MOLECULAR SHAPES
AND SOME OTHER MASS-DEPENDENT EFFECTS

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SEPARABILITY

Theory of many-body systems, in particular quantum chemistry, molecular physics, atomic physics, is based on approximations which impose separability to non-separable multi-dimensional Schrödinger equations.

Examples:
Hartree-Fock model, Born-Oppenheimer approximation.

In the resulting models, some features of non-separable effects related to interactions are obscured by the enforced separability.

Examples:
Electron correlation, non-adiabatic effects.

Exactly separable models of interacting particles are of particular interest in this context.

BORN-OPPENHEIMER MODEL

- The nuclei are not QM particles but classical sources of the external potential.
- Their fixed network is in rest in the laboratory reference frame.
- The shape of a molecule is determined by an arbitrarily prearranged distribution of the nuclei. This distribution may coincide with the the maxima in the nuclear charge/mass density derived from experimental data.
- By probing energy values for different nuclear distributions one can find minima in the potential energy hypersurface
- It is irrelevant whether the nuclei are defined as point charges or their spatial shapes are taken into account.

NON-BORN-OPPENHEIMER MOLECULE

- Fundamental chemical notions (e.g. potential energy surface or a molecular bond length) are inherent to the BO model.
- A non-BO Hamiltonian of a free molecule is spherically symmetric.
- Tracing the mass-dependence of the density distributions helps to understand how the molecular shape emerges from spherically-symmetric non-BO objects.
- The transition between a shapeless structure of two electrons and two positrons and a hydrogen molecule with a specific bond length implies a change of the way the molecule is described - separate treatment of electronic, vibrational and rotational degrees of freedom is specific for the BO model.

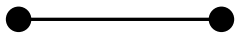
THE REFERENCE FRAME

- The form of the function which describes the mass distribution i.e. the shape of the molecule, depends on the choice of the reference frame.
- This problem is also known in the celectial mechanics – the difference between the Ptolomean and the Copernican representations of the Solar System stems from the choice of different reference points.
- In the BO model the network of fixed nuclei defines the reference frame.
- In non-BO description the shape of an N-body system is described by $3N-6$ 'shape coordinates' defined in the so called 'body frame'.

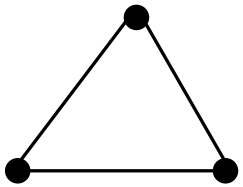
CONSTANTS OF THE MOTION

- For an isolated system of N bodies, the total momentum and total angular momentum are integrals of the motion.
- Consequently, the coordinates of the mass center and three global rotations can be separated,
- The total wave function is expressed as a linear combination of products of explicitly defined, universal functions of six collective variables and of unknown, system-specific, functions of $3N-6$ internal variables – “shape coordinates".

