 2\omega)^{-1/2}$$

# Dynamic polarizability of ${}^4\text{He}$ in $a_0^3$ at $\lambda = 632.9908$ nm.

static nonrelativistic	1.383 809 98641(1)
relativistic $1/c^2$	-0.000 080 4534(1)
QED $1/c^3$	0.000 030 657(1) <sup>†</sup>
QED $1/c^4$	0.000 000 56(14)
finite nuclear size	0.000 000 0217(1)
total	1.383 760 77(14)
$\lambda^{-2}$ nonrelativistic	0.007 995 798
relativistic $1/c^2$	-0.000 000 172
QED $1/c^3$	-0.000 000 32(3)
total	0.007 995 95(3)
$\lambda^{-4}$ nonrelativistic	0.000 054 836
relativistic $1/c^2$	0.000 000 0001
QED $1/c^3$	0.000 000 0031(3)
total	0.000 054 840
$\lambda^{-6}$ nonrelativistic	0.000 000 408
total present, PRA 2016	1.391 811 97(14)
Bhatia and Drachman	1.391 780 800

<sup>†</sup> The contribution of the electric field derivative of Bethe logarithm is 0.000 000 183(1)

## Virial expansion of the refractive index

$$n = 1 + \frac{3}{2}a_r\rho + b_n\rho^2 + \mathcal{O}(\rho^3)$$

$a_r(0)^\dagger$	Present	<b>0.517 254 13(6)<sup>a,b</sup></b>
	Experimental, Schmidt et al, 2007	<b>0.517 253 5(47)</b>
	Experimental, Geiser al, 2017	<b>0.517 255 03(98)</b>
$a_r(632.9908)$	Present	<b>0.520 263, 69(6)</b>
	Experimental, Achtermann et al	<b>0.521 3(1)</b>
	Experimental, Birch	<b>0.522 0(3)</b>
$b_n(0)$	present, 273.16 °K	<b>0.0245(2)<sup>c</sup></b>
$b_n(632.9908)$	Present, 273.16 °K	<b>0.0238(2)<sup>c</sup></b>
	Present, 323 °K	<b>0.0151(2)<sup>c</sup></b>
	Experimental, Achtermann et al	<b>0.000(15)</b>

<sup>a</sup>Wavelength  $\lambda$  in nm,  $a_r$  and  $b_n$  in  $\text{cm}^3/\text{mol}$  and  $\text{cm}^6/\text{mol}^2$ , respectively.

<sup>b</sup>Computed using  $\chi = -0.000021194(1) a_0^3$  from Bruch and Weinhold.

<sup>c</sup>Computed using  $b_\epsilon = -0.0978(2) \text{ cm}^3/\text{mol}$  from Rizzo et al.

<sup>†</sup>Magnetic contribution subtracted to allow comparison with Schmidt and Gaiser.

## Summary of the polarizability part of the talk

The uncertainty of current theoretical value of  $\alpha$  at  $\lambda$  equal to 632.9908 nm amounts to **0.1 ppm**. This accuracy level is sufficient for the proposed pressure standard.

To achieve such high accuracy several subtle effects were taken into account including:

- The electric-field dependence of the Bethe logarithm
- The relativistic recoil correction of order  $1/(Mc^2)$
- The QED recoil contribution to static polarizability of the order of  $1/(Mc^3)$  .
- The leading QED contribution to the polarizability dispersion .

We can now predict  $n - 1$ , to better than 1 ppm up to the pressure of 3 MPa. To increase this limit, more accurate ab initio values of the dielectric virial coefficients are needed.

## Pair potential for helium

The pair (two-body) interaction potential  $V(\mathbf{R})$  for helium is constructed in the following way

$$V(\mathbf{R}) = V_{\text{BO}}(\mathbf{R}) + V_{\text{ad}}(\mathbf{R}) + V_{\text{rel}}(\mathbf{R}) + V_{\text{QED}}(\mathbf{R}) + V_{\text{ret}}(\mathbf{R}) + V_{\text{nad}}(\mathbf{R})$$

where

$V_{\text{BO}}(\mathbf{R})$  – the nonrelativistic Born-Oppenheimer (clamped nuclei) potential

$V_{\text{ad}}(\mathbf{R})$  – the adiabatic correction for the coupling of electronic and nuclear motion

$V_{\text{rel}}(\mathbf{R})$  – the relativistic correction from the electronic Breit-Pauli Hamiltonian

$V_{\text{QED}}(\mathbf{R})$  – the leading QED correction (of the order of  $\alpha^3 E_h$ ,  $\alpha$  is here the f.s.c.)

