

Some Remarks on the Mass Density Distribution[†]

Jacek Karwowski

*Institute of Physics, Nicolaus Copernicus University, Grudziadzke 5, PL-87-100 Toruń, Poland
 (E-mail: jka@fizyka.umk.pl)*

RECEIVED JUNE 25, 2013; REVISED AUGUST 26, 2013; ACCEPTED AUGUST 27, 2013

Abstract. The distribution of the density of mass in several simple model systems is analyzed. In particular, the relation between the localization of a particle and its mass is studied in detail. The dependence of the function describing mass density distribution on the choice of the reference point and, in this context, the process of emerging the molecular shape as a function of masses of the constituent particles is briefly discussed. (doi: [10.5562/cca2312](https://doi.org/10.5562/cca2312))

Keywords: Schrödinger equation, density of mass, molecular shape, reference point, Born-Oppenheimer approximation

INTRODUCTION

In the Born-Oppenheimer (BO) approximation the nuclei are treated as sources of the external potential. Their network is fixed and, as long as we are interested in the electronic structure, may be, without any loss of generality, assumed to be in rest in the laboratory reference frame. The distribution of the BO nuclei in the reference frame determines the shape of a molecule. In this context it is irrelevant whether the nuclei are defined as point charges or their spatial shapes are taken into account. This influences the form of the nuclear potential but does not change the basic assumption about strict, prearranged, localization of the nuclei. A very complete review on finite nuclear charge density distributions has been published a decade ago by Andrae.¹ An interesting idea of introducing softened nuclear potentials, in which charge density extends far beyond the limits determined by the nuclear radii, has been recently presented by Besalú and Carbó-Dorca.²

In order to treat all particles forming an atom or a molecule on the same level, one has to abandon the BO approximation. Let us note that the most fundamental chemical notions like potential energy surface or geometry of a molecule, are inherent in the BO model.³ A non-BO Hamiltonian of a free molecule is always spherically symmetric. The transition between a shapeless structure composed of, say, two electrons and two positrons, and a hydrogen molecule with a specific bond length is not only a consequence of changing masses of the particles but also of modifying

the way the molecule is described. The ro-vibrational motion of the nuclei, present as a non-separable component of the complete quantum description, has to be frozen. Last but not least, the form of the function which describes the mass distribution depends on the choice of the reference point in the laboratory frame.^{3–5} This technical problem, appearing also in the celestial mechanics, adds another difficulty to the way the transition between the free and frozen nuclei models may be performed.

Quantum-chemical calculations without assuming BO approximation, feasible for systems composed of several particles by using most recent computer installations and highly sophisticated software, are computationally very demanding and time-consuming.^{6,7} The most attractive and appealing to the chemical intuition are investigations of the relations between the structure of quantum objects and the masses of the constituent particles based on simple, exactly solvable models.^{8–16} By an easy tracing the mass-dependence of the analytical solutions they lead to a better understanding of some specific features of the BO approximation and allow to trace the process of the emergence of the molecular structure from the spherically-symmetric non-BO objects.^{4,5,12–16}

In this report we investigate the distribution of the density of mass in three exactly solvable model systems: two particles bound by the Coulomb force, and two and three particles connected by the Hooke force. In particular, the relation between the degree of the localization of a particle and its mass is described in

[†] Dedicated to Professor Douglas Jay Klein on the occasion of his 70th birthday.

some detail. This relation is crucial for the process of formation of the molecular shapes and for the validity of models based on the BO approximation. Some special attention is given to the issue of the choice of the reference point. This subject has been discussed by Piela in Appendix I of Ref. 3. Very recently, in two very interesting works^{4,5} Luděna *et al.* have demonstrated that the one-particle density of mass distribution, for a state described by a given wavefunction, strongly depends on the choice of the reference point. In a way, this issue may be traced back to the very beginning of the modern science: the difference between the Ptolemean and the Copernican representations of the Solar System may also be reduced to a difference in the choice of the reference point.

Hereafter we use the following conventions concerning the notations: a boldfaced symbol always corresponds to a vector while the standard one – to its length, *e.g.* $r_i = |\mathbf{r}_i|$; $\mathbf{p}_i \equiv \mathbf{p}(\mathbf{r}_i)$ is the momentum operator in the original coordinates while after a transformation $\mathbf{r}_i \rightarrow \mathbf{r}'_i$ it is denoted $\mathbf{P}(\mathbf{r}'_i)$. Two and more-particle Hamiltonians are denoted H while the one-particle Hamiltonians are denoted h_x with index x referring to a specific particle or pseudo-particle. We use atomic units however masses of particles are always written explicitly.

TWO PARTICLES

The simplest form of the nuclear wavefunction may be easily derived from an analysis of two-particle systems. In this section we discuss an exactly solvable model of two particles from which the analytic form of the wavefunction of these particles and, consequently, the mass density distributions are derived. If one of the particles is much heavier than the other then the heavy particle corresponds to a nucleus.

