

Bohr, scaling and molecular physics

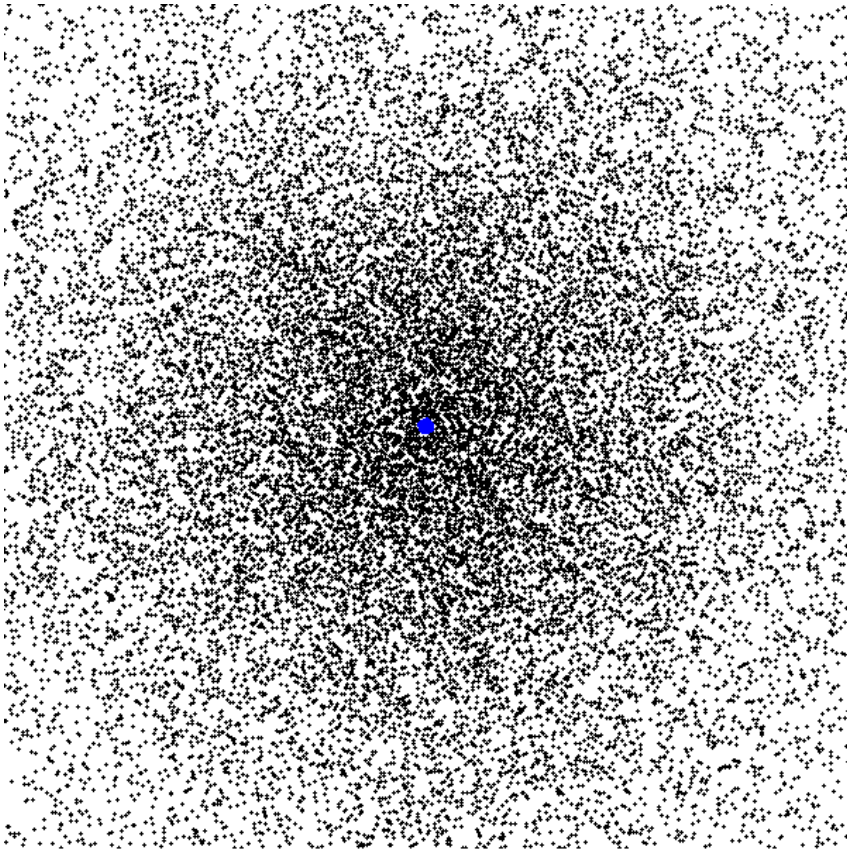
A. Sergeev

- Traditional scaling (full Jacobian)
- Alternative approach (without scaling angular-dependent terms)
- Method of empirically chosen effective potentials

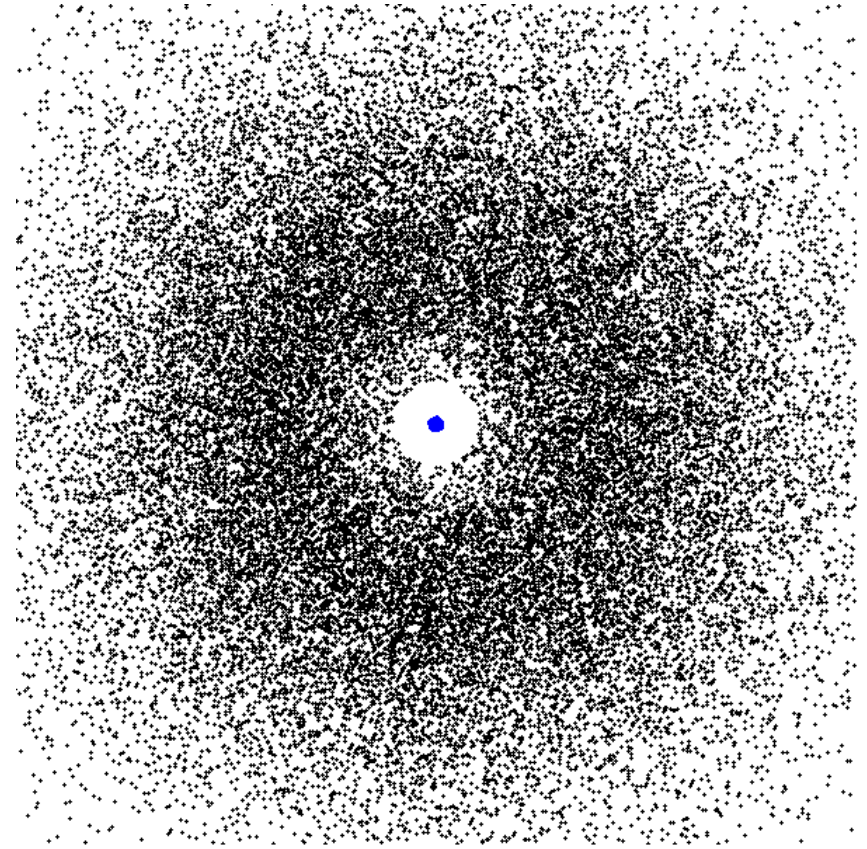
Results for CH and CH₄ molecules

Hydrogen atom in space of D dimensions

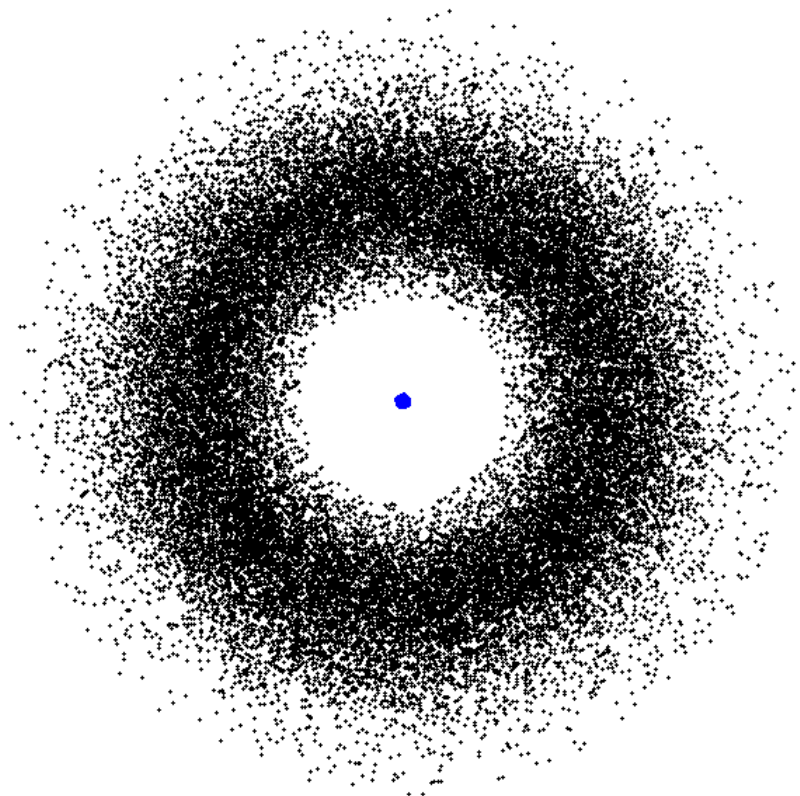
$$\psi_D(r) = N_D r^{(D-1)/2} \exp\left(-\frac{2r}{D-1}\right)$$



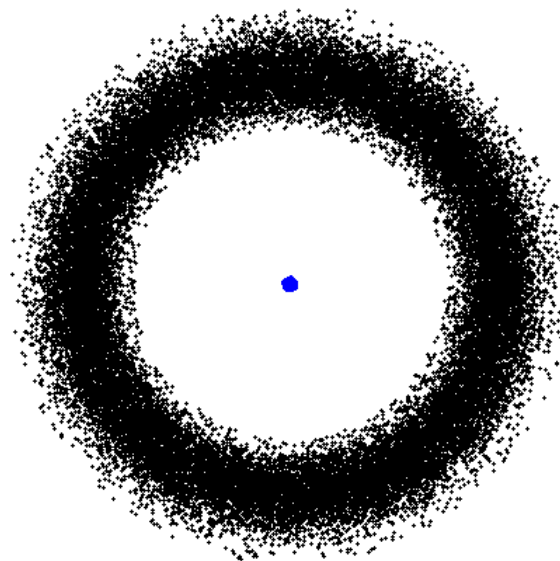
$D = 2$



$D = 5$



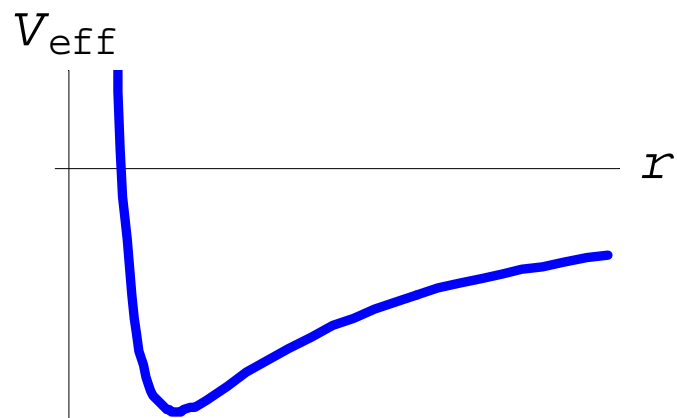
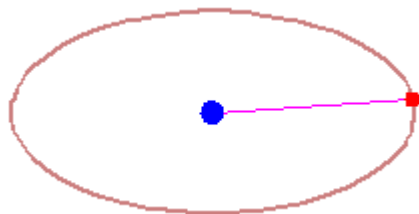
$D = 20$