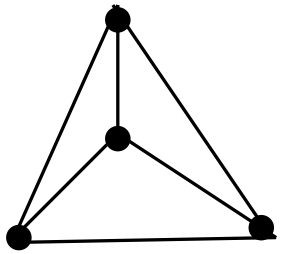
SHAPE COORDINATES



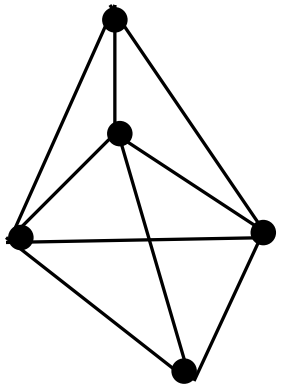
N=2, 3N−5=1



N=3, 3N−6=3



N=4, 3N−6=6



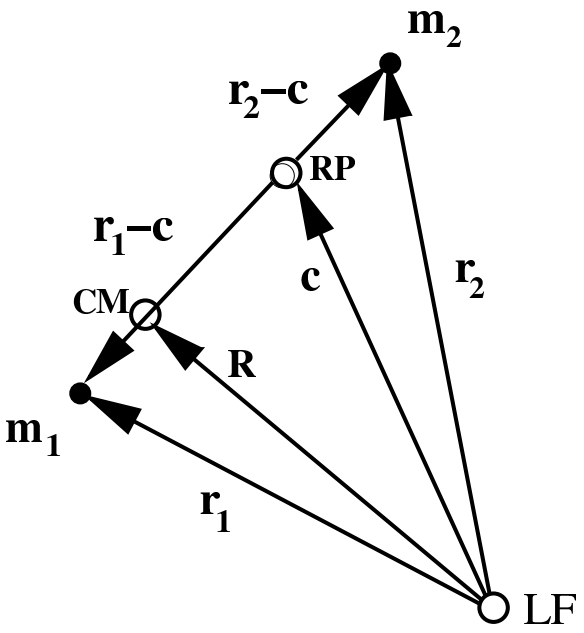
N=5, 3N−6=9

The number of independent coordinates of the particles is equal to the number of degrees of freedom, i.e. to $(3N-6)$.

These coordinates specify the "shape".

The total number of interparticle distances, $N(N-1)/2$, is larger than $(3N-6)$ if $N>4$.
Only $(3N-6)$ of them are independent.

THE REFERENCE FRAME – TWO PARTICLES



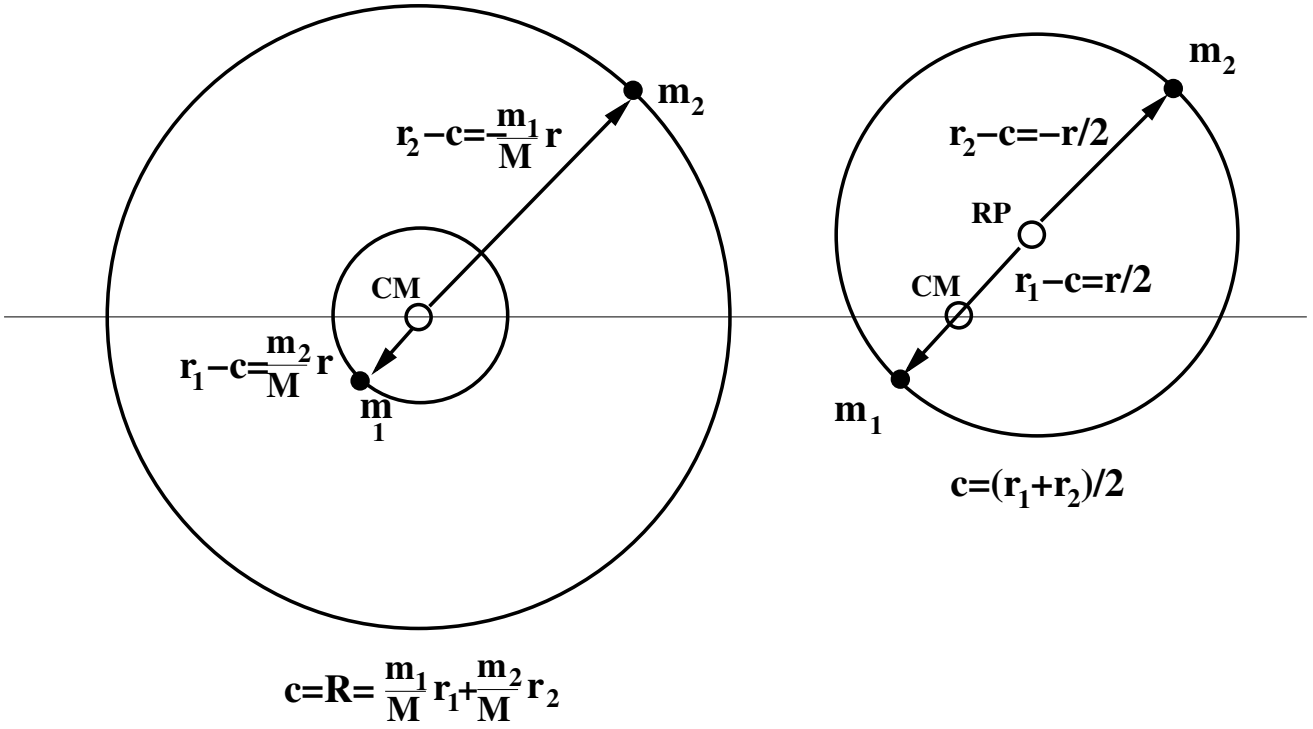
LF - laboratory frame;
RP - reference point;
CM - center of mass

Not all legitimate reference frames (RF) approach the Born-Oppenheimer one when the mass of one of the particles approaches infinity – for example, the one centered in the middle of the distance between the particles.

