# High-precision calculations of the hydrogen molecule

Michał Siłkowski, Krzysztof Pachucki

University of Warsaw

12th June, 2019, FFK-2019, Tihany, Hungary

H2SOLV - Schrödinger equation solver for two-electron, two-center molecule in the Born-Oppenheimer approximation (currently $\Sigma$ and $\Pi$ states), with non-relativistic hamiltonian:

$$H = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z_A}{r_{1A}} - \frac{Z_B}{r_{1B}} - \frac{Z_A}{r_{2A}} - \frac{Z_B}{r_{2B}} + \frac{1}{r_{12}} + \frac{Z_A Z_B}{R}. \quad (1)$$

The most efficient basis set to solve this equation is the generalization of one introduced by Kołos and Wolniewicz[1]

```
input nuclear charge A
input nuclear charge B
input A <-> B symmetry (1:gerade, -1:ungerade, 0:nosym)
input r1 <-> r2 symmetry (1:sym, -1:asym)
input ang momentum (0:Sigma, 1:Pi)
input internuclear distance
input basis restriction type 1 (=-1..2; -1:auto)
input basis restriction type 2 (=-1..2; -1:auto)
input basis rank OMEGA
input length of Taylor series NMAX
input working precision for MPRF in digits  (max:134)
input approximate energy EN
input nonlinear parameter Y
input nonlinear parameter X
input nonlinear parameter U
input nonlinear parameter W
input 0 for evaluation,
      1 for optimization without restriction,
      2 for optimization with restriction
1 recommended for the lowest state of given symmetry
2 will require value of energy of a lower-lying state
Auto selection: RESTRICT1 =            0
Auto selection: RESTRICT2 =            0
```
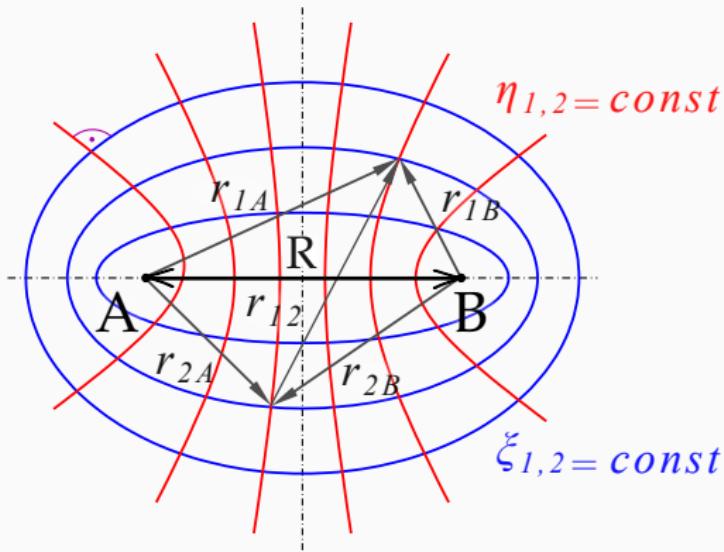
$$\xi_i = r_{iA} + r_{iB}, \ \eta_i = r_{iA} - r_{iB} \qquad i = 1, 2$$

$$R \leq \xi_i \leq \infty, \ -R \leq \eta_i \leq R, \ 0 \leq \varphi \leq 2\pi,$$

**Molecular hydrogen polarizability**
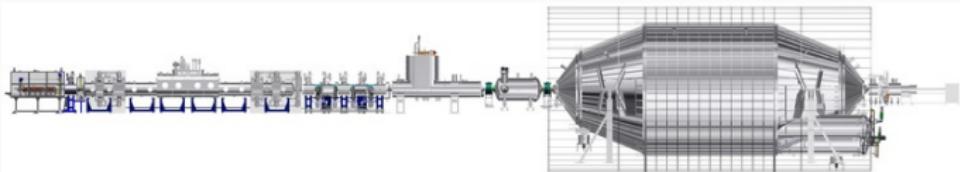


KATRIN experiment:

- Need for precise polarizability calculation (with reliable uncerainties!) for quantitative identification of $T_2$ gas concentration (and other isotopologues)

- To which electronic states does ground-state Tritium go after beta decay $\mathbf{T_2 \rightarrow\ ^3HeT^+}$

### Master Integral

We are capable of variational calculation using the explicitly correlated exponential Kołos-Wolniewicz basis functions:

$$\Psi\left(r_{1A}, r_{1B}, r_{2A}, r_{2B}, r_{12}\right) \equiv \\ \hat{S}_{12}\hat{S}_{AB} \sum_{n_1 \ldots n_5} c_{n_1 \ldots n_5} \phi_{n_1 \ldots n_5}\left(r_{1A}, r_{1B}, r_{2A}, r_{2B}, r_{12}\right), \tag{2}$$

where

$$\phi_{n_1 n_2 n_3 n_4 n_5}\left(r_{1A}, r_{1B}, r_{2A}, r_{2B}, r_{12}\right) \equiv \\ e^{-y(r_{1A}-r_{1B})-x(r_{2A}-r_{2B})-u(r_{1A}+r_{1B})-w(r_{2A}+r_{2B})-w_1 r_{12}} \\ r_{12}^{n_1}\left(r_{1A}-r_{1B}\right)^{n_2}\left(r_{2A}-r_{2B}\right)^{n_3}\left(r_{1A}+r_{1B}\right)^{n_4}\left(r_{2A}+r_{2B}\right)^{n_5} \\ R^{-n_1-n_2-n_3-n_4-n_5-3},$$

$$\tag{3}$$

where $x, y, u, w, w_1$ are nonlinear parameters.

**Master Integral $\leftrightarrow$ differential equation**

Corresponding differential equation

$$\left[\sigma_4 \frac{d^2}{dr^2} r \frac{d^2}{dr^2} + \sigma_2 \frac{d}{dr} r \frac{d}{dr} + \sigma_0 r\right] f(r) = F(r), \tag{4}$$

where $\sigma_0, \sigma_2, \sigma_4$ are polynomials in nonlinear parameters $y, x, u, w, w_1$:

$$\begin{aligned}
\sigma_0 &= w_1^2 \left(u + w - x - y\right)\left(u - w + x - y\right)\left(u - w - x + y\right)\left(u + w + x + y\right) \\
&\quad + 16 \left(w x - u y\right)\left(u x - w y\right)\left(u w - x y\right) \\
\sigma_2 &= w_1^4 - 2 w_1^2 \left(u^2 + w^2 + x^2 + y^2\right) + 16 u w x y \\
\sigma_4 &= w_1^2, \tag{5}
\end{aligned}$$

6

## Master Integral ↔ differential equation

$$
\begin{aligned}
F(r) &= w_1 \left( \frac{1}{r^2} + \frac{2\,w_1 + u + w + x - y}{r} \right) e^{-r\,(u + w + w_1 + x - y)} \\
&+ w_1 \left( \frac{1}{r^2} + \frac{2\,w_1 + u + w - x + y}{r} \right) e^{-r\,(u + w + w_1 - x + y)} \\
&- w_1 \left( \frac{1}{r^2} + \frac{u + w - x - y}{r} \right) e^{-r\,(u + w - x - y)} \\
&- w_1 \left( \frac{1}{r^2} + \frac{u + w + x + y}{r} \right) e^{-r\,(u + w + x + y)} \\
&+ \left[ \frac{w_1^2}{2}\,(u - w + x - y) + 2\,u\,w\,(y - x) + 2\,x\,y\,(w - u) \right] F_1 \\
&+ \left[ \frac{w_1^2}{2}\,(u - w - x + y) + 2\,u\,w\,(x - y) + 2\,x\,y\,(w - u) \right] F_2 \\
&+ \left[ \frac{w_1^2}{2}\,(u + w + x + y) + 2\,u\,w\,(x + y) + 2\,x\,y\,(u + w) \right] F_3 \\
&+ \left[ \frac{w_1^2}{2}\,(u + w - x - y) - 2\,u\,w\,(x + y) + 2\,x\,y\,(u + w) \right] F_4 \,, \qquad (6)
\end{aligned}
$$