$D = 100$

$$V_{\text{eff}} = \frac{m^2 - 1/4}{2r^2} - \frac{1}{r}$$

$$m = D/2 - 1$$



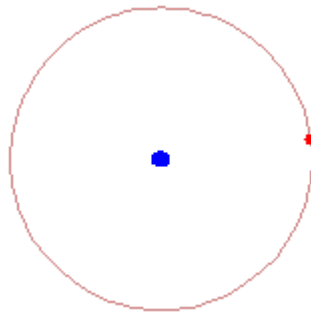
Classical mechanics as the limit of $D \rightarrow \infty$

$$\tilde{\psi}(\tilde{r}) = \psi\left((m^2 - 1/4)^{1/2} \tilde{r}\right) \quad \tilde{E} = (m^2 - 1/4)\mathcal{E}$$

$$\left[-\frac{1}{2(m^2 - 1/4)} \frac{d^2}{d\tilde{r}^2} + \frac{1}{2\tilde{r}^2} - \frac{1}{\tilde{r}} - \tilde{E} \right] \tilde{\psi}(\tilde{r}) = 0$$

$$\hbar \leftrightarrow (m^2 - 1/4)^{-1/2}$$

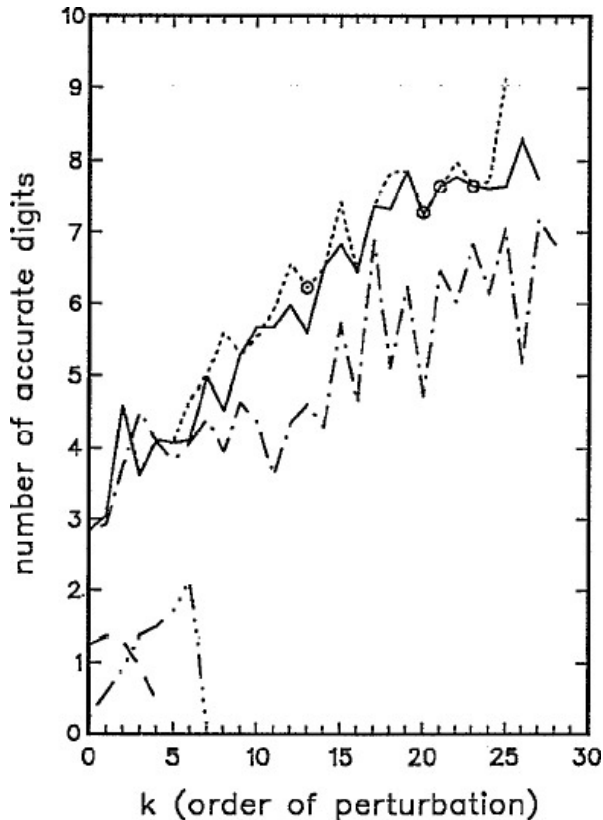
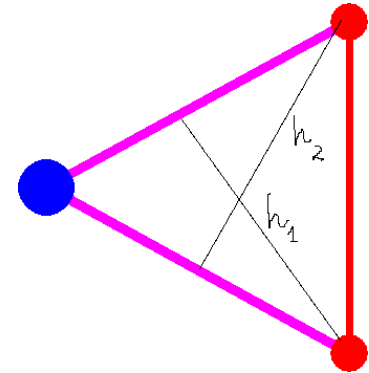
$\hbar \rightarrow 0$



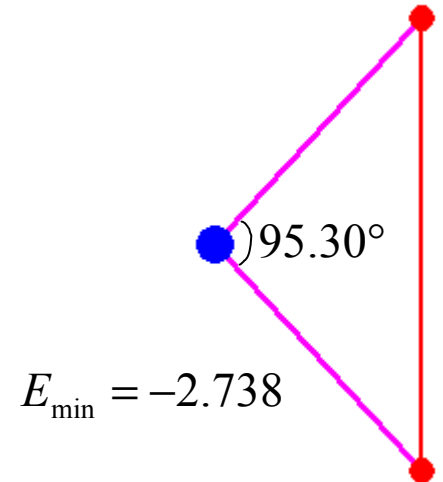
Helium atom in space of D dimensions

$$E = T + V = V_{\text{eff}}(r_1, r_2, r_{12})$$

$$V_{\text{eff}}(r_1, r_2, r_{12}) = -\frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} + \frac{L^2}{2} \left(\frac{1}{h_1^2} + \frac{1}{h_2^2} \right), \quad L = (D-1)/2$$



D. Goodson et al., J. Chem. Phys.,
97, 8481 (1992)

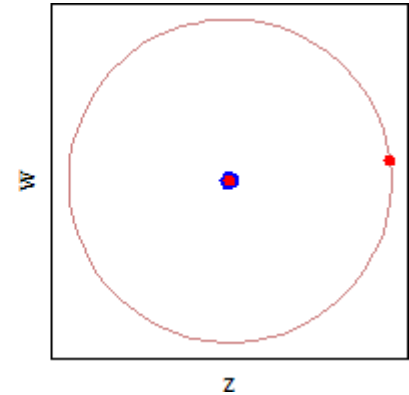
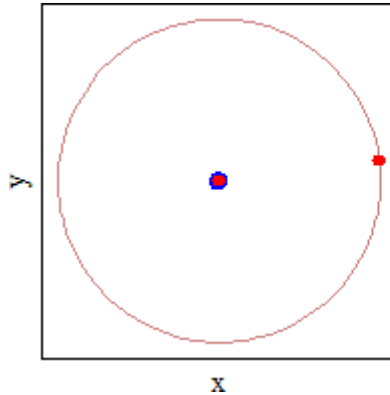


Stable Bohr orbits for helium in four dimensions (x, y, z, w)

The case of non-interacting electrons

$$1/r_{12} \rightarrow g/r_{12}, \quad g = 0$$

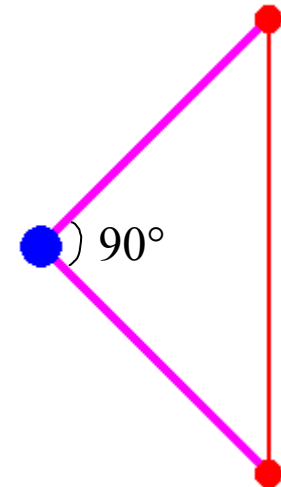
$$\begin{aligned} x_1(t) &= R \cos \omega t & x_2(t) &= 0 \\ y_1(t) &= R \sin \omega t & y_2(t) &= 0 \\ z_1(t) &= 0 & z_2(t) &= R \cos \omega t \\ w_1(t) &= 0 & w_2(t) &= R \sin \omega t \end{aligned}$$



$$r_1(t) = (x_1^2 + y_1^2 + z_1^2 + w_1^2)^{1/2} = R$$

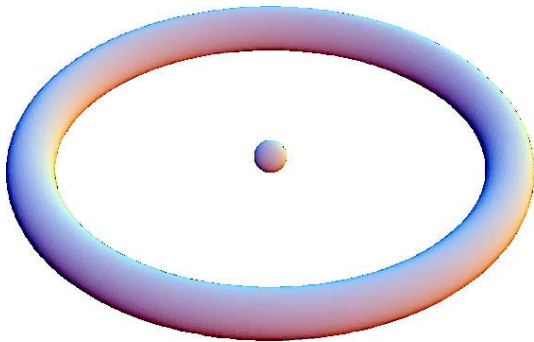
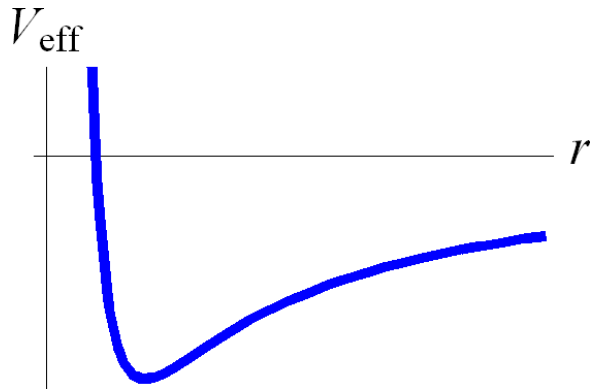
$$r_2(t) = (x_2^2 + y_2^2 + z_2^2 + w_2^2)^{1/2} = R$$

$$r_{12}(t) = ((x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2 + (w_1 - w_2)^2)^{1/2} = \sqrt{2}R$$