$V_{\text{ret}}(\mathbf{R})$  – the residual retardation correction (of the order of  $\alpha^4 E_h$ )

$V_{\text{nad}}(\mathbf{R})$  – the diagonal nonadiabatic correction (of the order of  $(m_e/m_\alpha)^2$ )

To account for the nonadiabatic effects we computed also two  $\mathbf{R}$ -dependent masses defined rigorously in Pachucki-Komasa's nonadiabatic perturbation theory (NAPT):

$m_{\parallel}(\mathbf{R})$  – the vibrational (longitudinal) mass

$m_{\perp}(\mathbf{R})$  – the rotational (transverse) mass

that interpolate between the nuclear mass at small  $\mathbf{R}$  and atomic mass at  $\mathbf{R}=\infty$

## Born-Oppenheimer potential $V_{\text{BO}}(\mathbf{R})$

We used the four-electron explicitly correlated Gaussian (ECG) wave function

$$\Psi = \mathcal{A}\Xi(1 + \hat{i}) \left[ c_0 \phi_0 + \sum_{k=1}^K c_k \phi_k(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \right],$$

where  $\mathcal{A}$  is the antisymmetrizer,  $\Xi$  is an appropriate spin function,  $\hat{i}$  inverts the wave function through the center of  $\text{He}_2$ , and  $\phi_k$ ,  $k > 0$  are the ECG basis functions:

$$\phi_k(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \prod_{i=1}^4 e^{-\alpha_{ki} |r_i - A_{ki}|^2} \prod_{i>j=1}^4 e^{-\beta_{kij} |r_i - r_j|^2},$$

The term  $\phi_0 = \psi^A(1, 2) \psi^B(3, 4)$  is the product of atomic wave functions.

We were increasing the expansion length  $K$  in the geometric progression up to  $K=6788$  (95000 nonlinear parameters).

This leads to errors in  $V(\mathbf{R})$  of 1ppm at short range, 20 ppm (0.2mK) at the minimum and 60 ppm at  $\mathbf{R} = 9$  bohr.

At larger  $\mathbf{R}$  the error decreases since the correct asymptotics is imposed by fitting to

$$V_{\text{BO}}(\mathbf{R}) = \sum_{k=1}^3 e^{-a_k R} \sum_{i=-1}^2 P_{ik} R^i - \sum_{n=6}^{16} f_n(\zeta R) \frac{C_n}{R^n},$$

## Adiabatic, relativistic, and QED corrections

The adiabatic corrections  $V_{\text{ad}}(\mathbf{R})$  is expressed as

$$V_{\text{ad}}(\mathbf{R}) = \frac{\hbar^2}{m_n} \langle \nabla_{\mathbf{R}} \Psi | \nabla_{\mathbf{R}} \Psi \rangle + \frac{1}{4m_n} \langle \Psi | P^2 | \Psi \rangle - 2E_{\text{ad}}^A,$$

$\mathbf{R}$  is the vector joining the nuclei,  $m_n$  is the nuclear mass,  $P$  is the total electronic momentum operator.

As proposed by Pachucki and Komasa  $\nabla_{\mathbf{R}} \Psi$  is obtained from the equation

$$(\hat{H}_{\text{el}} - E_{\text{BO}}) \nabla_{\mathbf{R}} \Psi = -(\nabla_{\mathbf{R}} \hat{H}_{\text{el}}) \Psi.$$

The solution for  $\nabla_{\mathbf{R}} \Psi$  was obtained by representing  $\nabla_{\mathbf{R}} \Psi$  and  $\Psi$  as full configuration interaction (FCI) expansions and solving linear equations for the CI coefficients.

Similar FCI expansion was used to compute relativistic corrections.

Gaussian bases with up to 500 orbitals and wave functions containing up to  $2 \times 10^9$  terms (Slater determinants) were used.

If  $l$  is the maximal angular momentum included in the basis, the error decays as:  $l^{-3}$  for  $V_{\text{ad}}(\mathbf{R})$ ,  $l^{-3/2}$  for the orbit-orbit interaction, and  $l^{-1}$  for the Darwin and  $P^4$  contributions.