Commonly used is the center-of-mass RF.

J. Karwowski, "Some remarks on the mass density distribution", Croat. Chem. Acta 86 (2013) 531-539 (Douglas Klein Issue)

MOTION OF TWO PARTICLES

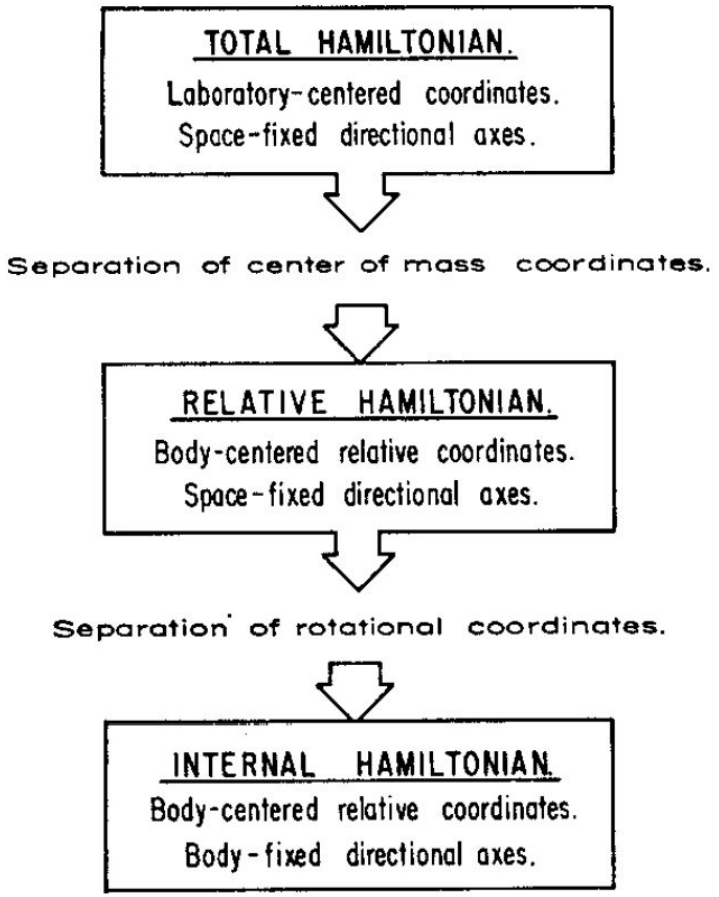


The maximum probability radii in the ground state.

Left panel – center of mass RF.

Right panel – the RF origin is in the middle of the distance between the particles.

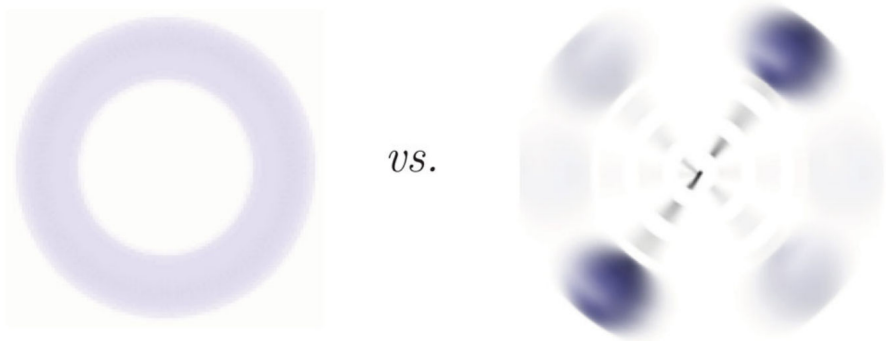
CONSTRUCTION OF THE BODY-FRAME HAMILTONIAN



R. T. Pack and J. O. Hirschfelder, "Separation of rotational coordinates from the N-electron diatomic Schrödinger equation" J. Chem. Phys. 49 (1968) 4009.