The non-relativistic Hamiltonian of a two-particle system reads

$$H(\mathbf{r}_1, \mathbf{r}_2) = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} + V(|\mathbf{r}_1 - \mathbf{r}_2|) \quad (1)$$

By introducing the center of mass and the relative coordinates,

$$\mathbf{R} \equiv \mathbf{r}_{12}^+ = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2}, \text{ and } \mathbf{r} \equiv \mathbf{r}_{12}^- = \mathbf{r}_1 - \mathbf{r}_2, \quad (2)$$

one may express $H(\mathbf{r}_1, \mathbf{r}_2)$ as a sum of two Hamiltonians: one for the center of mass and another one for the relative motion. The resulting Schrödinger equation may be separated accordingly and its spectrum is composed of two parts: the continuous spectrum of the free motion of the center of mass and the spectrum of the relative mo-

tion which depends on the form of V . Thus,

$$H(\mathbf{r}_1, \mathbf{r}_2) = h_{\mathbf{R}}(\mathbf{R}) + h_{\mathbf{r}}(\mathbf{r}) \quad (3)$$

where

$$h_{\mathbf{R}}(\mathbf{R}) = -\frac{1}{2M} \nabla_{\mathbf{R}}^2, \quad (4)$$

$$h_{\mathbf{r}}(\mathbf{r}) = -\frac{1}{2\mu} \nabla_{\mathbf{r}}^2 + V(r), \quad (5)$$

$$M \equiv M_{12} = m_1 + m_2, \mu \equiv \mu_{12} = \frac{m_1 m_2}{m_1 + m_2}. \quad (6)$$

We are interested in the bound states of $h_{\mathbf{r}}$. More specifically, in its bound ground state.

Since there are no external potentials, the interaction potential $V(r)$ is spherically symmetric. Therefore the eigenfunctions of $h_{\mathbf{r}}(\mathbf{r})$ may be expressed as

$$\Psi_{nml}(\mathbf{r}) = \Phi(r)_{nl} Y_{lm}(\theta, \phi) \quad (7)$$

In particular, the ground-state wavefunction reads

$$\Psi_{100}(\mathbf{r}) = \Phi_{10}(r) Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}} \Phi_{10}(r). \quad (8)$$

We denote $\Phi_{10}(r) \equiv \psi(r)$. The radial function $\psi(r)$ is nodeless and is real. We assume that it is normalized and the normalization condition reads:

$$\int_0^\infty [\psi(r)r]^2 dr = 1. \quad (9)$$

The one-particle density of mass operator of the two-particle system is defined as^{4,12}

$$\hat{\rho}(\boldsymbol{\tau}; \mathbf{r}) = m_1 \delta(\boldsymbol{\tau} - \mathbf{r}_1 + \mathbf{c}) + m_2 \delta(\boldsymbol{\tau} - \mathbf{r}_2 + \mathbf{c}), \quad (10)$$

where⁴

$$\mathbf{c} = \alpha \mathbf{r}_1 + \pi(1 - \alpha) \mathbf{r}_2, \quad (11)$$

where α is a parameter. From here, after some simple algebra, we get

$$\begin{aligned} \mathbf{r}_1 - \mathbf{c} &= (1 - \alpha) \mathbf{r} \\ \mathbf{r}_2 - \mathbf{c} &= -\alpha \mathbf{r}. \end{aligned} \quad (12)$$

Then,

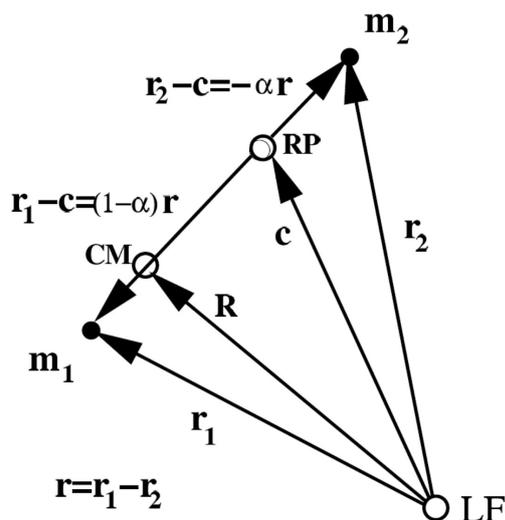


Figure 1. The two-particle system: CM – center of mass; RP – reference point; LF – the origin of the laboratory frame; the meaning of the remaining symbols is explained in the text.

$$\begin{aligned} \rho(\boldsymbol{\tau}; \mathbf{r}) &= m_1 \delta(\boldsymbol{\tau} - (1-\alpha)\mathbf{r}) + m_2 \delta(\boldsymbol{\tau} + \alpha\mathbf{r}) \\ &= \frac{m_1}{(1-\alpha)^3} \delta\left(\frac{\boldsymbol{\tau}}{1-\alpha} - \mathbf{r}\right) + \frac{m_2}{\alpha^3} \delta\left(\frac{\boldsymbol{\tau}}{\alpha} + \mathbf{r}\right). \end{aligned} \quad (13)$$

The mutual relations between vectors defining the locations of the particles, the reference point, the center of mass and the origin of the laboratory frame are illustrated in Figure 1.