Performing these angular momentum extrapolations we could compute  $V_{\text{ad}}(\mathbf{R})$  and  $V_{\text{rel}}(\mathbf{R})$  with errors below 0.1%. (2% for QED)

## Relation with the Casimir-Polder theory

The bad news is that a finite QED expansion of the potential  $V(R)$  in powers of  $\alpha$

$$V_{\text{int}}(R) = V_0(R) + \alpha^2 V_2(R) + \alpha^3 V_3(R) + \alpha^4 V_4(R) + \dots$$

blows up at large  $R$  since:

$$V_0(R) \sim C_6^{(0)} R^{-6} \quad V_2(R) \sim C_4^{(2)} R^{-4} \quad V_3(R) \sim C_3^{(3)} R^{-3} \quad V_4(R) \sim C_2^{(4)} R^{-2}$$

The good news is that the  $C_{6-n}^{(n)}$  constants are the same as the constants appearing in the expansion of the Casimir-Polder potential

$$V_{\text{CP}}(R) = -\frac{1}{\pi R^6} \int_0^\infty \alpha_d^2(i\omega) e^{-2R\omega/c} P(R\omega/c) d\omega,$$

in powers of  $\alpha$ :

$$V_{\text{CP}}(R) = C_6^{(0)} R^{-6} + \alpha^2 C_4^{(2)} R^{-4} + \alpha^3 C_3^{(3)} R^{-3} + \alpha^4 C_2^{(4)} R^{-2} + O(\alpha^5)$$

To see how the  $R^{-7}$  asymptotics is possible consider the expansion

$$\frac{1}{\alpha R^7} \left[ 2 - (2 + \alpha R) e^{-\alpha R} \right] = \frac{1}{R^6} - \frac{\alpha^2}{6R^4} + \frac{\alpha^3}{12R^3} - \frac{\alpha^4}{40R^2} + \dots$$

## Additive retardation corrections

If  $V(\mathbf{R})$  is computed at the nonrelativistic level,  $V(\mathbf{R})=V_{\text{BO}}(\mathbf{R})$ , then  $\alpha^2$ ,  $\alpha^3$ , , etc., terms from  $V_{\text{CP}}(\mathbf{R})$  can be added to  $V_{\text{BO}}(\mathbf{R})$ , which leads to the retardation correction:

$$\delta V_{\text{ret}}^{(0)}(\mathbf{R}) = V_{\text{CP}}(\mathbf{R}) - C_6^{(0)} R^{-6}$$

Adding  $\delta V_{\text{ret}}^{(0)}(\mathbf{R})$  to  $V_{\text{BO}}(\mathbf{R})$  we improve accuracy accounting for the QED effects through infinite order in  $\alpha$  and, simultaneously, we entirely eliminate the **unphysical  $R^{-6}$  contribution** to the potential.

When the relativistic potential  $V_{\text{BO}}(\mathbf{R})+\alpha^2 V_{\text{rel}}(\mathbf{R})$  is available then  $\alpha^3$ ,  $\alpha^4$ , etc., terms from  $V_{\text{CP}}(\mathbf{R})$  can be added to it leading to the correction:

$$\delta V_{\text{ret}}^{(2)}(\mathbf{R}) = V_{\text{CP}}(\mathbf{R}) - C_6^{(0)} R^{-6} - \alpha^2 C_4^{(2)} R^{-4}$$