A.V. Meremianin, J.S. Briggs, "The irreducible tensor approach in the separation of collective angles in the quantum N -body problem", Physics Reports 384 (2003) 121 – 195

TWO PARTICLES

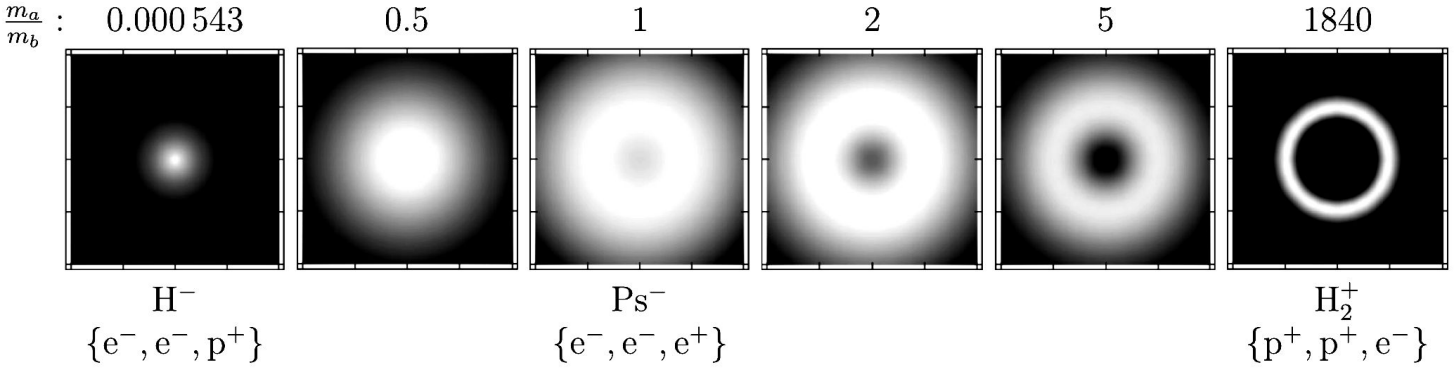


Left: In the CM **space-fixed** reference frame represented using the "**Relative Hamiltonian**".

Right: In the CM **body-fixed** reference frame represented using the "**Internal Hamiltonian**".

MASS DENSITY

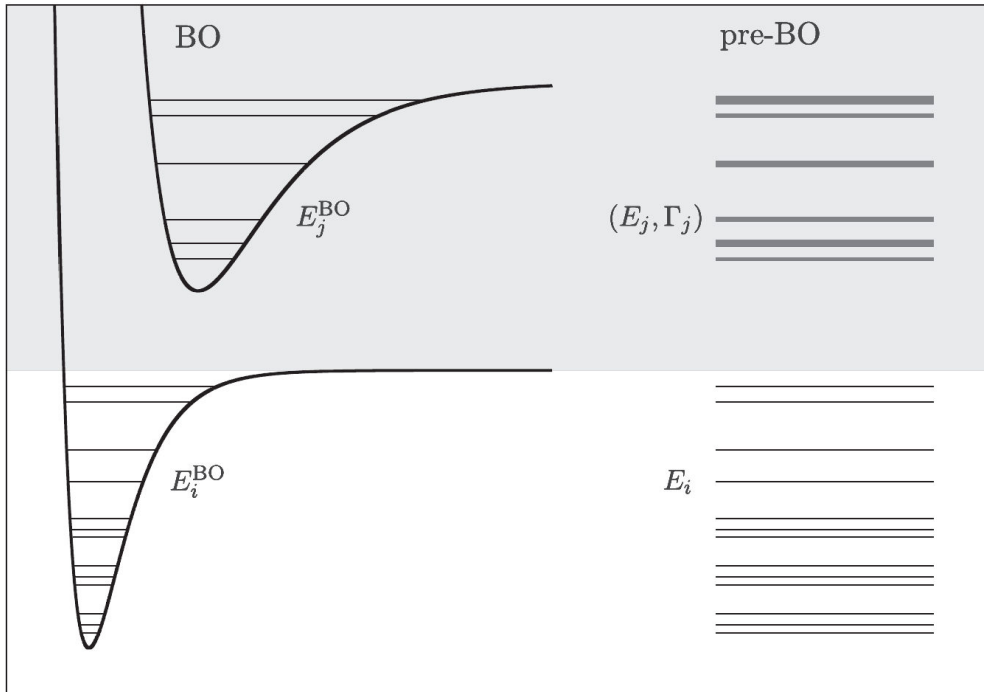
Three-particle systems: H^- ion and H_2^+ molecule.