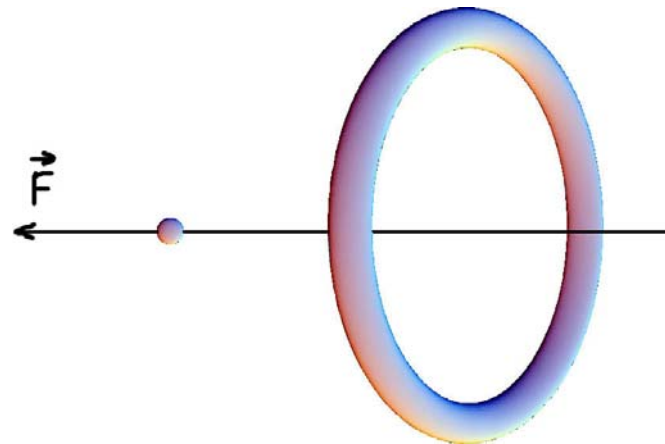
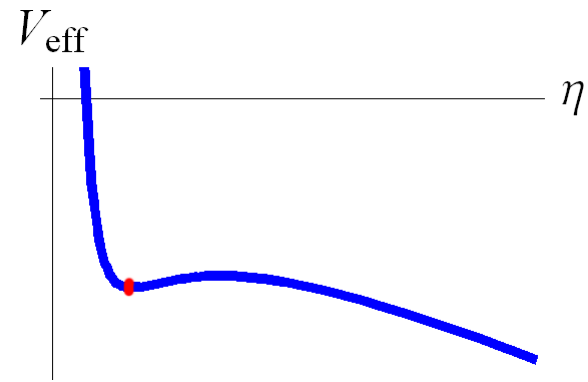


Atom in an electric field and quasistationary states

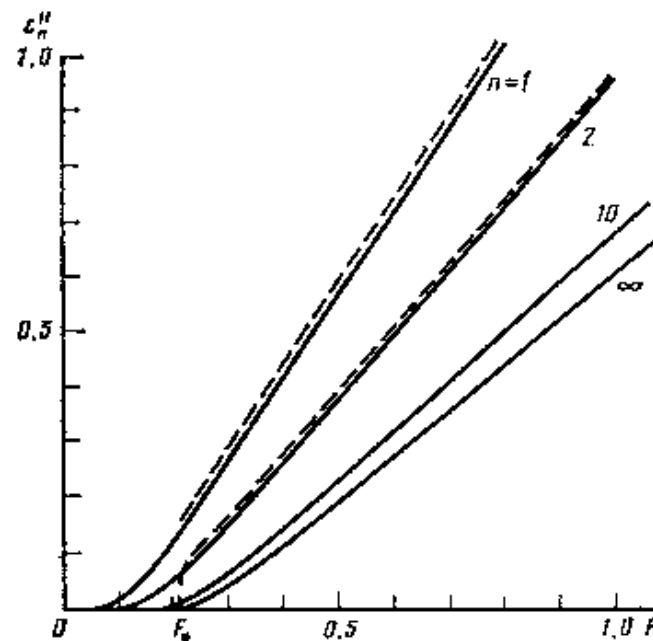
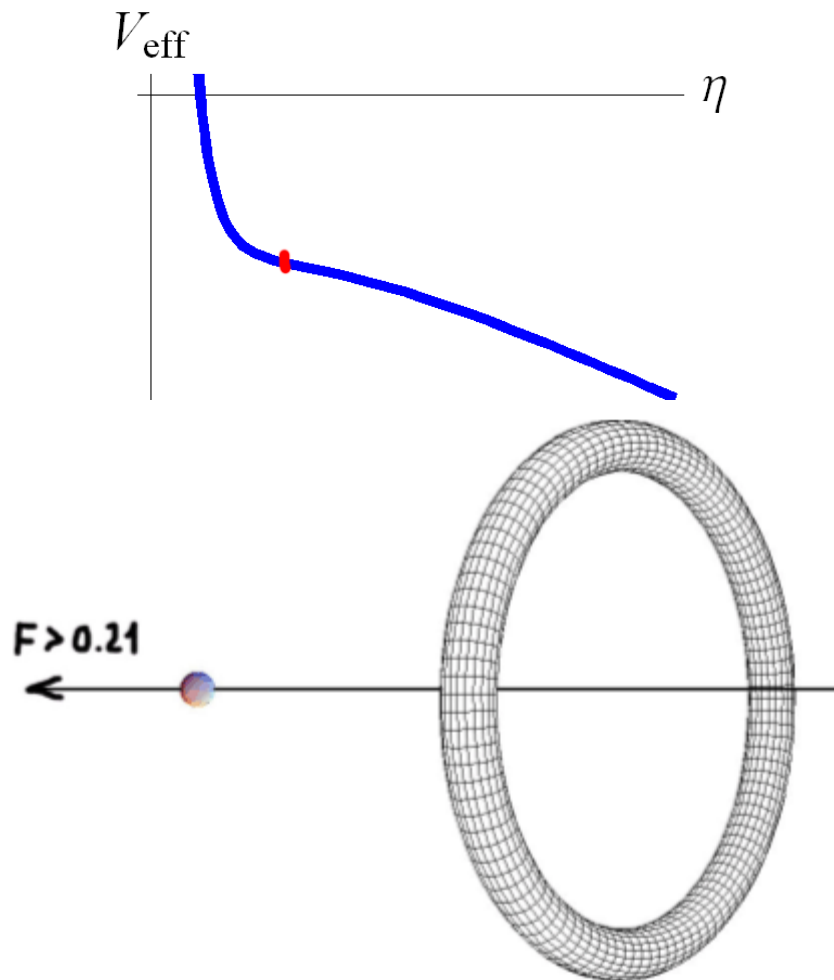
$F = 0$



$0 < F < 0.21$



Stark effect in strong field

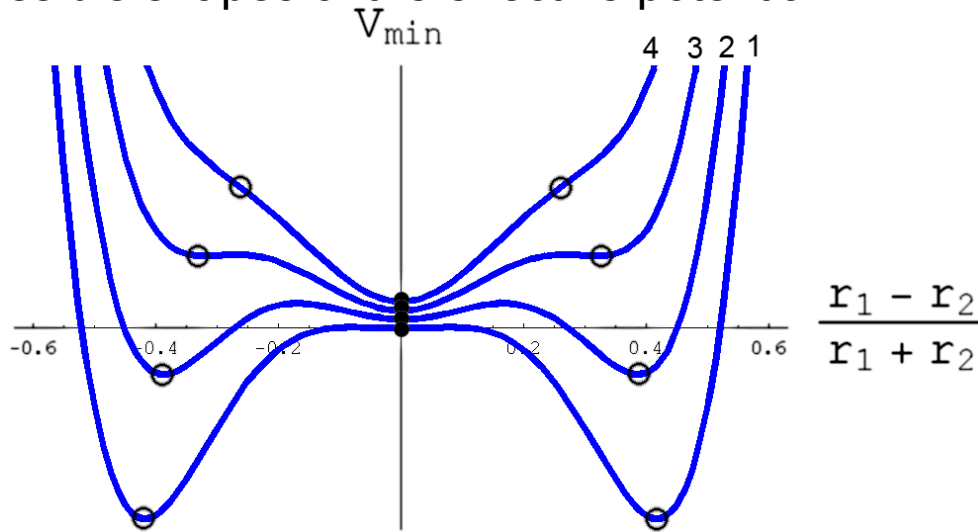


$\epsilon_n^n = n^2 \Gamma_n$ as a function of the external field for the $(0, 0, n-1)$ states.

Atom with variable nuclear charge.

Instability of molecules and a negative ion H^- at large D

Possible shapes of the effective potential

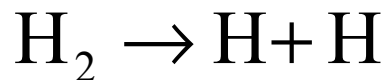
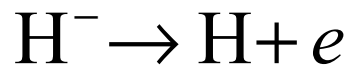


(1) $Z = 1.229$ (2) $Z = 1.232$ (3) $Z = 1.235$ (4) $Z = 1.238$

V_{\min} is the minimum of V_{eff} for the given value of the parameter of asymmetry,

$$\frac{r_1 - r_2}{r_1 + r_2}$$

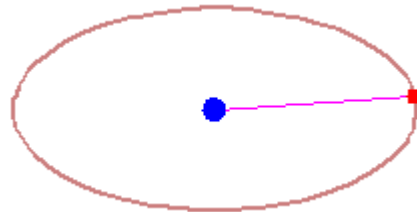
Curves for different values of Z are shifted along vertical axis for easier plotting.