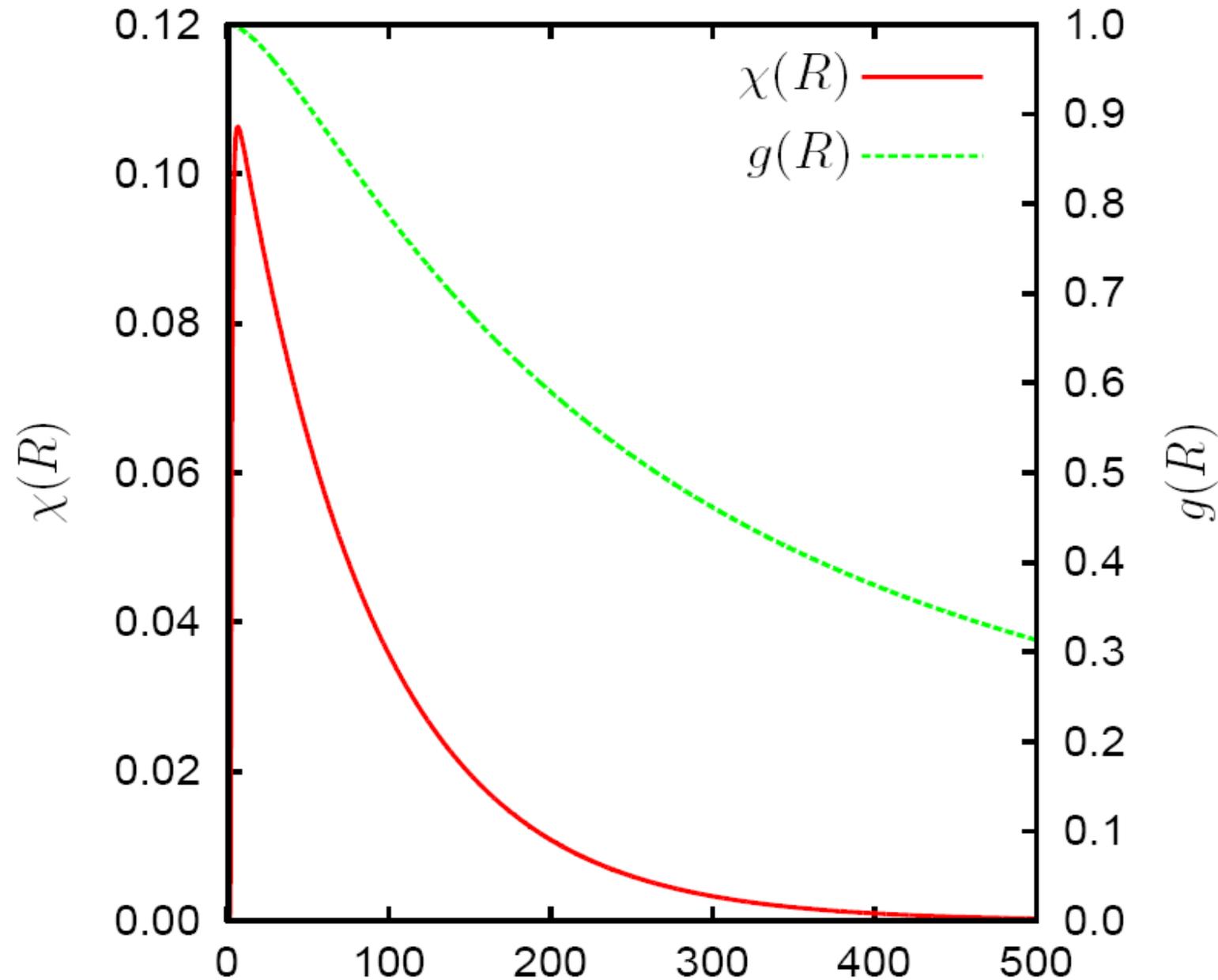
Adding  $\delta V_{\text{ret}}^{(2)}(\mathbf{R})$  we eliminate the **unphysical  $R^{-4}$  term** from the asymptotics.

Quite similarly one defines the retardation correction appropriate for the potential  $V_{\text{BO}}(\mathbf{R})+\alpha^2 V_{\text{rel}}(\mathbf{R})+\alpha^3 V_{\text{QED}}(\mathbf{R})$  :