## Master Integral $\leftrightarrow$ differential equation

where

$$F_1 = \text{Ei}[-r\,(w_1+2\,u)]\,\exp[r\,(u-w+x-y)]-\text{Ei}[-r\,(w_1+2\,w)]\,\exp[-r\,(u-w+x-y)]\,,$$

$$F_2 = \text{Ei}[-r\,(w_1+2\,u)]\,\exp[r\,(u-w-x+y)]-\text{Ei}[-r\,(w_1+2\,w)]\,\exp[-r\,(u-w-x+y)]\,,$$

$$F_3 = \text{Ei}[-2\,r\,(u+w)]\,\exp[r\,(u+w+x+y)]+\left\{\text{Ei}[2\,r\,(x+y)]-\text{Ei}[-r\,(w_1-2\,x)]\right.$$
$$\left.-\text{Ei}[-r\,(w_1-2\,y)]-\ln\left[\frac{(w_1+2\,u)\,(w_1+2\,w)\,(x+y)}{(u+w)\,(w_1-2\,x)\,(w_1-2\,y)}\right]\right\}\,\exp[-r\,(u+w+x+y)]\,,$$

$$F_4 = \text{Ei}[-2\,r\,(u+w)]\,\exp[r\,(u+w-x-y)]+\left\{\text{Ei}[-2\,r\,(x+y)]-\text{Ei}[-r\,(w_1+2\,x)]\right.$$
$$\left.-\text{Ei}[-r\,(w_1+2\,y)]-\ln\left[\frac{(w_1+2\,u)\,(w_1+2\,w)\,(x+y)}{(u+w)\,(w_1+2\,x)\,(w_1+2\,y)}\right]\right\}\,\exp[-r\,(u+w-x-y)]\,,$$

$$(7)$$

and $\text{Ei}$ is the exponential integral function.

**Explicitly correlated Exponential functions**

$$\phi_{n_1 n_2 n_3 n_4 n_5} (r_{1A}, r_{1B}, r_{2A}, r_{2B}, r_{12}) \equiv$$
$$e^{-y(r_{1A}-r_{1B})-x(r_{2A}-r_{2B})-u(r_{1A}+r_{1B})-w(r_{2A}+r_{2B})-w_1 r_{12}}$$
$$r_{12}^{n_1} (r_{1A} - r_{1B})^{n_2} (r_{2A} - r_{2B})^{n_3} (r_{1A} + r_{1B})^{n_4} (r_{2A} + r_{2B})^{n_5}$$
$$R^{-n_1-n_2-n_3-n_4-n_5-3},$$

$$(8)$$

where $x, y, u, w, w_1$ are nonlinear parameters.
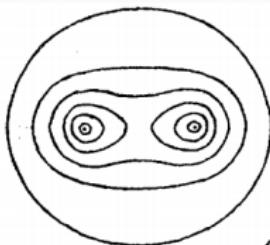
$$E_{exch} := E(^3\Sigma_u^+) - E(^1\Sigma_g^+).$$



source: *The Quantum Theory of Valence* (1935), J. H. Van Vleck, A. Sherman

Wechselwirkung neutraler Atome
und homöopolare Bindung nach der Quantenmechanik[1].

Von W. Heitler und F. London in Zürich.

Mit 2 Abbildungen. (Eingegangen am 30. Juni 1927.)

In Heitler-London theory[2] exchange energy behaves asymptotically like:[3]

$$E_{HL} = - \left( \frac{28}{45} - \frac{2}{15} \left[ \ln(R) + \gamma \right] \right) R^3 \exp(-2R) + \mathcal{O}(R^2 \exp(-2R)), \tag{9}$$

where $R$ is internuclear distance and $\gamma$ is the Euler-Mascheroni constant.