Alternative scaling of the kinetic energy

Hydrogen atom

$$V_{\text{kin}} \sim \frac{1}{r^2}$$



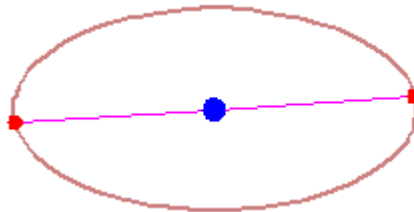
ground state

Helium atom

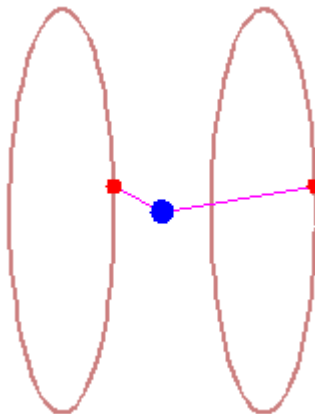
$$V_{\text{kin}} \sim \frac{1}{r_1^2} + \frac{1}{r_2^2}$$

instead of

$$V_{\text{kin}} \sim \frac{1}{\sin^2 \theta} \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right)$$

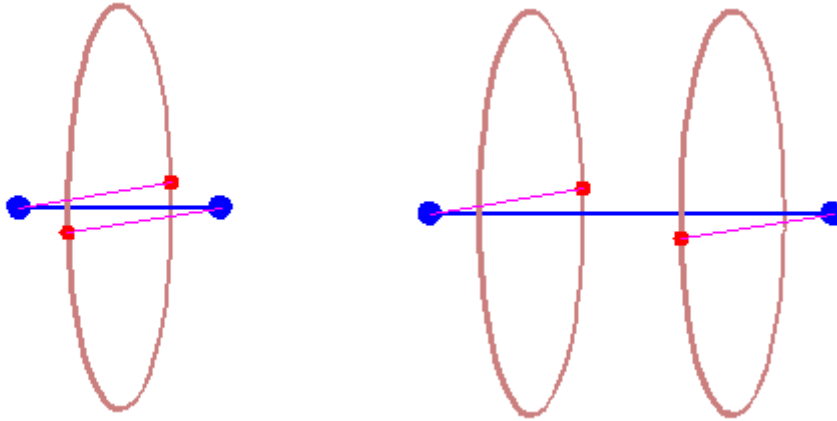


ground state

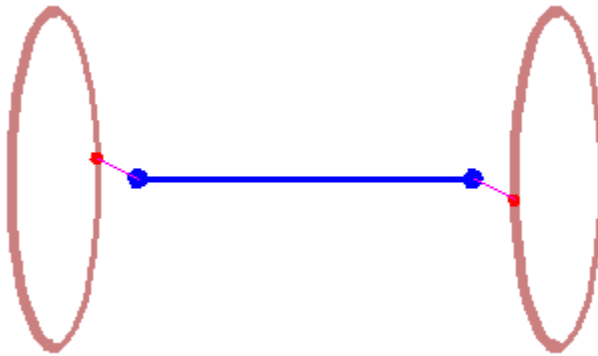


lowest triplet state

Hydrogen molecule

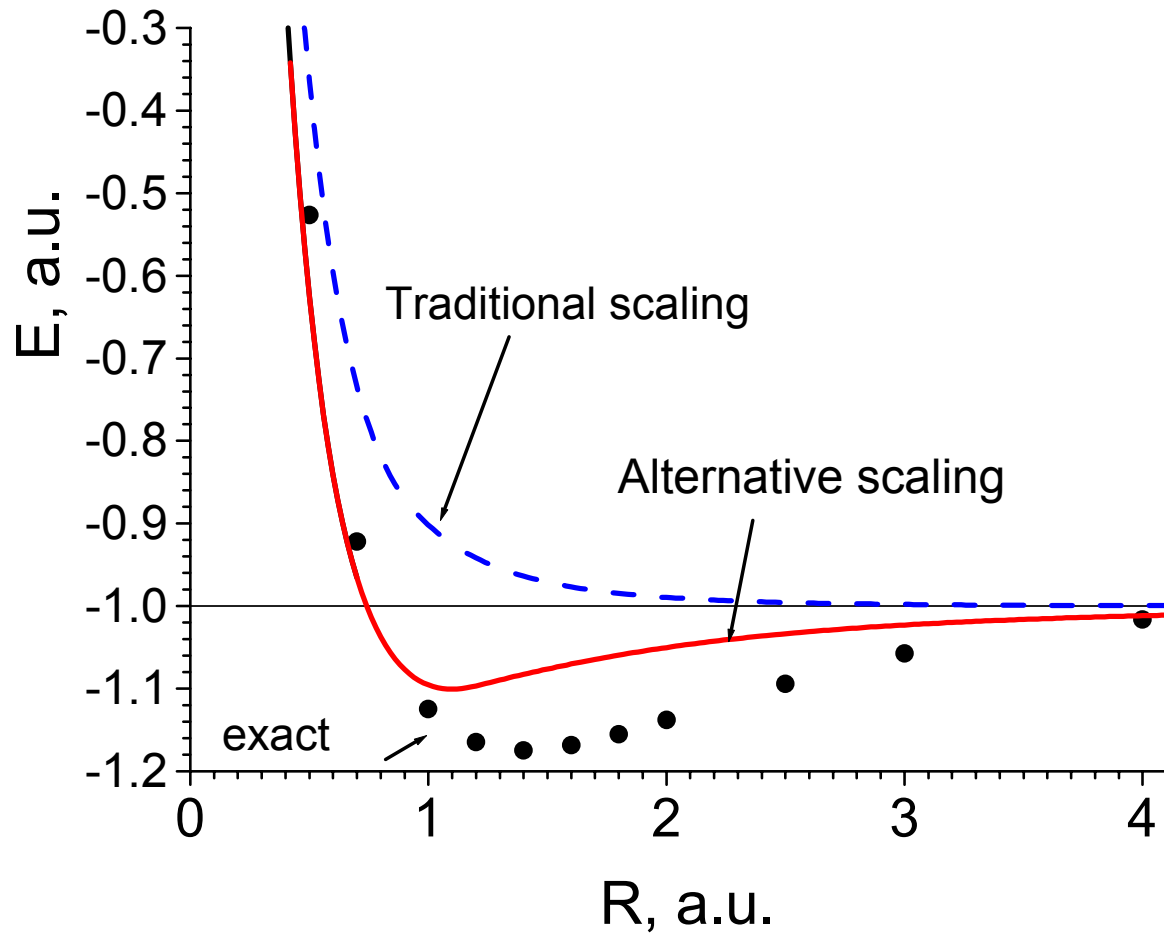


ground state

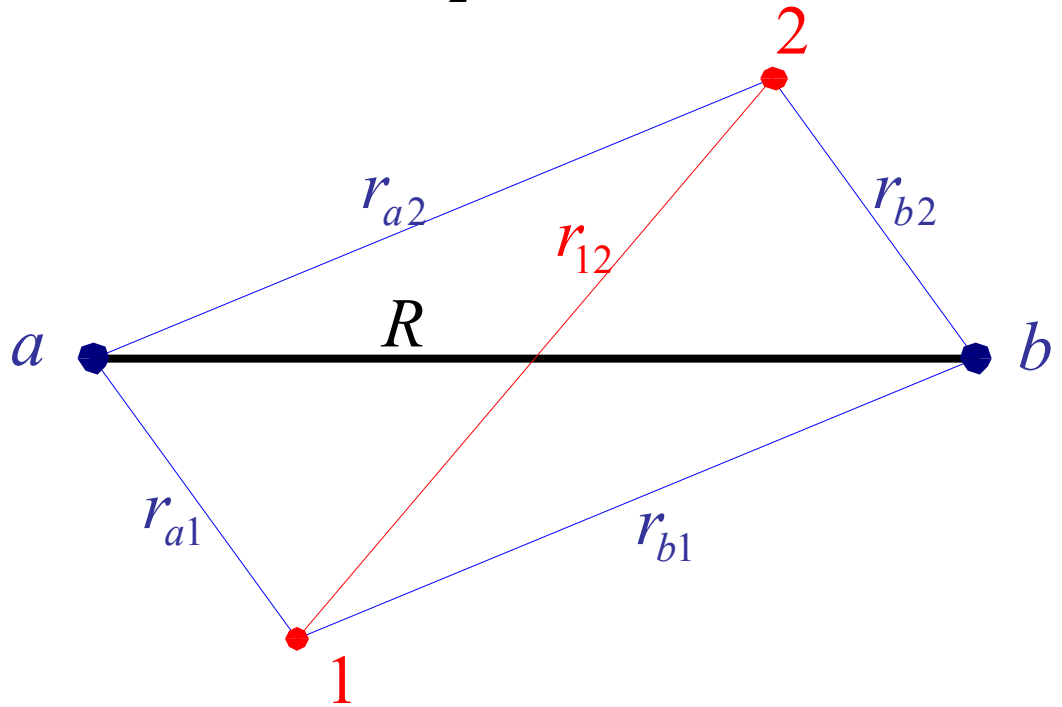


lowest triplet state

Results for H₂



Empirical effective potential for H₂



$$V_{\text{eff}} = V + T$$

$$V = \frac{1}{R} - \frac{1}{r_{a1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}}$$