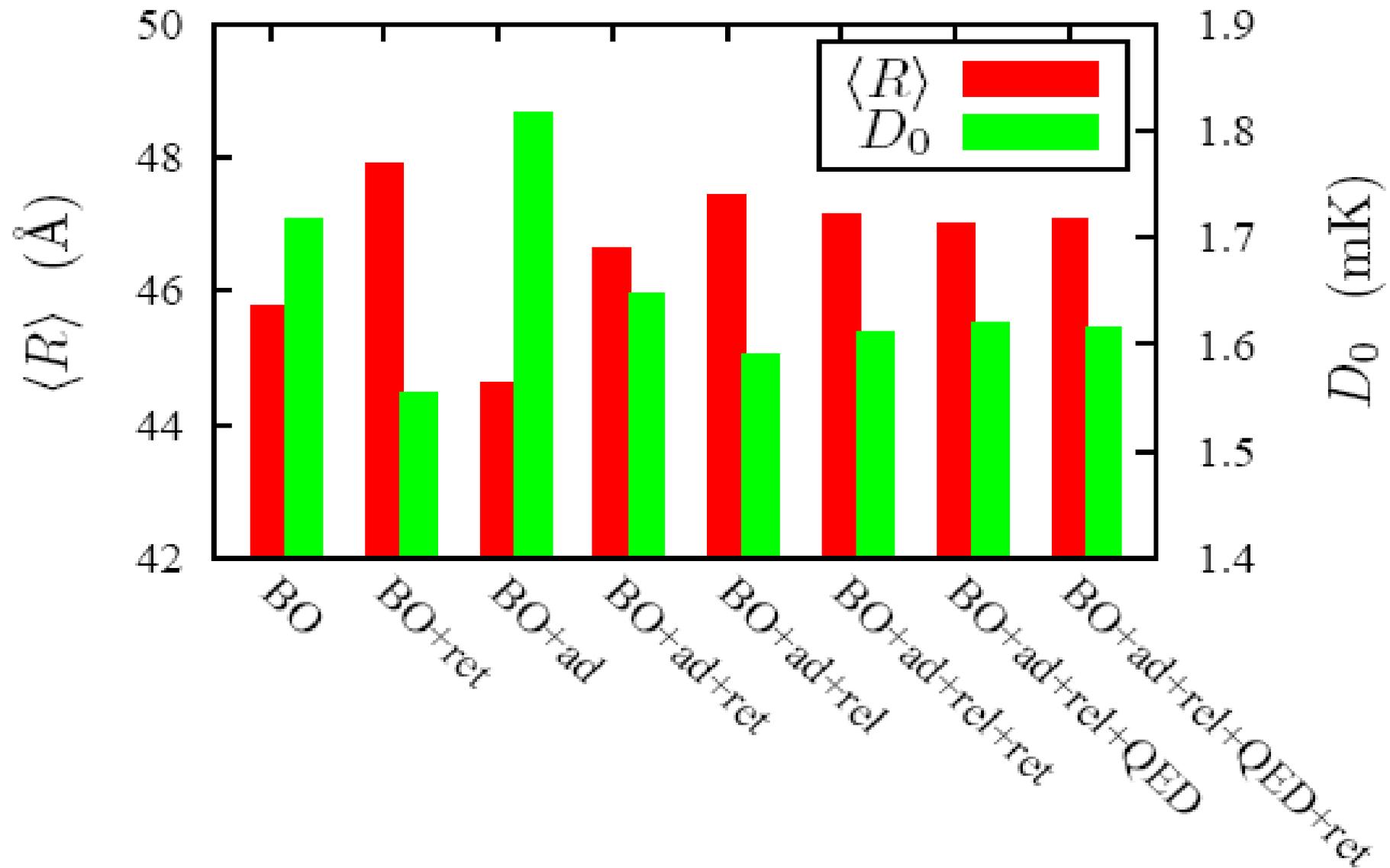
$$\delta V_{\text{ret}}^{(3)}(\mathbf{R}) = V_{\text{CP}}(\mathbf{R}) - C_6^{(0)} R^{-6} - \alpha^2 C_4^{(2)} R^{-4} - \alpha^3 C_3^{(3)} R^{-3}$$

eliminating the **unphysical  $R^{-3}$  term** from the asymptotics of  $V(\mathbf{R})$ .

Vibrational wave function  $\chi(\mathbf{R})$  and the retardation factor  $g(\mathbf{R}) = V_{\text{CP}}(\mathbf{R})R^6/C_6$  for  ${}^4\text{He}_2$ . The unit of  $\mathbf{R}$  is Å.



Dissociation energy  $D_0$  (in mK) and the bond length  $\langle R \rangle$  (in Å) for  $^4\text{He}_2$ .



Components of the  $^4\text{He}$  dimer potential in kelvin with  $R$  in bohr.

$R$	$V_{\text{BO}}$	$V_{\text{ad}}$	$V_{\text{rel}}$	$V_{\text{QED}}$	$V$	$V_{\text{ret}}$
3.0	3767.7341(38)	1.3847(15)	-0.2125(17)	0.09376(22)	3769.000(4)	0.00045
4.0	292.58201(86)	0.10585(17)	0.03322(21)	0.00891(5)	292.7300(9)	0.00025
5.0	-0.47114(36)	-0.006992(10)	0.024012(25)	-0.00106(3)	-0.4552(4)	0.00015
5.6	<b>-11.00072(20)</b>	<b>-0.008905(10)</b>	<b>0.015403(15)</b>	<b>-0.001351(23)</b>	<b>-10.99557(20)</b>	<b>0.00012</b>
6.0	-9.68079(16)	-0.007170(4)	0.011438(11)	-0.00120(4)	-9.67772(16)	0.00010
7.0	-4.62260(10)	-0.0033168(24)	0.005768(4)	-0.00074(3)	-4.62089(11)	0.00007
9.0	-0.98971(6)	-0.0007328(8)	0.0019306(6)	-0.000316(29)	-0.98883(7)	0.00004
12.0	-0.16592(2)	-0.0001261(1)	0.0005768(1)	-0.000133(26)	-0.16560(3)	0.00002