The mass density distribution in a state $\Psi(\mathbf{r})$ may be calculated as

$$\rho(\boldsymbol{\tau}) = \langle \Psi(\mathbf{r}) | \hat{\rho}(\boldsymbol{\tau}; \mathbf{r}) | \Psi(\mathbf{r}) \rangle. \quad (14)$$

Since the two particles are distinguishable, the density distribution may be split to two independent densities, each corresponding to one particle. Thus, we have

$$\rho(\boldsymbol{\tau}) = \rho_1(\boldsymbol{\tau}) + \rho_2(\boldsymbol{\tau}), \quad (15)$$

where

$$\rho_1(\boldsymbol{\tau}) = \frac{m_1}{(1-\alpha)^3} \left| \Psi\left(\frac{\boldsymbol{\tau}}{1-\alpha}\right) \right|^2, \quad \rho_2(\boldsymbol{\tau}) = \frac{m_2}{\alpha^3} \left| \Psi\left(-\frac{\boldsymbol{\tau}}{\alpha}\right) \right|^2. \quad (16)$$

In the case under consideration, after the integration over the angular part, one obtains the radial mass density distributions as

$$\rho_1(\tau) = \frac{m_1}{(1-\alpha)^3} \left| \psi\left(\frac{\tau}{1-\alpha}\right) \tau \right|^2, \quad \rho_2(\tau) = \frac{m_2}{\alpha^3} \left| \psi\left(\frac{\tau}{\alpha}\right) \tau \right|^2. \quad (17)$$

The further discussion, *i.e.* defining the way the distribution of masses of the two particles is seen from the reference point, depends on the choice of α . In particular, if $\mathbf{c} = \mathbf{R}$ then the reference point coincides with the center of mass. For this particular choice

$$\alpha = \frac{\mu}{m_2} = \frac{m_1}{M}, \quad (18)$$

$$\mathbf{r}_1 - \mathbf{c} = \frac{\mu}{m_1} \mathbf{r} = \frac{m_2}{M} \mathbf{r}, \quad \mathbf{r}_2 - \mathbf{c} = -\frac{\mu}{m_2} \mathbf{r} = -\frac{m_1}{M} \mathbf{r}, \quad (19)$$

and

$$\rho_1(\tau) = \frac{m_1^4}{\mu^3} \left| \psi\left(\frac{m_1}{\mu} \tau\right) \tau \right|^2, \quad \rho_2(\tau) = \frac{m_2^4}{\mu^3} \left| \psi\left(\frac{m_2}{\mu} \tau\right) \tau \right|^2. \quad (20)$$

As one can see, in this case the distribution of the density of mass depends on the masses of the two particles not only due to the mass dependence of $\psi(r)$, but also because α is mass-dependent. Let us note that the difference between the mass-dependence of ρ_1 and ρ_2 is exclusively due to the mass-dependence of α (except for the normalization factors m_1 and m_2). In particular, if $m_1 \gg m_2$ and $m_2 = 1$, then $m_1/\mu \approx m_1$, $m_2/\mu \approx 1$ and, if $\psi(r)$ is an exponential function of r , then $\rho_1(\tau)$ is represented by a narrow peak (strongly localized particle) while $\rho_2(\tau)$ is diffuse. The picture is entirely different if we take $\alpha = 1/2$. This corresponds to the reference point selected in the middle of the distance between the particles. Then

$$\rho_1(\tau) = 8m_1 \left| \psi(2\tau) \tau \right|^2, \quad \rho_2(\tau) = 8m_2 \left| \psi(2\tau) \tau \right|^2. \quad (21)$$

In this case the densities depend on the masses of the particles only due to the mass dependence of $\psi(r)$ and the normalization factors.

To illustrate the behavior of the density of mass distribution as it is given by Eq. 17 we present two examples: the ground states of the hydrogen atom and of the spherical harmonic oscillator.

Ground States of the Hydrogen Atom and of the Spherical Harmonic Oscillator

The 'hydrogen atom' we discuss is composed of a point nucleus with mass m_1 and charge $+1$. The mass and the charge of the second particle are, respectively, m_2 and -1 . The interaction potential is given by

$$V(r) = -\frac{1}{r}, \quad (22)$$

and the corresponding ground state wavefunction is equal to

$$\psi(r) = 2\mu^{3/2} \exp(-\mu r). \quad (23)$$

The radial mass density distribution of each of the particles, according to Eqs. 17 and 23, is composed of two concentric ring-shape clouds:

$$\begin{aligned} \rho_1(\tau) &= \frac{m_1}{2} \left(\frac{2\mu}{1-\alpha} \right)^3 \tau^2 \exp\left(-\frac{2\mu\tau}{1-\alpha}\right), \\ \rho_2(\tau) &= \frac{m_2}{2} \left(\frac{2\mu}{\alpha} \right)^3 \tau^2 \exp\left(-\frac{2\mu\tau}{\alpha}\right). \end{aligned} \quad (24)$$

The maximum probability (the classical orbits) corresponds to the radii for which $d\rho_j/d\tau = 0$, $j = 1, 2$. This condition implies

$$\tau_1^0(\alpha) = \frac{1-\alpha}{\mu}, \quad \tau_2^0(\alpha) = \frac{\alpha}{\mu}. \quad (25)$$

The motion of the particles is fully correlated: According to Eq. 19 the directions of $\mathbf{r}_1 - \mathbf{c}$ and $\mathbf{r}_2 - \mathbf{c}$ are opposite to each other. The classical distance between the two particles is equal to

$$r_0 = \tau_1^0(\alpha) + \tau_2^0(\alpha) = \frac{1}{\mu}. \quad (26)$$

If the reference point is taken at the center of mass then, using Eqs. 18 and 25, we get

$$\tau_1^0(\mu/m_2) = \frac{1}{m_1}, \quad \tau_2^0(\mu/m_2) = \frac{1}{m_2}. \quad (27)$$

They are the same as the radii of the classical orbits: according to Eqs. 19 and 26

$$|\mathbf{r}_1 - \mathbf{c}|_0 = \frac{\mu}{m_1} r_0 = \frac{1}{m_1}, \quad |\mathbf{r}_2 - \mathbf{c}|_0 = \frac{\mu}{m_2} r_0 = \frac{1}{m_2}. \quad (28)$$

In the case of $\alpha = 1/2$ we get two identical circles. Their radii are equal to

$$\tau_1^0(1/2) = \frac{1}{2\mu}, \quad \tau_2^0(1/2) = \frac{1}{2\mu}, \quad (29)$$

and also, as one can easily check, are the same as in the classical orbits. If the masses are equal (as it is in the case of positronium or of a system composed of a proton and an antiproton), then for both choices of the

reference point we get the same picture since the center of mass is at the middle of the distance between the particles.