True scaling,
or “quantization to the axis”

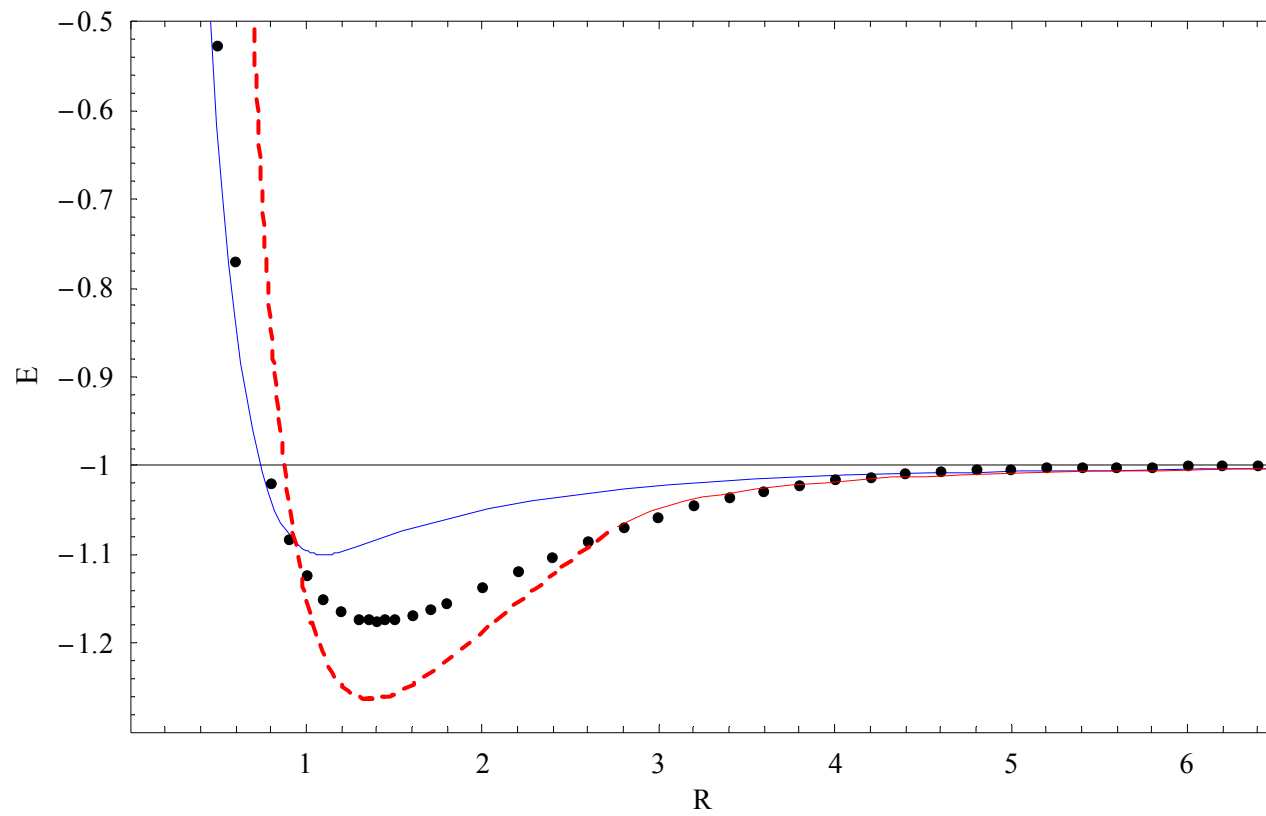
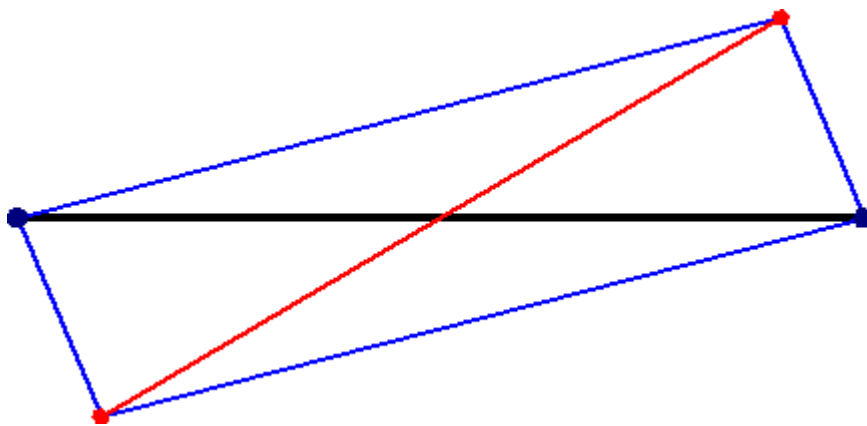
$$T = \frac{1}{2\rho_1^2} + \frac{1}{2\rho_2^2}$$

$$\tilde{V}_{\text{eff}} = V + \tilde{T}$$

$$\tilde{T} = \frac{1}{2r_{a1}^2} + \frac{1}{2r_{b2}^2}$$

Empirical effective potential,
or “quantization to the nearest
nucleus”

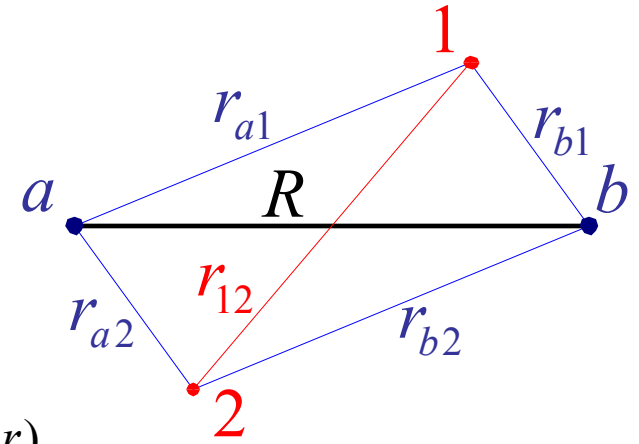
Results



Combining method of effective potential
with Heitler – London variational method
for H₂ molecule

$$E(R) = \min_r E_{\text{HL}}(r, R), \quad E_{\text{HL}}(r, R) = \frac{\langle \Psi_r | H | \Psi_r \rangle}{\langle \Psi_r | \Psi_r \rangle}$$

$$\Psi_r(\vec{r}_1, \vec{r}_2) = \exp(-r_{a1}/r) \exp(-r_{b2}/r) + \exp(-r_{b1}/r) \exp(-r_{a2}/r)$$