## Thermophysical properties of helium

The thermal contribution to the quantum density virial  $B(T)$  is given by

$$B_{\text{th}}(T) \propto \int_0^{\infty} e^{-E/(kT)} \mathcal{S}(E) dE,$$

where, for the bosonic  ${}^4\text{He}$ ,

$$\mathcal{S}(E) \equiv \sum_{\ell=0,2,4,\dots}^{\infty} (2\ell + 1) \delta_{\ell}(E)$$

can be sensitive to very large values of  $R$ . Indeed, for  $\ell > 2$  the Born approximation for the phase shift of the  $C_3/R^3$  potential gives

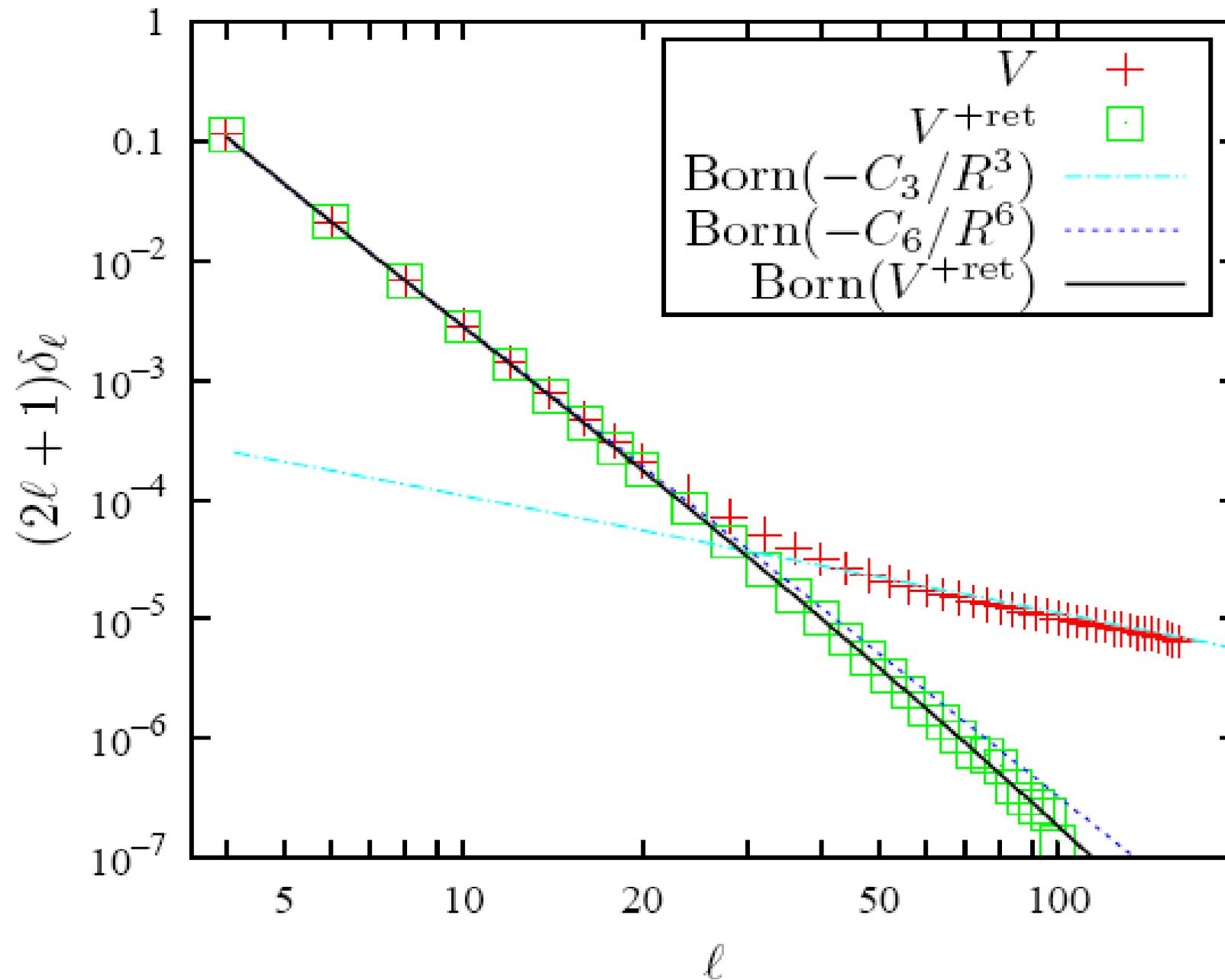
$$\delta_{\ell}^{\text{B}}(E) = \frac{\mu^{3/2} C_3 \sqrt{2E}}{\ell(\ell + 1)},$$

while for the  $C_6/R^6$  potential one obtains

$$\delta_{\ell}^{\text{B}}(E) = \frac{12\pi\mu^3 C_6 E^2}{(2\ell - 3)(2\ell - 1)(2\ell + 1)(2\ell + 3)(2\ell + 5)}.$$

where  $\mu$  is the reduced atomic mass of the dimer.