[2]W. Heitler and F. London, Z. Phys. **44** (1927) 455.
[3]Sugiura, Y. Z. Physik (1927) **45**: 484.

## Critique of Heitler-London

Asymptotically unphysical negative value due to domination of negative term $\sim R^3 \ln(R) \exp(-2R)$.
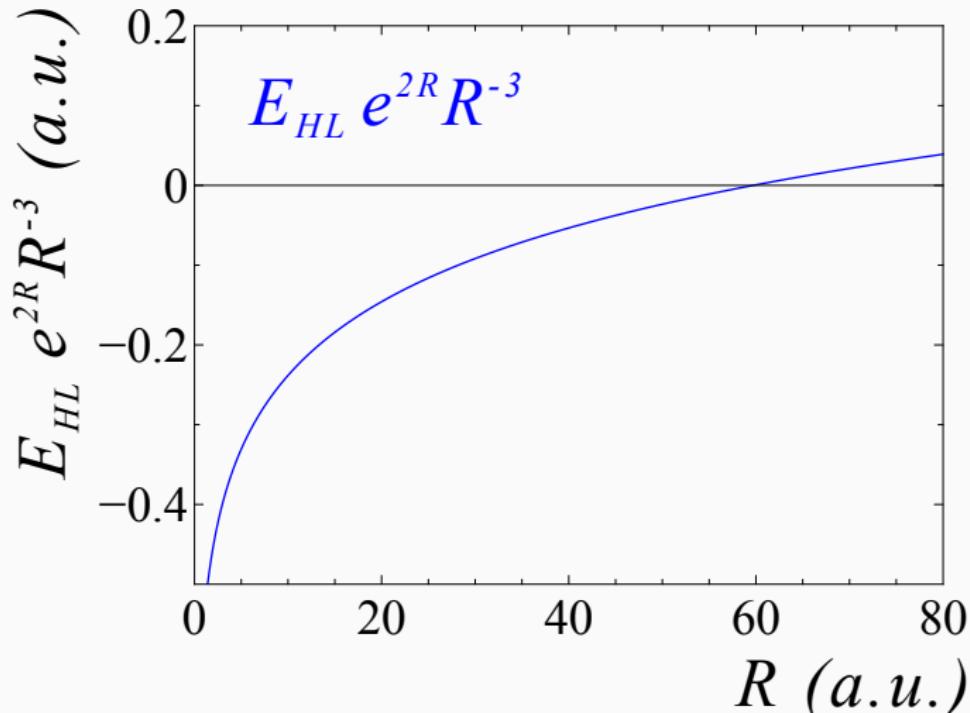
## Critique of the Heitler-London Method of Calculating Spin Couplings at Large Distances

CONYERS HERRING

*Bell Telephone Laboratories, Murray Hill, New Jersey*

Herring[4](1962): *$J_{ij}$ measures the rate at which an electron exchange would take place between atoms i and j if each atom started with a known set of individually distinguishable electrons. In the course of such an exchange process, the mutual avoidance of the exchanging electrons is bound to be important, and this correlation effect is ignored in the Heitler-London approximation. (…)*

[4]C. Herring, Rev. Mod. Phys. **34** (1962), 631.