In the case of the spherical harmonic oscillator we have two particles with masses m_1 and m_2 interacting by the Hooke force with the potential

$$V(r) = \frac{\mu\omega^2}{2} r^2. \quad (30)$$

If, for simplicity, we set $\omega = 1$ then the relative motion of these particles in the ground state, is described by the wavefunction:

$$\psi(r) = \frac{2\mu^{3/4}}{\pi^{1/4}} \exp(-\mu r^2/2). \quad (31)$$

According to Eqs. 17 and 31 the radial mass density distributions are given by

$$\begin{aligned} \rho_1(\tau) &= \frac{4}{\sqrt{\pi}} \left(\frac{\sqrt{\mu}}{1-\alpha} \right)^3 \tau^2 \exp\left(-\frac{\mu\tau^2}{(1-\alpha)^2}\right), \\ \rho_2(\tau) &= \frac{4}{\sqrt{\pi}} \left(\frac{\sqrt{\mu}}{\alpha} \right)^3 \tau^2 \exp\left(-\frac{\mu\tau^2}{\alpha^2}\right). \end{aligned} \quad (32)$$

The maximum probability radii for which $d\rho_j/dr = 0$, $j = 1, 2$ are given by

$$\tau_1^0(\alpha) = \frac{1-\alpha}{\sqrt{\mu}}, \quad \tau_2^0(\alpha) = \frac{\alpha}{\sqrt{\mu}} \quad (33)$$

and the classical distance between the particles is $r_0 = 1/\sqrt{\mu}$.

If the reference point is taken at the center of mass then, in the same way as in the case of the hydrogen atom, we get

$$\tau_1^0(\mu/m_2) = \frac{\sqrt{\mu}}{m_1}, \quad \tau_2^0(\mu/m_2) = \frac{\sqrt{\mu}}{m_2} \quad (34)$$

and in the case of $\alpha = 1/2$

$$\tau_1^0(1/2) = \frac{1}{2\sqrt{\mu}}, \quad \tau_2^0(1/2) = \frac{1}{2\sqrt{\mu}}. \quad (35)$$

General Remarks

The diagrams showing the form of the maxima of $\rho_j(\tau)$, $j = 1, 2$, seen from the center of mass and from the reference point in the middle of the distance be-

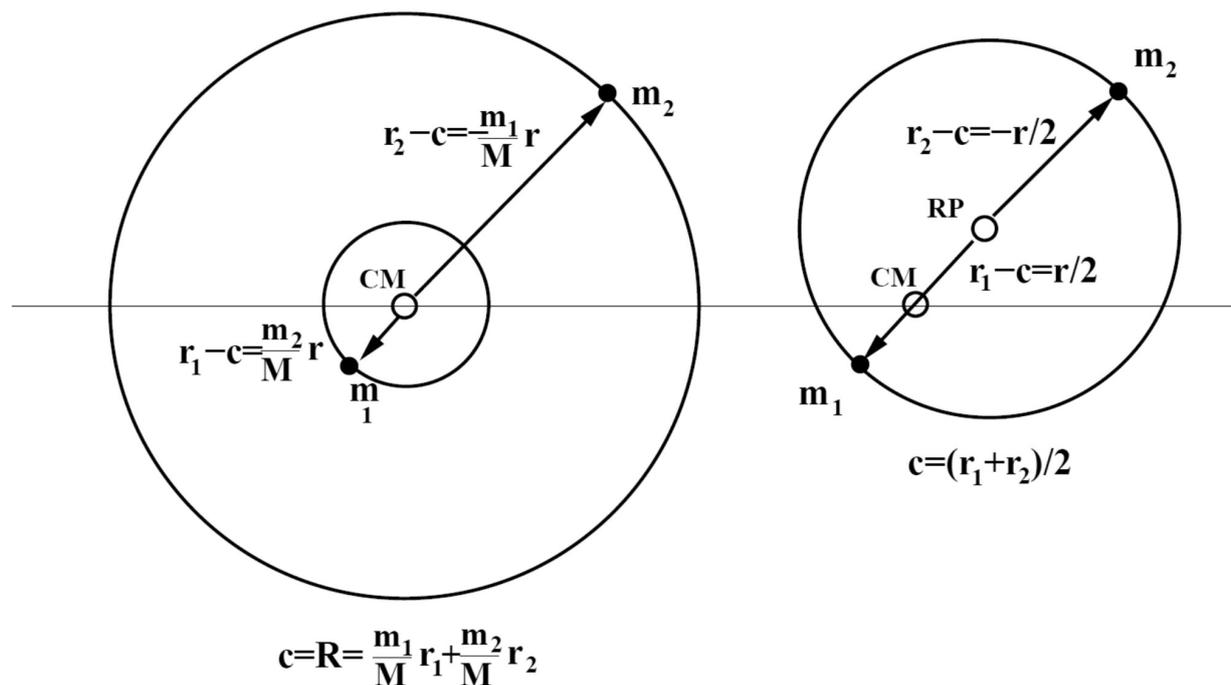


Figure 2. Orbits in the circular motion of two-particles. The diagram represents the maximum probability radii in the ground states of both hydrogen atom and spherical harmonic oscillator (the magnitudes of m_1 and m_2 have been selected arbitrarily). It may also be interpreted as a representation of the orbital motion of two macroscopic bodies interacting by the gravitational force, with properly selected masses and initial conditions. In the left panel the reference point coincides with the center of mass. In the right panel the reference point is in the middle of the distance between m_1 and m_2 . The notation is explained in the text.