Phase shifts for  $E = 3\text{K}$  computed with retarded and non-retarded potentials



## Nonadiabatic treatment of dimer bound state

According to the NAPT theory of Pachucki and Komasa the wave function for the dimer is obtained by solving the effective Schrodinger equation:

$$\left[ -\frac{\hbar^2}{R^2} \frac{\partial}{\partial R} \frac{R^2}{2\mu_{\parallel}(R)} \frac{\partial}{\partial R} + \frac{J(J+1)\hbar^2}{2\mu_{\perp}(R)R^2} + \mathcal{Y}(R) - E \right] \chi(R) = 0,$$

where  $\mu_{\parallel}(R)$  and  $\mu_{\perp}(R)$  are the  $R$ -dependent vibrational and rotational reduced masses

$$\frac{1}{2\mu_{\parallel}(R)} = \frac{1}{m_n} + \mathcal{W}_{\parallel}(R), \quad \frac{1}{2\mu_{\perp}(R)} = \frac{1}{m_n} + \mathcal{W}_{\perp}(R),$$

and  $\mathcal{Y}(R) = V(R) + V_{\text{ret}}(R) + V_{\text{na}}(R)$ . Expressions for  $\mathcal{W}_{\parallel}(R)$ ,  $\mathcal{W}_{\perp}(R)$ , and  $V_{\text{na}}(R)$  were given by Pachucki and Komasa in their 2008 NAPT paper.

One can show that

$$\mathcal{W}_{\parallel}(\infty) = \mathcal{W}_{\perp}(\infty) = -2m_e/m_n^2,$$

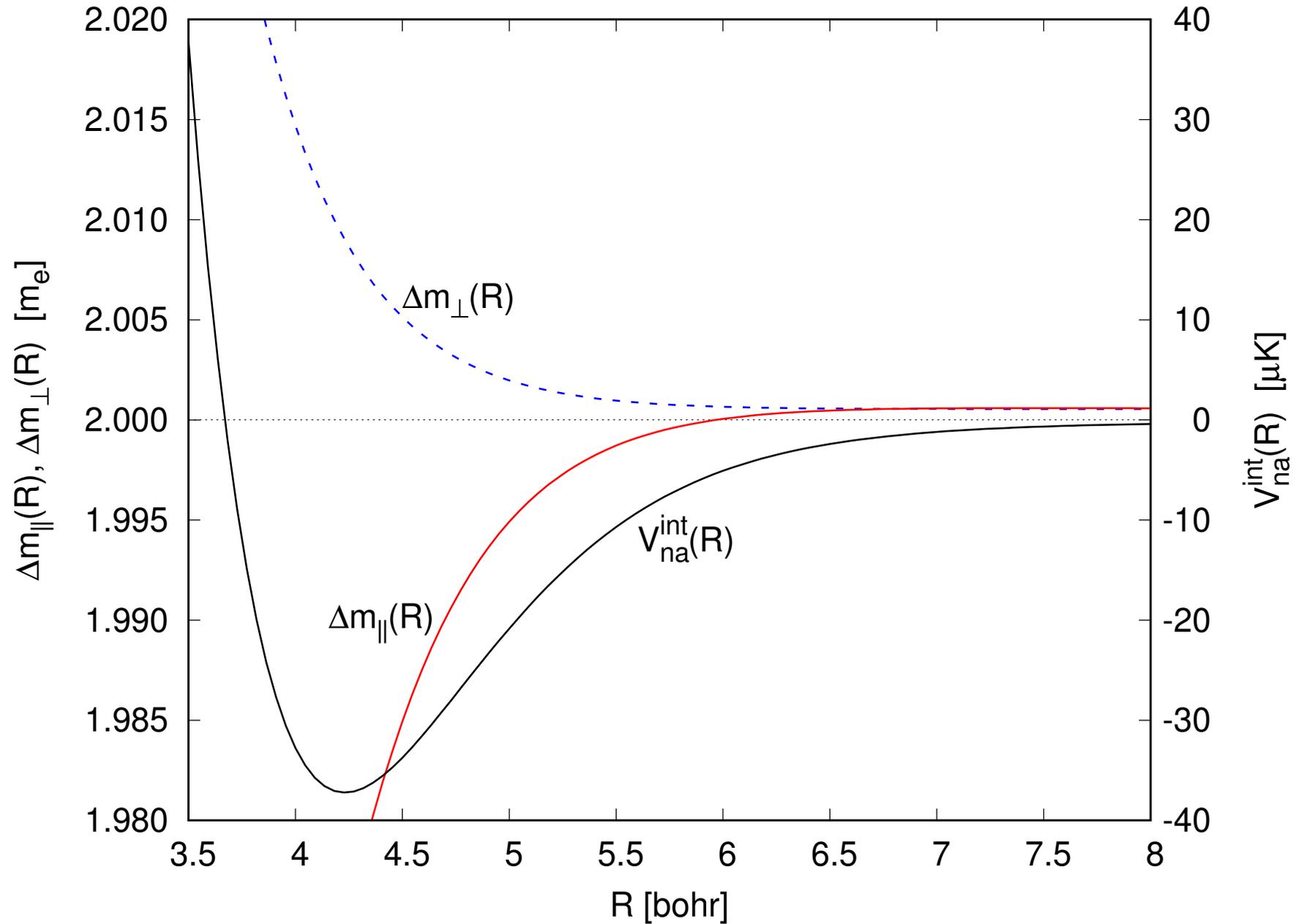
where  $m_e$  is the electron mass, and that