13

Molecular hydrogen hamiltonian:

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r_{A1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}} + \frac{1}{R} + \frac{1}{r_{12}} \qquad (10)$$
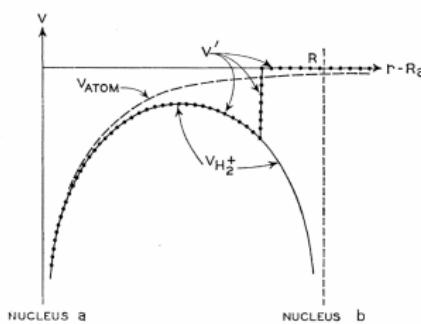


$$\int_{\Omega_{near}} d^6r \left(\phi_u H \phi_g - \phi_g H \phi_u\right) = \frac{1}{2} \int_{\Sigma} \mathbf{dS} \cdot \left(\hat{P}\phi_A \nabla\phi_A - \phi_A \nabla\hat{P}\phi_A\right), \quad (11)$$

where $\hat{P}$ denotes permutation operator $(1 \leftrightarrow 2)$

$$LHS = \int_{\Omega_{near}} d^6r \left(\phi_u H \phi_g - \phi_g H \phi_u\right) = (E_g - E_u)\left(\frac{1}{2} + \mathcal{O}(e^{-2R})\right) \quad (12)$$

14

**1964** – L. P. Gor'kov and L. P. Pitaevskii and C. Herring and M. Flicker proposed the form,

$$E_{exch} = C \ R^{5/2} e^{-2R} + \mathcal{O}(R^2 \exp(-2R)), \tag{13}$$

$$C = -4\pi^{-1/2} \int_0^1 dq e^{-q} q^{3/2} (2-q)^{1/2} = -1.63657... \tag{14}$$

## Still controversial

| Year | Authors | Coefficient | Asymptotics |
|------|---------|-------------|-------------|
| 1927 | Heitler, London | $\left(\frac{28}{45} - \frac{2}{15}\left(\gamma + \ln R\right)\right)$ | $R^3 e^{-2R}$ |
| 1964 | Gor'kov, Pitaevskii | $-1.47$ | $R^{5/2} e^{-2R}$ |
| 1964 | Herring, Flicker | $-1.636572$ | $R^{5/2} e^{-2R}$ |
| 1993 | Tang, Toennies | $\frac{4}{15}$ | $R^3 e^{-2R}$ |
| 2012 | Burrows, Dalgarno, Cohen | $\left(0.30167 + \frac{2.455}{R}\right)$ | $R^3 e^{-2R}$ |
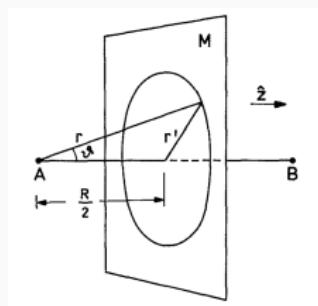


All approaches based on the Surface Integral Method.

$$E_{exch} \xrightarrow{?} \begin{cases} R^{5/2}e^{-2R} + \mathcal{O}(R^2 e^{-2R}) \\ R^3 e^{-2R} + \mathcal{O}(R^2 e^{-2R}) \quad for R >> a_0 \\ R^3 e^{-2R} + \mathcal{O}(R^{5/2} e^{-2R}) \end{cases}$$

## Basis of wavefunctions

In usual applications, trial wavefunction basis is characterized by the principal number $\Omega$

$$\sum_{i=1}^{5} n_i \leq \Omega, \tag{15}$$

In usual applications, trial wavefunction basis is characterized by the principal number $\Omega$

$$\sum_{i=1}^{5} n_i \leq \Omega, \qquad (15)$$

However we conjecture, following argumentation by Herring that the essential behaviour of wavefunctions (for the sake of exchange energy splitting calculations) depend on $\eta_{1,2}$ and $r_{12}$.
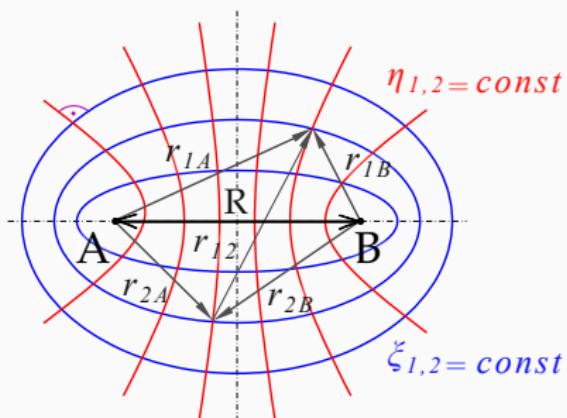
$$\phi_{n_1 n_2 n_3 n_4 n_5}\left(r_{1A}, r_{1B}, r_{2A}, r_{2B}, r_{12}\right) \equiv$$