tween the particles, are shown in Figure 2. Since Eqs. 10–21 may also be interpreted as describing the distributions of mass in the classical mechanics, the circles may represent the time-averaged density of mass distribution in the orbital motion of two bodies interacting by the gravitational force [*i.e.* the circular orbits in which the linear density of mass is equal to $m_j / (2\pi|r_j - c|)$, $j = 1, 2$] with properly selected initial conditions.

The density distribution depends on the choice of the reference point. Nevertheless, it is a very convenient tool in studies of the structure of the models describing quantum systems of several particles and the molecular properties. The decision about the choice of the reference point is determined by our aims and by the mathematical simplicity of the resulting model. The reference point located at the Sun is a good choice if one wants to describe the planetary motion but for the description of the motion of the satellites of a planet it is better to locate the reference point at this very planet. If we wish to describe the process of emerging the molecular shape due to the increasing masses of the particles playing the role of the nuclei then we have to select the reference point in such a way that in the limit of infinite masses of these particles we get the BO model. The idea of the adiabatic connection between the BO limit and a model with all particles equally treated may be here very use-

ful. The selections of the reference point at the center of mass of the nuclei (as recommended by Sutcliffe¹⁷) or at the total center of mass of the molecule, approach the BO model at the limit of infinite nuclear masses. The ones in which the coordinates of the reference point are mass-independent – do not. The formulation of strict mathematical criteria which define these reference points which are adiabatically connected to the BO model certainly deserves some attention.

THREE PARTICLES

Let us consider a system of three particles with masses m_1 , m_2 , m_3 . The Hamiltonian of this system may be written as

$$H(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \frac{p_3^2}{2m_3} + W(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3). \quad (36)$$

We assume that the interaction potential is composed of two parts:

$$W(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = W_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + V(r_{12}^-), \quad (37)$$

where

$$W_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{\omega^2}{2M_{123}} \left[\begin{array}{l} m_1 m_2 (r_{12}^-)^2 + m_1 m_3 (r_{13}^-)^2 \\ + m_2 m_3 (r_{23}^-)^2 \end{array} \right] \quad (38)$$

with

$$M_{123} = m_1 + m_2 + m_3 \quad (39)$$

corresponds to the Hooke-type harmonic attractions and $V(r_{12}^-)$ describes a repulsive interaction between particles {1} and {2} dependent only on the distance between these particles. A similar form of the interaction potential has been used to the modeling the so called Hookean molecules.⁸⁻¹²

Introducing coordinates of the center of mass

$$\mathbf{R}_0 = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2 + m_3 \mathbf{r}_3}{M_{123}} \quad (40)$$

and two vectors describing the relative positions of the particles:

$$\mathbf{r}_a = \mathbf{r}_{12}^-, \quad \text{and} \quad \mathbf{r}_b = \mathbf{r}_{12}^+ - \mathbf{r}_3 \quad (41)$$

one can rewrite the Hamiltonian (36) as

$$H = h_0(\mathbf{R}_0) + h_a(\mathbf{r}_a) + h_b(\mathbf{r}_b) \quad (42)$$

where $h_0(\mathbf{R}_0)$ describes the kinetic energy of the center of mass and

$$h_a(\mathbf{r}_a) = \frac{P(\mathbf{r}_a)^2}{2\mu_{12}} + \frac{\mu_{12}\omega^2}{2} r_a^2 + V(r_a) \quad (43)$$

$$h_b(\mathbf{r}_b) = \frac{P(\mathbf{r}_b)^2}{2\mu_{12,3}} + \frac{\mu_{12,3}\omega^2}{2} r_b^2, \quad (44)$$

where

$$\mu_{12,3} = \frac{M_{12}m_3}{M_{12} + m_3}. \quad (45)$$

Then, the wavefunction describing stationary states of the relative motion of the particles reads

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \Phi(\mathbf{r}_a) \Xi(\mathbf{r}_b). \quad (46)$$

The eigenvalue equation of $h_b(\mathbf{r}_b)$ is solvable analytically.^{18,19} The eigenvalue problem of $h_a(\mathbf{r}_a)$, depending on the form of V , may be solvable exactly, quasi-

exactly or numerically. In particular, for $V = 0$ we have exactly-solvable model known as the *Moshinsky atom*.¹⁸ If $V \sim 1/r_a^2$, the equation is reduced to the one describing a spherical harmonic oscillator and is also exactly solvable. For $V \sim 1/r_a$ we have a very interesting quasi-exactly solvable model known as *harmonium*.^{20,21} The equation is quasi-exactly solvable for several other potentials (see e.g. Refs. 10, 15). Since we are interested in the ground-state properties, the most essential is the behavior of the effective potential in Eq. 43 close to its minimum. In fact, for each kind of interaction V which monotonically increases with decreasing distance between the interacting particles, the effective interaction $A r_a^2 + V(r_a)$, $A > 0$, may be expanded in a power series around its minimum. If we retain only the quadratic term then Eq. 43 is also reduced to an exactly solvable equation describing a shifted harmonic oscillator.