$$2\mu_{\parallel}(\infty) = 2\mu_{\perp}(\infty) = m_n + 2m_e + 4m_e^2/m_n + \mathcal{O}(m_e^3/m_n^2).$$

Thus, at  $R=\infty$  the effective reduced masses are very close to the reduced atomic mass.

The  $R$ -dependence of the excess effective masses

$$\Delta m_{\parallel} = m_{\parallel} - m_n \text{ and } \Delta m_{\perp} = m_{\perp} - m_n$$



Dissociation energy  $D_0$  (in neV) and the average separation  $\langle R \rangle$  (in Å) for the  $^4\text{He}$  dimer.

potential	$D_0$		$\langle R \rangle$	
	nuclear	atomic	nuclear	atomic
$V_{\text{BO}}$	145.2(5)	147.8(5)	46.20(7)	45.80(7)
$V_{\text{BO}}+V_{\text{ad}}$	153.5(5)	156.3(5)	45.03(7)	44.65(7)
$V_{\text{BO}}+V_{\text{ad}}+V_{\text{rel}}$	134.1(5)	136.7(5)	47.90(8)	47.48(8)
$V^a$	136.7(5)	139.3(5)	47.48(8)	47.07(8)
$V+V_{\text{ret}}$	136.3(5)	138.9(5)	47.55(8)	47.13(8)
$V+V_{\text{ret}}+\text{nonad}$		138.9±0.5		47.13±0.08
Experiment		151.9±13.3 <sup>b</sup>		52±4 <sup>c</sup>

<sup>a</sup>  $V=V_{\text{BO}}+V_{\text{ad}}+V_{\text{rel}}+V_{\text{QED}}$

<sup>b</sup> S. Zeller et al, PNAS 2016 (via Coulomb explosion).

<sup>c</sup> R. E. Grisenti, PRL 2000 (via nanosieve transmission).

## Conclusions

- A new helium pair potential, an order of magnitude more accurate than earlier ones has been obtained
- This potential includes the effects of relativity, QED, retardation and the nonadiabatic coupling of the electronic and nuclear motion
- The uncertainty of the nonrelativistic BO component still dominates the error budget
- The nonadiabatic calculation shows that for the dimer properties it is sufficient to use atomic masses in an adiabatic treatment. It remains to be seen if this is also true for thermophysical properties
- Our calculations agree with the first experimental determination of the dimer binding energy from Dörner group (via the Coulomb explosion technique)
- Calculations of thermophysical properties with the new potential will follow soon

## Collaboration

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## Publications on the polarizability of helium

W. Cencek, K. Szalewicz, and B.J., *Phys. Rev. Lett.* **86**, 5675 (2001).

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M. Przybytek, W. Cencek, J. Komasa, G.Łach, B.J., and K. Szalewicz, *Phys. Rev. Lett.*, **104**, 183003 (2010).

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