$$e^{-y(r_{1A}-r_{1B})-x(r_{2A}-r_{2B})-u(r_{1A}+r_{1B})-w(r_{2A}+r_{2B})-w_1 r_{12}}$$

$$r_{12}^{n_1}\left(r_{1A}-r_{1B}\right)^{n_2}\left(r_{2A}-r_{2B}\right)^{n_3}\left(r_{1A}+r_{1B}\right)^{0}\left(r_{2A}+r_{2B}\right)^{0}$$

$$R^{-n_1-n_2-n_3-n_4-n_5-3},$$

$$(16)$$

The difference between the "full-shell" basis and $\Omega_\xi = 0$ basis is
**exponentially decreasing with internuclear distance** $R$.
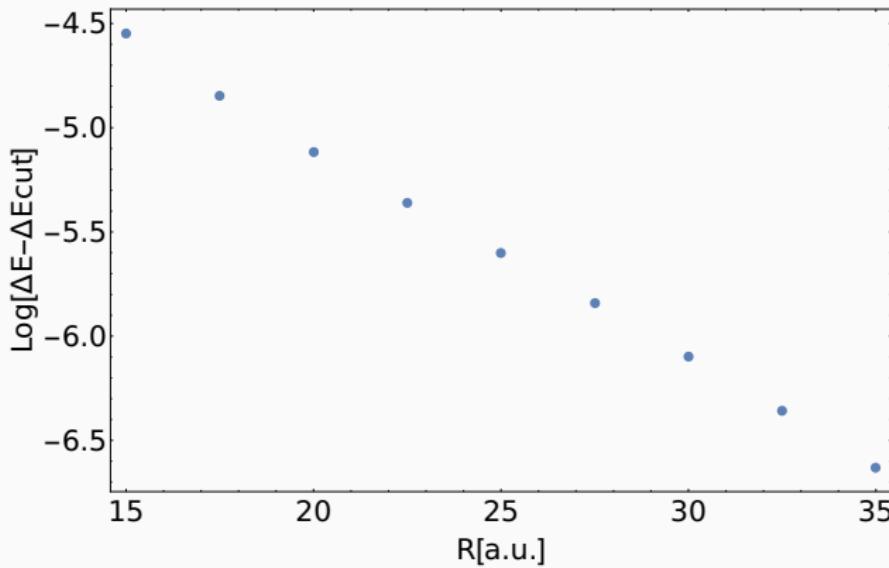
**Exemplary output**

Exemplary excerpt from program output for $R = 60$, $\Omega_\eta = 120$:

```
ENG =
-1.0000000000274459828249920579331790798823550367364664613
ENU =
-1.0000000000274459828249920579331790798823550367335077709
ENU - ENG = 2.95869075e-48
(ENU - ENG)*EXP(2R)*R^(-5/2) = 1.38375523
```

Fit to Herring-Flicker asymptotic series:

$\sum_{i=0}^{\infty} c_i \left( \frac{x}{\sqrt{R}} \right)^i$, where $x := \Delta E R^{-5/2} e^{2R}$
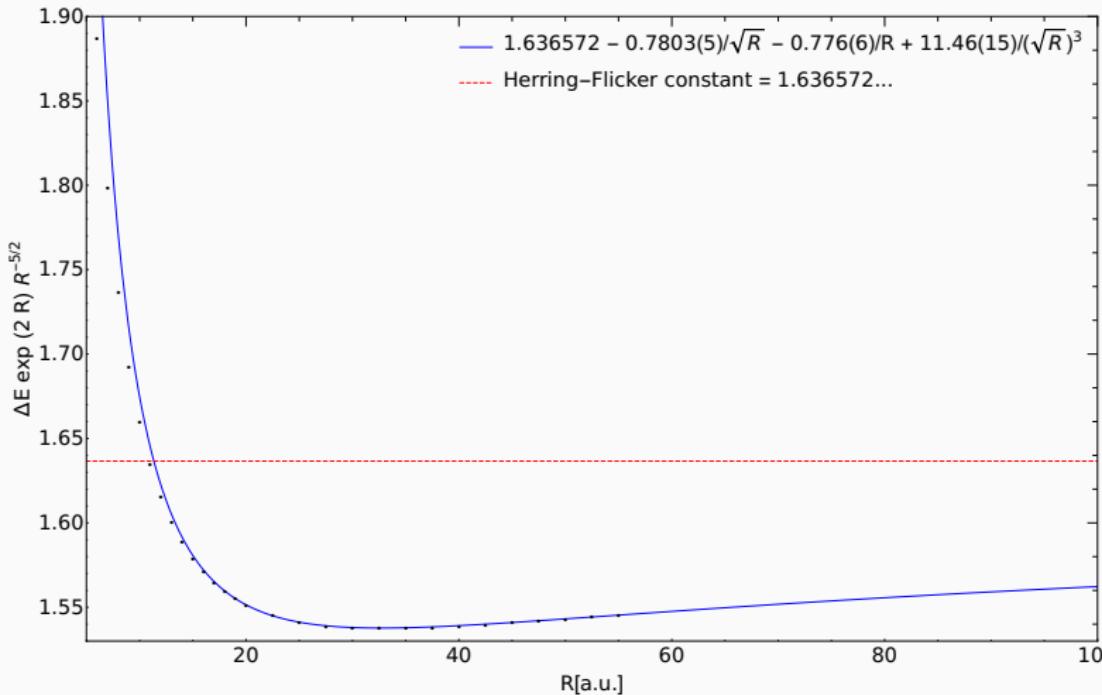
Whereas, insisting on leading term in the asymptotic series being $R^3 \exp(-2R)$

leads to **almost zero** leading coefficient.