Transition of the ground-state mass density, from H^- to H_2^+.
The space-fixed reference frame - the "Relative Hamiltonian".

Edit Mátyus, "Pre-Born-Oppenheimer molecular structure theory",
Mol. Phys. 117 (2019) 590-609.

MOLECULAR BO AND PRE-BO SPECTRA



Molecular energy levels:
BO – left; pre-BO – right.
Center-of-mass (CM) reference frame.

In both electronic states the rovibratiotional BO states are bound.

In the pre-BO model all states linked to the excited electronic state are resonances.

In the laboratry reference frame with no separation of the free motion of CM, all discrete states are degenerate with the CM continuum states.

THREE-PARTICLE SYSTEMS

Density of mass operator:

$$\hat{\rho}(r;r_1,r_2,r_3) = m_1\,\delta(r-r_1) + m_2\,\delta(r-r_2) + m_3\,\delta(r-r_3)\,.$$

Density of mass:

$$\rho(r) = \langle \Psi(r_1,r_2,r_3)|\hat{\rho}(r;r_1,r_2,r_3)|\Psi(r_1,r_2,r_3)\rangle$$

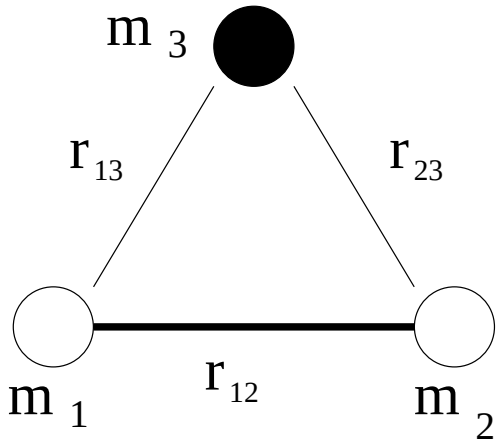
Density of mass of particle $\{3\}$:

$$\begin{aligned}\rho(r)_{m_3} &= m_3\langle \Psi(r_1,r_2,r_3)|\delta(r-r_3)|\Psi(r_1,r_2,r_3)\rangle_{1,2} \\ &= m_3\langle \Xi(r_3)|\delta(r-r_3)|\Xi(r_3)\rangle = m_3\,|\Xi(r)|^2\end{aligned}$$

A SEPARABLE MODEL OF N INTERACTING PARTICLES

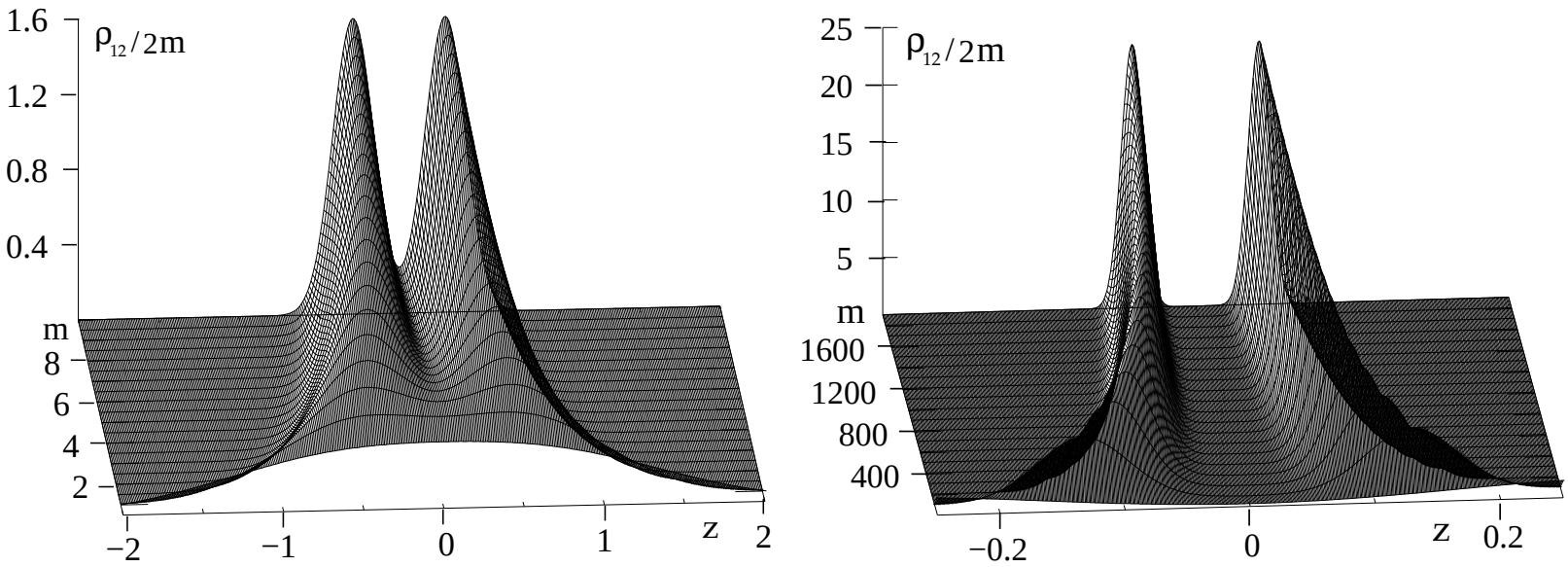
A system of K disjoint pairs of particles interatcing by two-body potentials and coupled by Hooke forces is separable.