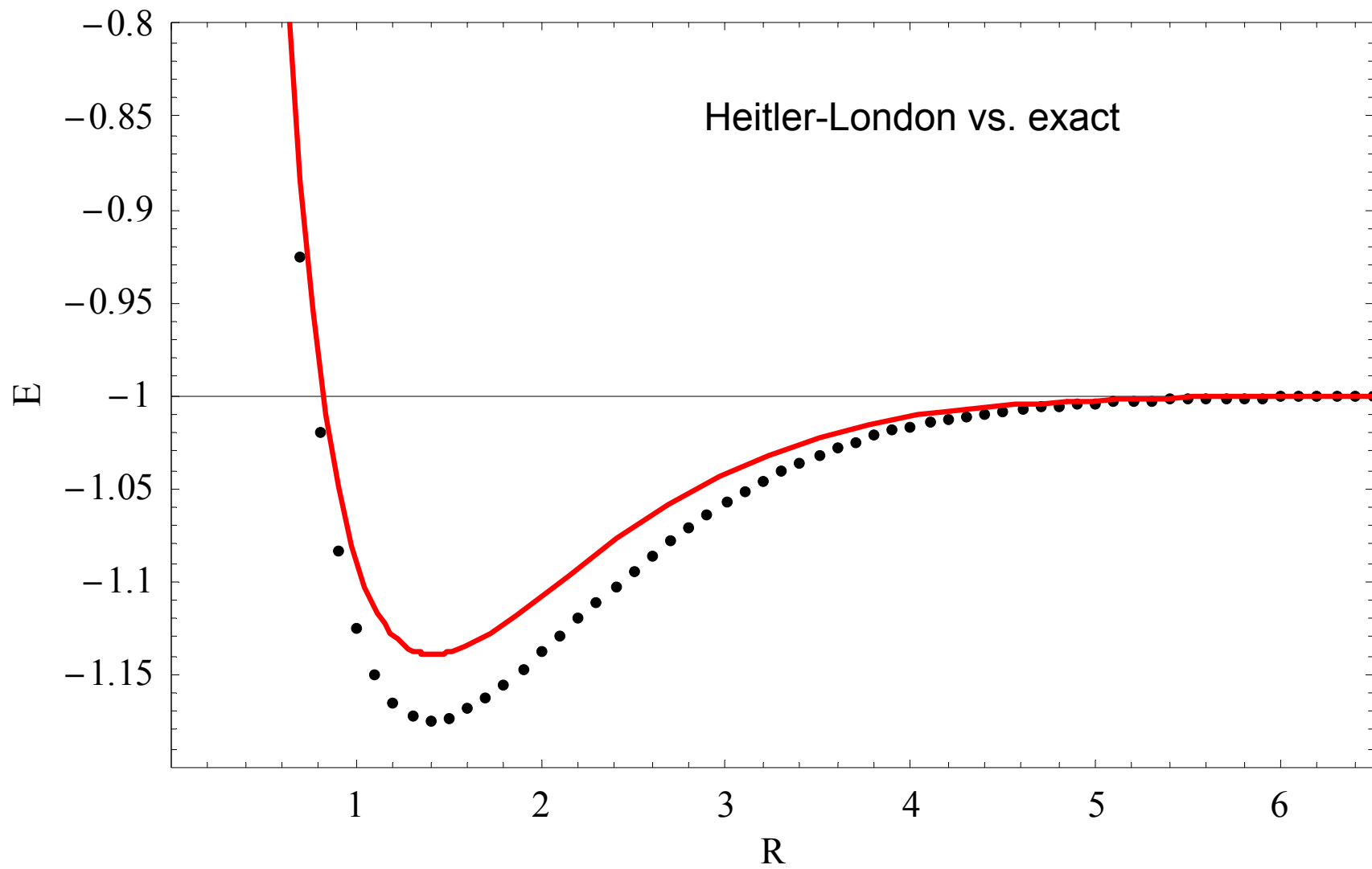


$$E_{\text{HL}}(r, R) = \underset{\substack{\uparrow \\ \text{electron} \\ \text{kinetic} \\ \text{energy}}}{T_{\text{HL}}(r, R)} + \underset{\substack{\uparrow \\ \text{interaction} \\ \text{between} \\ \text{electrons} \\ \text{and nuclei}}}{V_{\text{HL}}^{(1)}(r, R)} + \underset{\substack{\uparrow \\ \text{interaction} \\ \text{between} \\ \text{electrons}}}{V_{\text{HL}}^{(2)}(r, R)} + \frac{1}{R}$$

$$\left\langle \frac{1}{r_{12}} \right\rangle$$

$$T_{\text{HL}}(r, R) = \frac{9 \left(1 + e^{\frac{2R}{r}}\right) r^4 + 18Rr^3 + 9R^2r^2 - R^4}{9e^{\frac{2R}{r}}r^6 + (3r^2 + 3Rr + R^2)^2 r^2} \quad V_{\text{HL}}^{(1)}(r, R) = -\frac{6(r+R) \left[3 \left(-1 + e^{\frac{2R}{r}}\right) r^3 + 6Rr^2 + 6R^2r + 2R^3\right]}{R \left[9e^{\frac{2R}{r}}r^4 + (3r^2 + 3Rr + R^2)^2\right]}$$

$$V_{\text{HL}}^{(2)}(r, R) = 3 \left[12 \left(-5 + 5e^{\frac{2R}{r}} + 6\gamma\right) r^4 + 9(-5 + 16\gamma)Rr^3 + 6(-19 + 20\gamma)R^2r^2 \right. \\ \left. + 2(-23 + 24\gamma)R^3r + 4(-1 + 2\gamma)R^4 + 8e^{\frac{4R}{r}} (3r^2 - 3Rr + R^2)^2 \text{Ei} \left(-\frac{4R}{r}\right) \right. \\ \left. - 16e^{\frac{2R}{r}} (9r^4 - 3R^2r^2 + R^4) \text{Ei} \left(-\frac{2R}{r}\right) + 8(3r^2 + 3Rr + R^2)^2 \log \left(\frac{R}{r}\right) \right] \\ \times \left\{ 20R \left[9e^{\frac{2R}{r}}r^4 + (3r^2 + 3Rr + R^2)^2 \right] \right\}^{-1} . \quad ($$

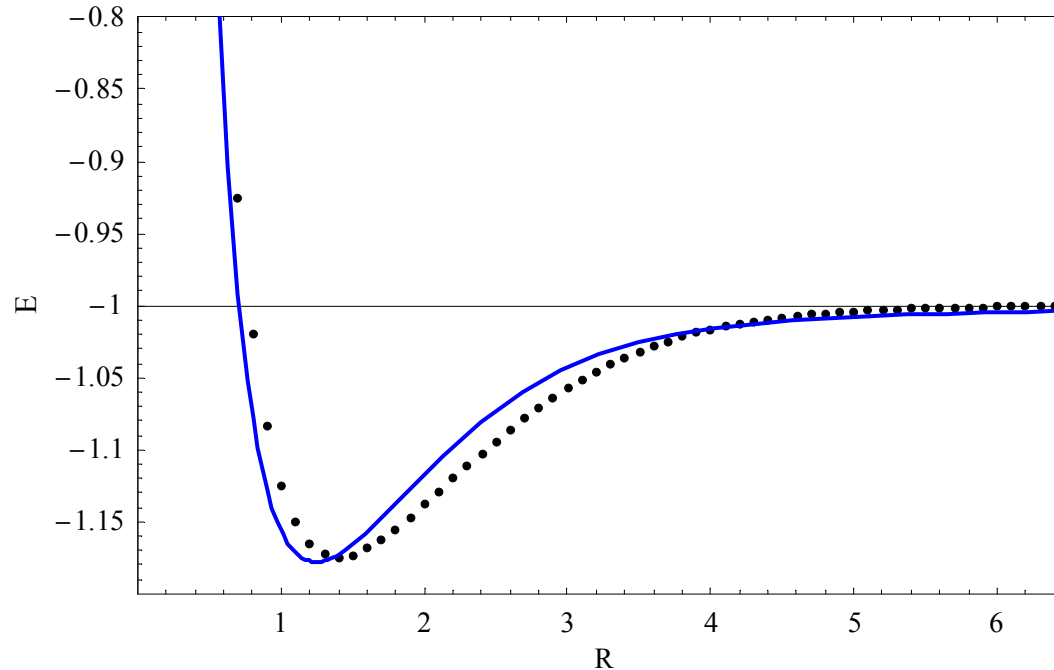
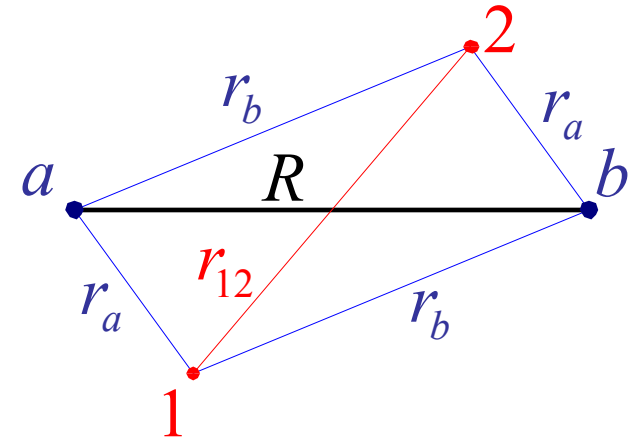