Let us take

$$V(r_a) = \frac{\zeta}{r_a}, \quad \zeta \geq 0, \quad (47)$$

$m_1 = m_2 \equiv m$. Since we are interested in tracing the process of emerging the molecular shape due to the increasing nuclear masses, we select the reference point at the center of mass coordinate system in which $\mathbf{R}_0 = 0$. Then

$$\mu_{12} = \frac{m}{2}, \quad M_{12} = 2m, \quad \mu_{12,3} = \frac{2mm_3}{2m + m_3} \equiv \mu. \quad (48)$$

The minimum of the effective potential in Eq. 43

$$V_{\text{eff}}(r_a) = \frac{m\omega^2}{4} r_a^2 + \frac{\zeta}{r_a} \quad (49)$$

is at

$$r_0 = \left(\frac{2\zeta}{m\omega^2} \right)^{1/3}. \quad (50)$$

The expansion of $V_{\text{eff}}(r_a)$ around $r_a = r_0$ reads

$$V_{\text{eff}}(r_a) = \frac{3m\omega^2}{4} [r_0^2 + (r_a - r_0)^2] + O[(r_a - r_0)^3]. \quad (51)$$

Let us note that the procedure described has been designed to solve the radial part of the eigenvalue problem of h_a . Therefore r_a and r_0 in Eqs. 49–51 denote the *radial* variables rather than the position vectors. Thus, the ground-state solutions of Eqs. 43 and 44 may be written as

$$\Phi(r_a) = \left(\frac{2}{\pi}\right)^{1/4} (\sqrt{3}\omega m)^{3/4} \exp\left[-\frac{\sqrt{3}\omega m}{4}(r_a - r_0)^2\right], \quad (52)$$

$$\Xi(r_b) = \frac{2}{\pi^{1/4}} (\omega\mu)^{3/4} \exp\left(-\frac{\omega\mu}{2}r_b^2\right). \quad (53)$$

It is convenient to introduce

$$\lambda_{12} = \frac{M_{123}}{2m}, \text{ and } \lambda_3 = \frac{M_{123}}{m_3} \quad (54)$$

connected by an obvious relation:

$$\frac{1}{\lambda_{12}} + \frac{1}{\lambda_3} = 1. \quad (55)$$

Then Eqs. 40 and 41 imply

$$\mathbf{r}_1 + \mathbf{r}_2 = -\frac{m_3}{m}\mathbf{r}_3 = \frac{2}{\lambda_3}\mathbf{r}_b, \text{ and } \mathbf{r}_b = -\lambda_{12}\mathbf{r}_3. \quad (56)$$

From Eqs. 41 and 56 we get

$$\begin{aligned} \mathbf{r}_1 &= \frac{1}{2}\mathbf{r}_a + \frac{1}{\lambda_3}\mathbf{r}_b \\ \mathbf{r}_2 &= -\frac{1}{2}\mathbf{r}_a + \frac{1}{\lambda_3}\mathbf{r}_b \\ \mathbf{r}_3 &= -\frac{1}{\lambda_{12}}\mathbf{r}_b \end{aligned} \quad (57)$$

In the present case the one-particle density of mass operator reads

$$\hat{\rho}(\boldsymbol{\tau}; \mathbf{r}_a, \mathbf{r}_b) = m_1\delta(\boldsymbol{\tau} - \mathbf{r}_1) + m_2\delta(\boldsymbol{\tau} - \mathbf{r}_2) + m_3\delta(\boldsymbol{\tau} - \mathbf{r}_3) \quad (58)$$

and, using Eqs. 57, we get

$$\begin{aligned} \hat{\rho}(\boldsymbol{\tau}; \mathbf{r}_a, \mathbf{r}_b) &= m\lambda_3^3 \left[\delta\left(\lambda_3\boldsymbol{\tau} - \frac{\lambda_3}{2}\mathbf{r}_a - \mathbf{r}_b\right) + \right. \\ &\quad \left. \delta\left(\lambda_3\boldsymbol{\tau} + \frac{\lambda_3}{2}\mathbf{r}_a - \mathbf{r}_b\right) \right] \\ &\quad + m\lambda_{12}^3\delta(\lambda_{12}\boldsymbol{\tau} + \mathbf{r}_b). \end{aligned} \quad (59)$$

If particles {1} and {2} are indistinguishable and particle {3} is different, then the mass density can be split to two independent densities. For particle {3} we have

$$\begin{aligned} \rho_3(\boldsymbol{\tau}) &= m_3\lambda_{12}^3 \langle \Phi(\mathbf{r}_a)\Xi(\mathbf{r}_b) | \delta(\lambda_{12}\boldsymbol{\tau} + \mathbf{r}_b) | \Phi(\mathbf{r}_a)\Xi(\mathbf{r}_b) \rangle \\ &= m_3\lambda_{12}^3 |\Xi(-\lambda_{12}\boldsymbol{\tau})|^2. \end{aligned} \quad (60)$$

From here, after the substitution of the explicit form of Ξ and integration over the angular variables we get the radial mass density of particle {3}

$$\rho_3(\tau) = \frac{4}{\sqrt{\pi}} \left(\frac{\omega}{\mu}\right)^{3/2} m_3^4 \tau^2 \exp\left(-\frac{\omega}{\mu}m_3^2\tau^2\right). \quad (61)$$

The maximum probability radius for which $d\rho_3 / dr = 0$ is given by

$$\tau_3^0 = \frac{1}{m_3} \sqrt{\frac{\mu}{\omega}}. \quad (62)$$

Let us note that Eqs. 61 and 62, by the appropriate change of the masses, become identical with, respectively, Eqs. 32 and 34 for the two-particle oscillator.