R=30,n1+n2+n3+n4+n5=Ω
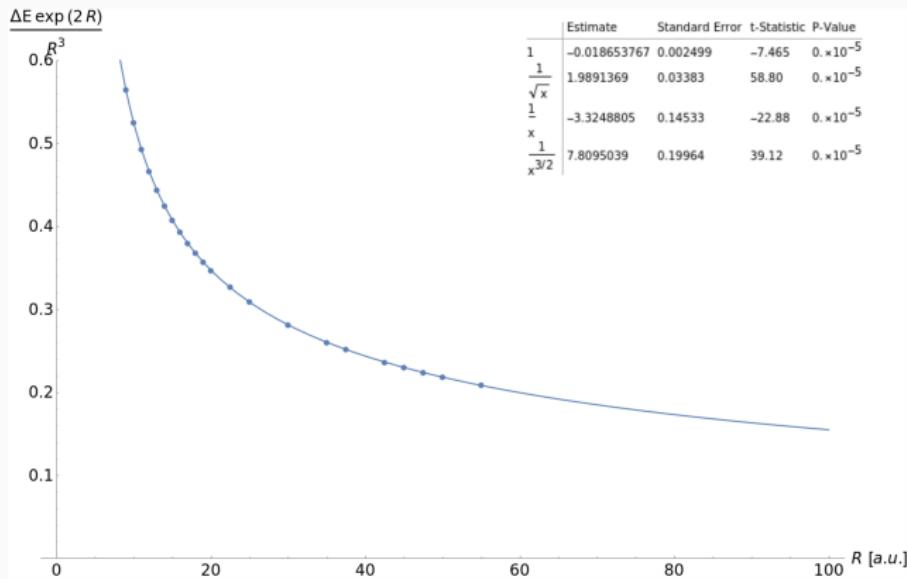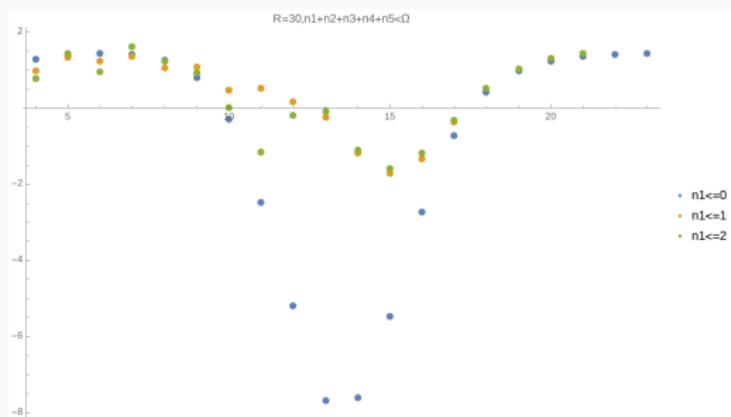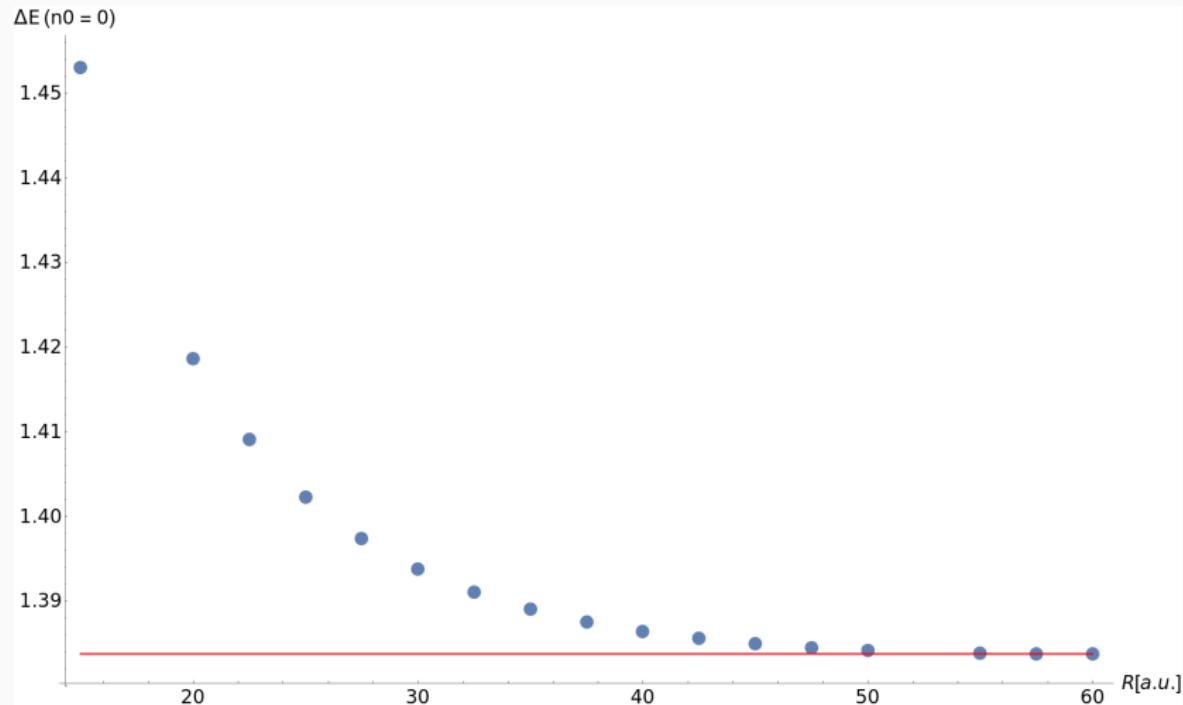
*Thank you for your attention*