Example: $N = 3$, $-$ Hookean H_2^+ , Ps^- , He , etc



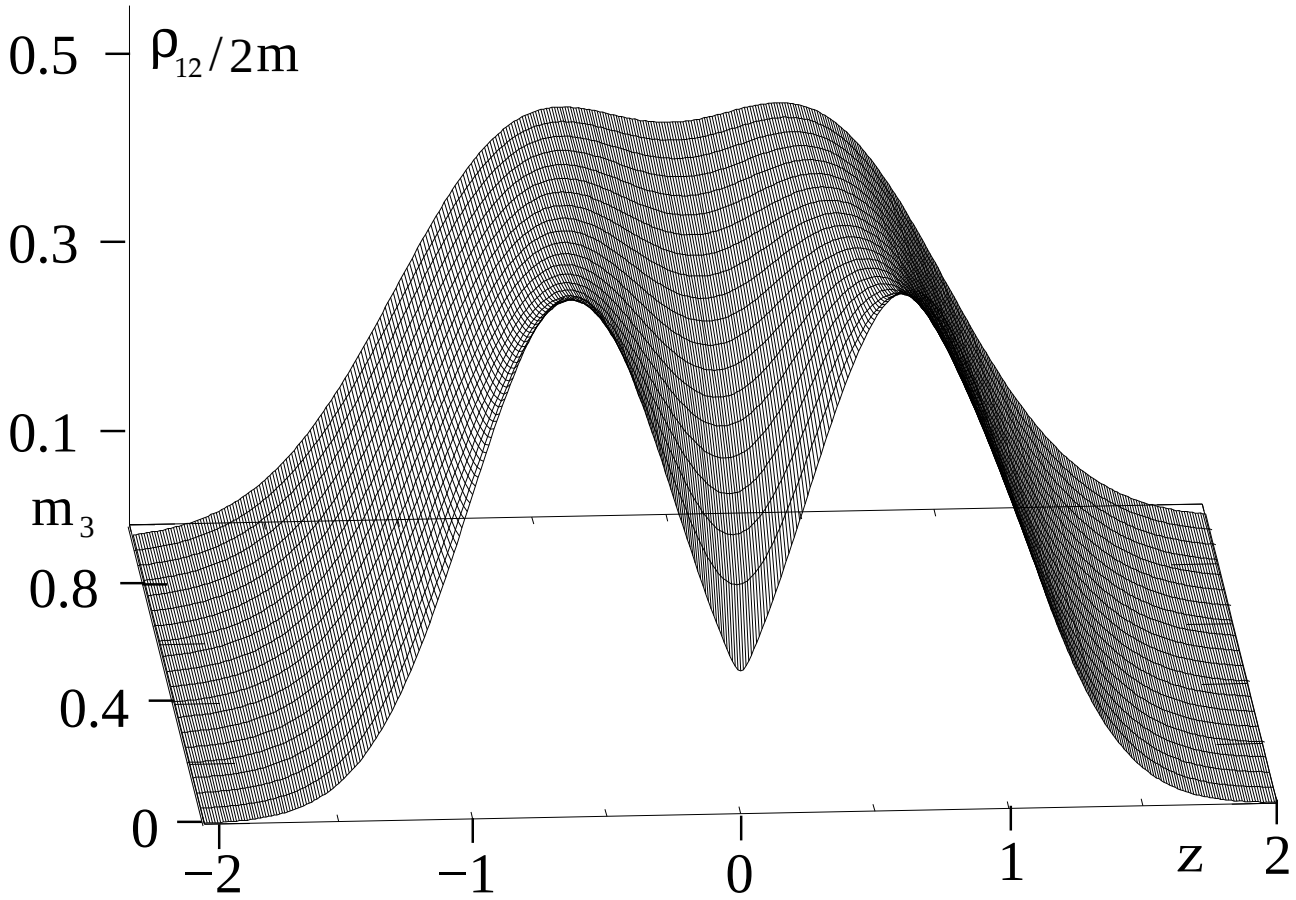
$$V_{12} = V(r_{12}), \quad V_{13} \sim r_{13}^2, \quad V_{23} \sim r_{23}^2.$$