A similar procedure for particles {1} and {2} gives:

$$\rho_{12}(\boldsymbol{\tau}) = m\lambda_3^3 \int_{v_a} |\Phi(\mathbf{r}_a)|^2 \left[\left| \Xi\left(\lambda_3\boldsymbol{\tau} - \frac{\lambda_3}{2}\mathbf{r}_a\right) \right|^2 + \left| \Xi\left(\lambda_3\boldsymbol{\tau} + \frac{\lambda_3}{2}\mathbf{r}_a\right) \right|^2 \right] d^3\mathbf{r}_a. \quad (63)$$

For simplicity we set hereafter $\omega = 1$ and $\zeta = 4$. We also skip the normalization factor in ρ_{12} since it is inessential for our consideration. It can also be easily recovered by the requirement that the density is normalized to $2m$. Due to the spherical symmetry of ρ , we may perform the calculations for z component of $\boldsymbol{\tau}$ only. This assumption considerably simplifies the integration. Now, the integration over the angle resulting from the scalar product $(\boldsymbol{\tau}_a \cdot \mathbf{r}_a)$ may be performed using the same approach as in Ref. 12. The result reads:

$$\rho_{12}(\tau_z) \sim \frac{I_+ - I_-}{\tau_z}, \quad (64)$$

where

$$I_{\pm} = \int_0^{\infty} |\Phi(r)|^2 \exp\left[-\frac{(2m)^2}{\mu} \left(\frac{r}{2} \pm \tau_z\right)^2\right] r dr \quad (65)$$

In general, the radial function $\Phi(r)$ in Eq. 65 may be obtained by solving the eigenvalue equation of the Hamiltonian (43) for an arbitrary interaction potential V . The substitution of the explicit form of $\Phi(r)$, as given by Eq. 52, yields

$$I_{\pm} \sim \int_0^{\infty} \exp\left[-\frac{\sqrt{3}m}{2}(r - r_0)^2 + \frac{m^2}{\mu}(r \pm 2\tau_z)^2\right] r dr. \quad (66)$$

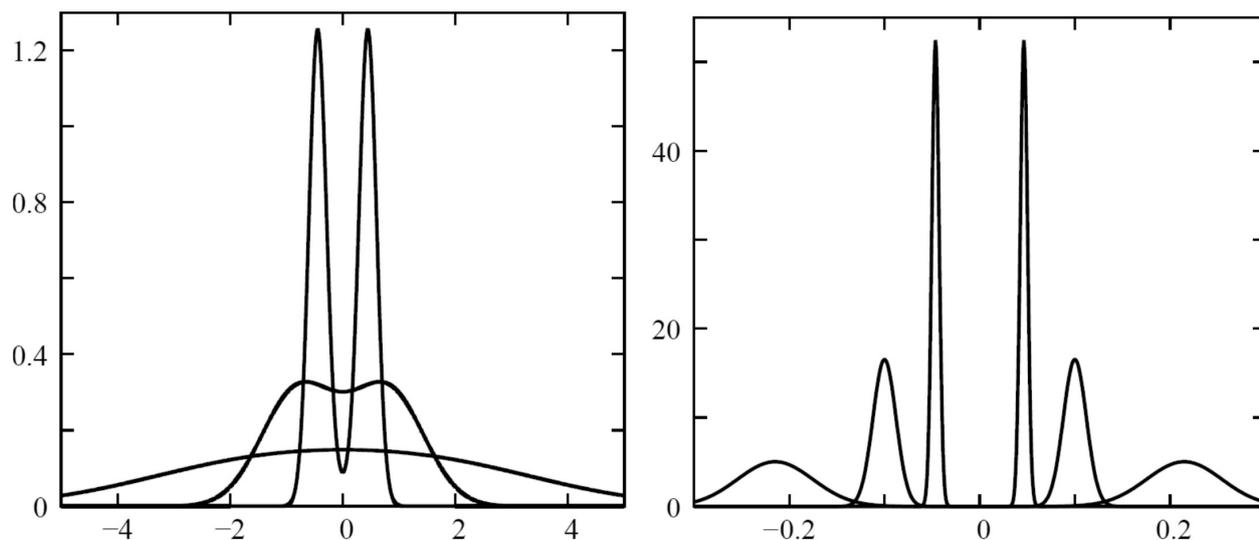


Figure 3. Density of mass $\rho_{12}(\tau)$ normalized to 1 for $m_3 = 10$. In the left panel plots for $m = 0.1, 1, 10$ and in the right panel – for $m = 100, 1000, 10000$ are displayed. The maxima of the curves increase with the increasing m . Note the difference of the scale in both panels.