Hybrid HL-B model

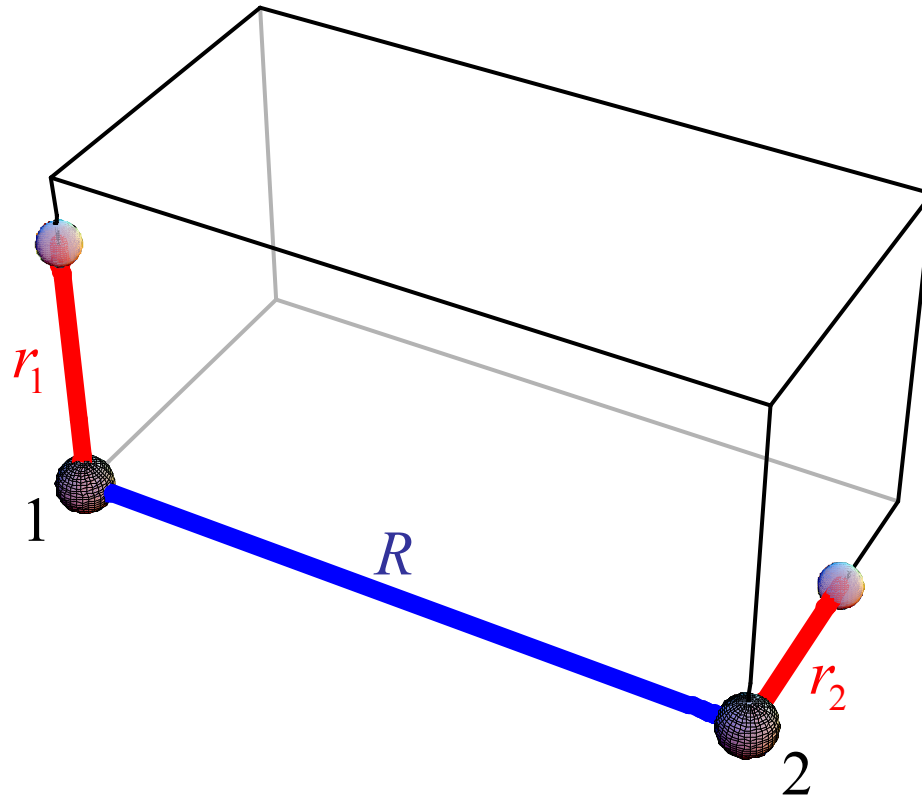
$$E(r_a, R) = T_{\text{HL}}(r_a, R) + V_{\text{HL}}^{(1)}(r_a, R) + \frac{1}{r_{12}} + \frac{1}{R}$$

Constraint

$$T_{\text{HL}}(r_a, R) + V_{\text{HL}}^{(1)}(r_a, R) = \left(\frac{1}{2r_a^2} - \frac{1}{r_a} - \frac{1}{r_b} \right) \times 2$$



Bohr + Hartree – Fock + variational



$$E(r_1, r_2, R) = T(r_1, r_2, R)$$

$$+ \frac{1}{R} - \frac{1}{r_1} - \frac{1}{r_2} - \frac{1}{\sqrt{R^2 + r_1^2}} - \frac{1}{\sqrt{R^2 + r_2^2}} + \frac{1}{\sqrt{R^2 + r_1^2 + r_2^2}}$$

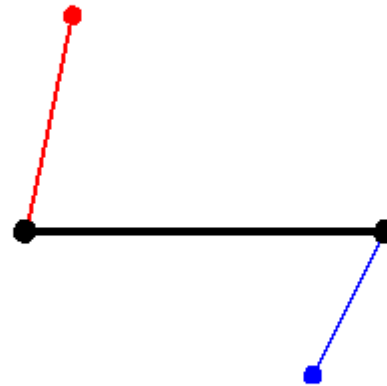
Kinetic energy

$$T(r_1, r_2, R) = \left\langle \Psi_{r_1, r_2} \left| \vec{\nabla}_1^2 + \vec{\nabla}_2^2 \right| \Psi_{r_1, r_2} \right\rangle$$

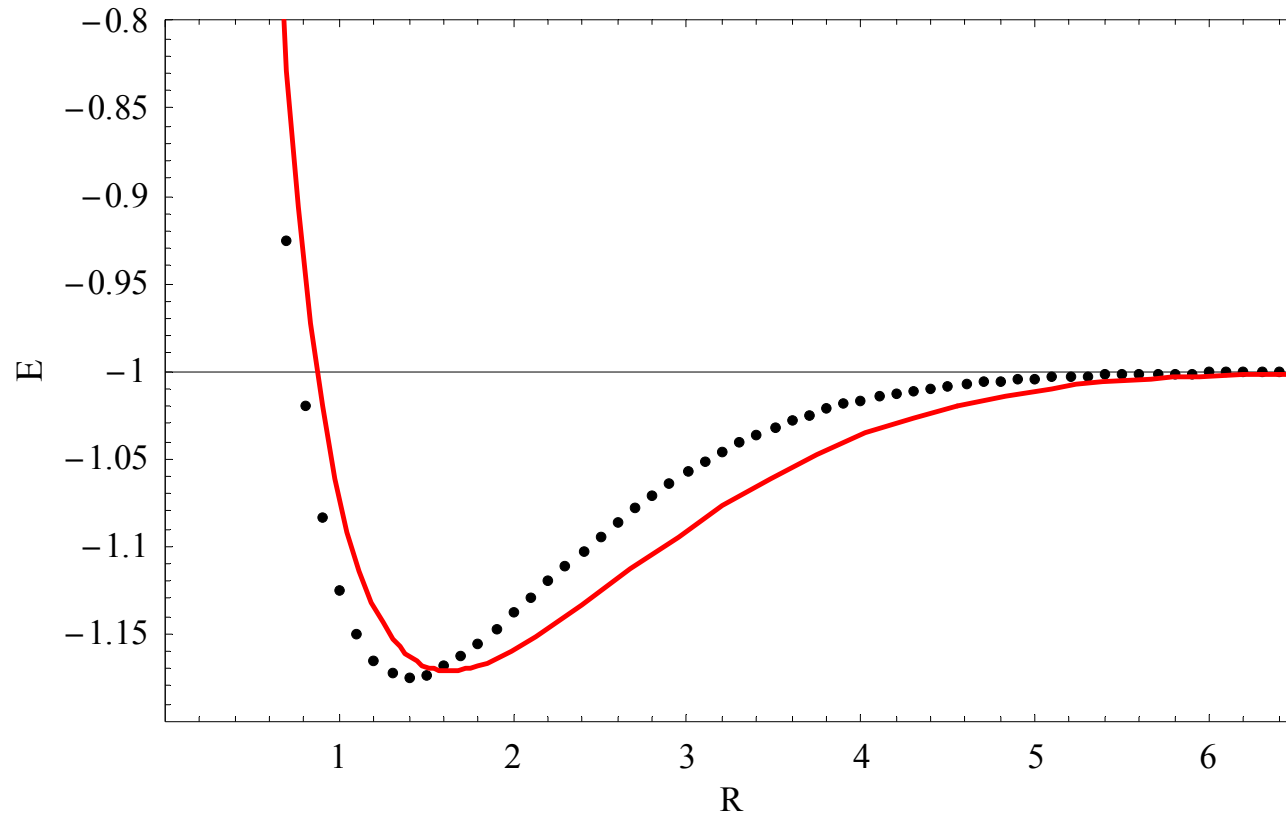
$$\Psi_{r_1, r_2}(\vec{r}_1, \vec{r}_2) = \exp(-r_{a1}/r_1) \exp(-r_{b2}/r_2) + \exp(-r_{b1}/r_2) \exp(-r_{a2}/r_1)$$

$$T(r_1, r_2, R) = \frac{1}{6} \left(-\frac{32(r_1^2 + r_2^2)}{r_1^4 + 14r_2^2 r_1^2 + r_2^4} + \frac{32}{r_1^2 + 6r_2 r_1 + r_2^2} + \frac{3}{r_1^2} + \frac{3}{r_2^2} \right)$$