MOLECULAR SHAPES



Distribution of normalized to 1 density of mass of particles $\{1\}$ and $\{2\}$ as a function of $m = m_1 = m_2$. $m_3 = 1$, $\mathrm{V} = 1/r_{12}$

J. Karwowski, "Three-particle non-Born-Oppenheimer systems", 503-518, in: R. Carbó-Dorca, T. Chakraborty (ed), "Theoretical and Quantum Chemistry at the Dawn of the 21st Century", Apple Academic Press, 2018.



Distribution of normalized to 1 density of mass of particles $\{1\}$ and $\{2\}$ as a function of m_3.

$m_1 = m_2 = 1$, $V(r_{12}) = 1/r_{12}$

STRUCTURE OF H_2^+

Length unit (Bohr radius):

$$a_0 = \frac{\hbar^2}{m\,e^2}$$

Energy unit (hartree):

$$E_h = \frac{m\,e^4}{\hbar^2}$$

If electron is replaced by muon, $m_\mathrm{e} \Rightarrow m_\mu = 207\,m_\mathrm{e}$, the length decreases and the energy increases **207 times**.

The muonic analog of H_2^+ is ~ 207 times smaller and its binding energy ~ 207 times larger compared to H_2^+.

The “effective nuclear mass" is 207 times smaller than in the electronic case – the nuclear density is more diffuse.

MUON CATALYSED FUSION

There were some hopes that this phenomenon may open a way to self-supporting muon catalyzed fusion with $DT\mu$ molecules – the probability of fusion strongly depends on the overlap of the nuclear densities.

The basic chain of reactions:

$$(DT\mu)^+ \rightarrow {}^4He^{2+} + \mu^- + n + 18MeV,$$
$$\mu^- + (D_2, DT, T_2) \rightarrow (T\mu) + \cdots,$$
$$(T\mu) + (D_2, DT, T_2) \rightarrow (DT\mu) + \cdots,$$

The fusion has been observed, but the number of muons produced is too small for the reaction being self-supported.

W. H. Breunlich et al., "Muon-catalyzed fusion", Ann. Rev. Nucl. Part. Sci. **39** (1989) 311.

PHENOMENA RELATED TO NON-B.O. DESCRIPTION

1. Stability conditions
2. Efimov effect and Borromean system
3. Molecular shapes

STABILITY OF THREE-PARTICLE SYSTEMS

$q_2 = q_3 = -q_1 = \pm 1$ bound by Coulomb forces

$$Ps^- = e^+ e^- e^- \quad - \quad \text{stable}$$
$$H_2^+ = e^- p\, p \quad - \quad \text{stable}$$
$$H^- = p\, e^- e^- \quad - \quad \text{stable}$$
$$p\, \mu^- e^- \quad - \quad \text{unstable}$$