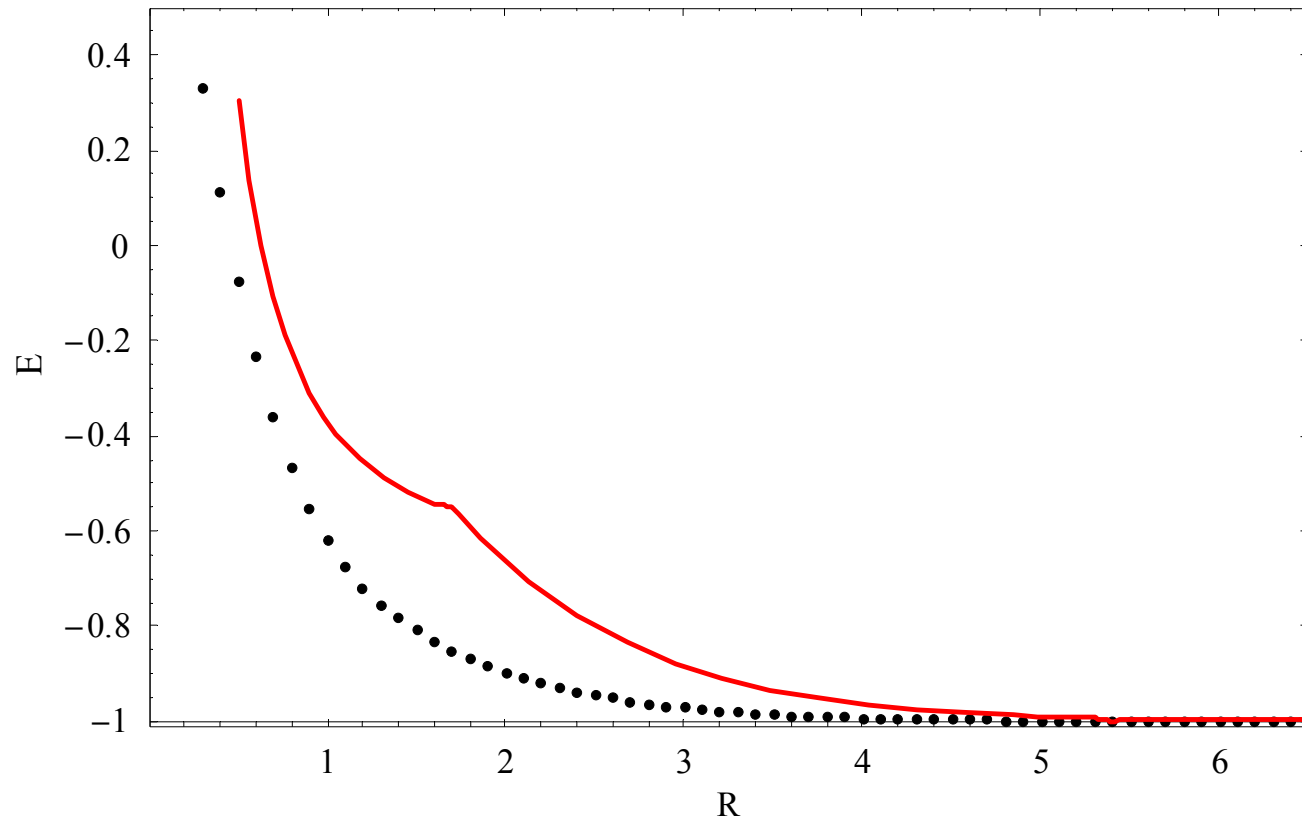
(This expression is given for $R=0$. For arbitrary R it is more lengthy)



Results for the ground state



Results for the lowest triplet state



Method of effective potential
(nearest-nucleus quantization)
for many-electron molecules

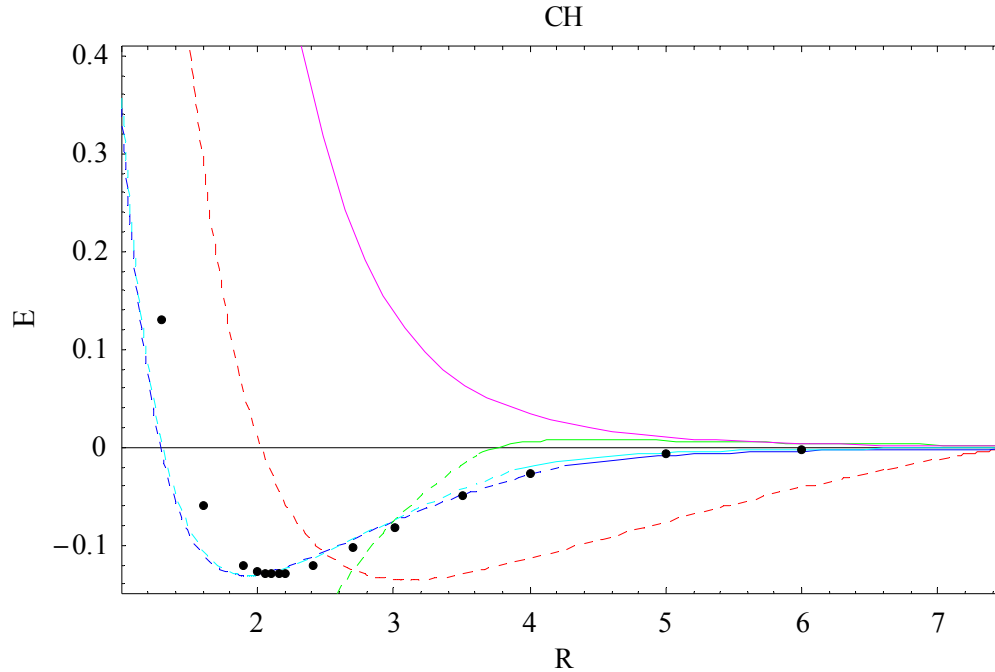
$$W(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = V + T$$

$$T(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_{i=1}^N \frac{n_i^2}{2|\vec{r}_i - \vec{R}_{n_i}|^2}$$

$$E = \min_{\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N} W(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

Results for CH molecule

$N = 5$



Dots – exact

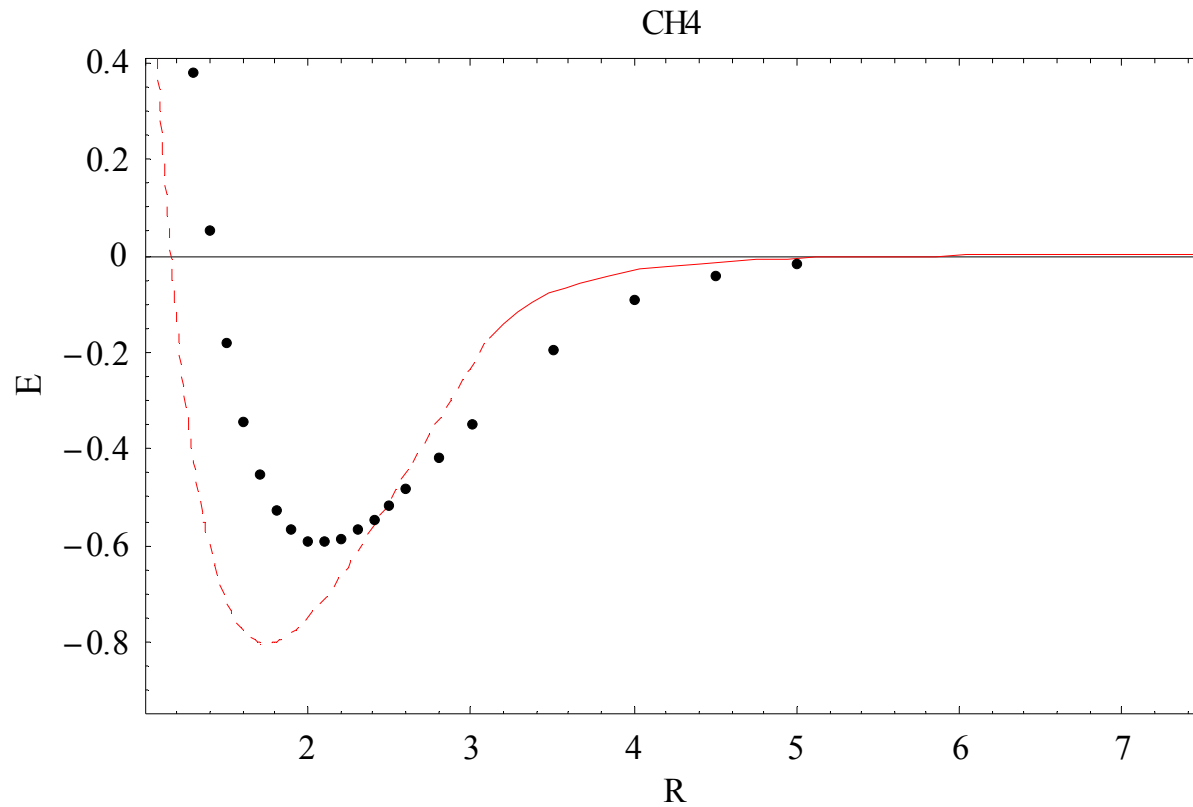
Red line - linear configuration

(unstable for $R < 7.2$)

Blue and green lines - planar configurations

Cyan and magenta lines - 3-dimensional
tetrahedral configurations

Results for CH₄ molecule $N = 8$



Totally symmetric
tetrahedron configuration of
electrons

Conclusions

- For all molecules, the effective potential in the infinite- D limit does not possess a minimum; a molecule is unstable in respect to dissociation.
- A modified dimensional scaling allows to reproduce binding energies of molecules.
- Minimization of a modified effective potential gives surprisingly accurate results for a hydrogen molecule, but it may fail for other molecules.
- For the first time, the method was used for molecules with up to eight active electrons.