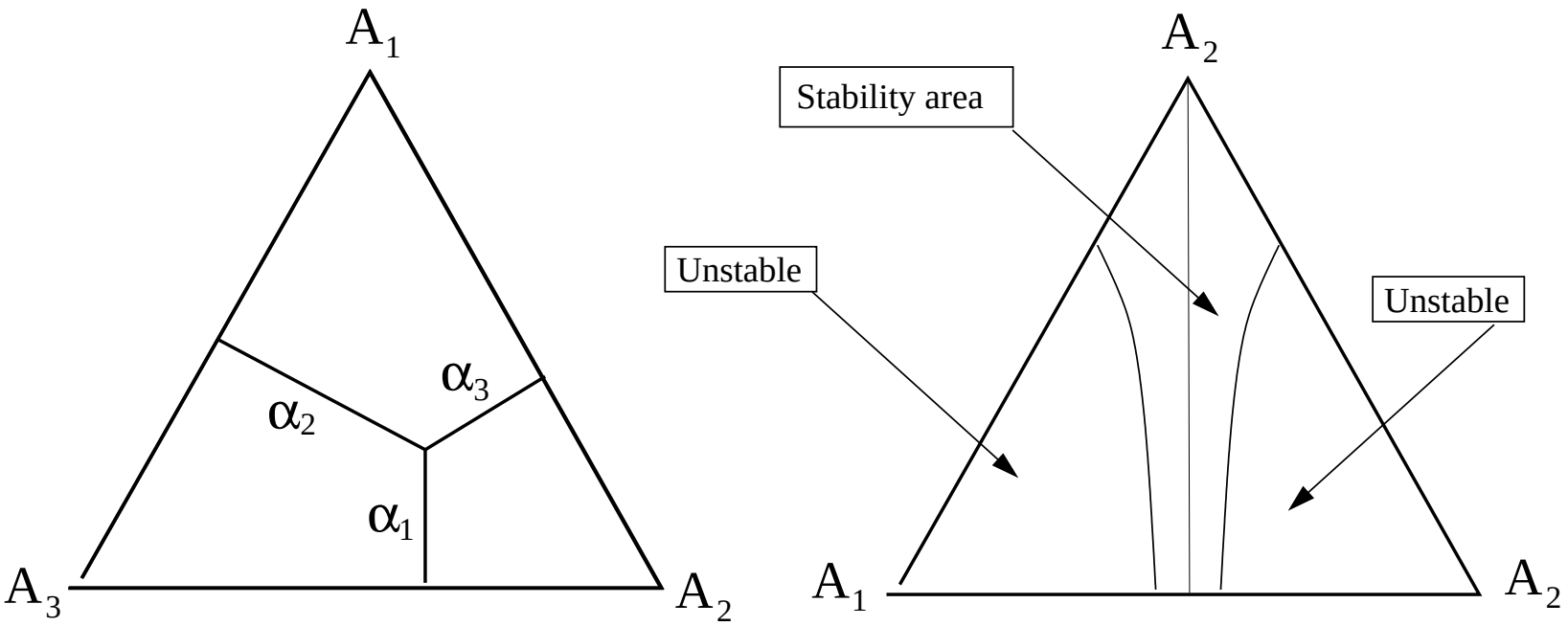
Let

$$\alpha_i = \frac{1/m_i}{1/m_1 + 1/m_2 + 1/m_3}, \quad \alpha_1 + \alpha_2 + \alpha_3 = 1.$$

Rule: A system is stable if $\alpha_2 \sim \alpha_3$.

Every symmetric system $(m_2 = m_3)$ is stable

STABILITY TRIANGLE



S. Kais, Q. Shi, "Quantum criticality and stability of three-body Coulomb systems", Phys. Rev. A 62 (2000) 060502.

FINAL REMARKS

Bound systems of particles, when described without imposing Born-Oppenheimer approximation, exhibit many interesting and unexpected features. Working with relatively strongly bound systems composed of electrons and thousands times more massive nuclei, for which the Born-Oppenheimer model is highly accurate, we frequently forget about the non-intuitive and full of surprizing phenomena the non-Born-Oppenheimer world.