After some calculus we finally obtain the density distribution

$$\rho_{12}(\tau) \sim \frac{\exp(C)}{\tau} \left[\frac{\exp(A_+^2) A_+ \operatorname{erfc}(A_+) - \exp(A_-^2) A_- \operatorname{erfc}(A_-)}{\exp(A_+^2) A_+ \operatorname{erfc}(A_+) + \exp(A_-^2) A_- \operatorname{erfc}(A_-)} \right], \quad (67)$$

where

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty \exp(-t^2) dt$$

is the complementary error function,

$$A_\pm = \frac{\beta_\pm}{\sqrt{\alpha}} \quad (68)$$

$$\beta_\pm = m \left(-\frac{\sqrt{3}}{2} r_0 \pm \frac{2m}{\mu} \tau \right) \quad (69)$$

$$\alpha = m \left(\frac{\sqrt{3}}{2} + \frac{m}{\mu} \right) \quad (70)$$

and

$$C = -m \left(\frac{\sqrt{3}}{2} r_0^2 + 4 \frac{m}{\mu} \tau^2 \right) \quad (71)$$

A plot of $\rho_{12}(\tau)$ (for convenience normalized to 1 rather than to $2m$) for $m_3 = 10$ and for several values of m is

presented in Figure 3. For $m \ll m_3$, when the system of three particles corresponds to an atom rather than to a molecule, the density of mass of two light particles is smooth, with a single diffuse maximum. With increasing masses of particles {1} and {2} the system transforms to a molecule and localized nuclei emerge. The maxima of the density are localized at approximately r_0 . In this model r_0 is inversely proportional to $m^{1/3}$. Therefore the bond length decreases with increasing m . If in Eq. 49 the repulsion was set proportional to m , *i.e.* if instead of ζ we had $m\zeta$, then the bond distance would be independent of m . A similar behavior of the mass density $\rho_{12}(\tau)$ is presented in Figure 4.

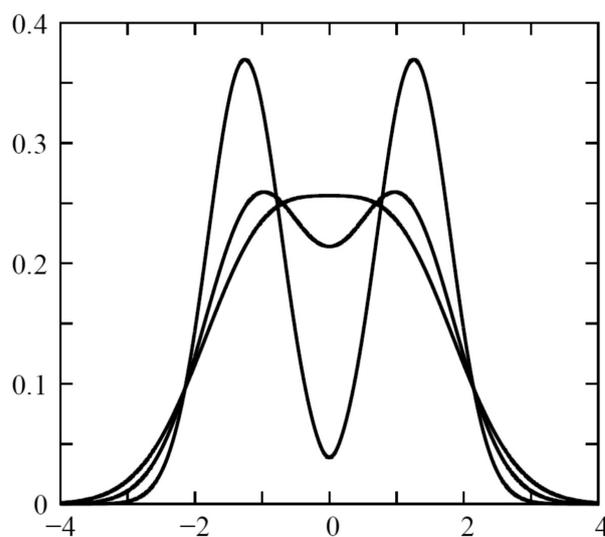


Figure 4. Density of mass $\rho_{12}(\tau)$ normalized to 1 for $m = 0.5$ and $m_3 = 0.01, 1, 100$. The maxima of the curves decrease with increasing m_3 .

Here the masses of particles {1} and {2} are fixed and equal 0.5 while the mass of particle {3} changes. Again, if $m \ll m_3$ the system corresponds to an atom and the density distribution of the light particles (with mass m) has one maximum. With increasing m the localization of the two particles with masses m (now much larger than m_3) increases and the system takes the shape of a diatomic molecule.

FINAL REMARKS

In the BO model the molecular shape is defined in a unique, though somehow arbitrary, way: we locate the nuclei in properly selected points and keep them fixed. These points may (but do not have to) correspond to the minima of a potential energy hyper-surface. If we treat all particles at the same level, the molecular shape, by definition, cannot be determined. However, we can define some auxiliary tools which may be helpful in understanding the process of emerging the molecular shape from a shapeless, spherically-symmetric structure given by the square of the many-body wavefunction. One of these tools is the operator of the one-particle density of mass^{4,12} exemplified in Eqs. 10 and 58. However, the expectation values of this operator depend on the choice of the reference point. Therefore, the studies on molecular properties in which this operator is applied have to rely on a proper selection of this point. This is somehow analogous to the selection of the initial conditions or the boundary conditions when solving a differential equation. The solution of such an equation has some physical meaning only after the appropriate boundary conditions are selected. In general, one can define a family of the reference points for which the one-particle density of mass converges to the same BO limit. Thus, the way a BO molecule is formed as a consequence of the increasing nuclear masses is not quite unique though, in order to get a basis for comparing this process in different systems, one can define some standards. In particular, the reference point linked to the center of mass of the system whose behavior we wish to study (*e.g.* a set of nuclei)

remains in a rather straightforward relation to the BO model.^{12–14}

Acknowledgements. I am grateful to Lutosław Wolniewicz for his criticism and to Ramon Carbó-Dorca for several inspiring discussions. Most useful comments of an anonymous referee, in particular his drawing my attention to references 4 and 5, are greatly appreciated.

REFERENCES

1. D. Andrae, *Phys. Rep.* **336** (2000) 413–525.
2. E. Besalú and R. Carbó-Dorca, *J. Mol. Graph. Model.* **39** (2013) 39–49.
3. L. Piela, *Ideas of quantum chemistry*, Chapter 6, Elsevier, Amsterdam 2007.
4. E. V. Ludeña, L. Echevarría, X. Lopez, and J. M. Ugalde, *J. Chem. Phys.* **136** (2012) 084103 (1–12).
5. C. G. Rodríguez, A. S. Urbina, F. J. Torres, D. Cazar, and E. V. Ludeña, *Comput. Theoret. Chem.* **1018** (2013) 26–34.
6. D. B. Kinghorn and L. Adamowicz, *Phys. Rev. Lett.* **83** (1999) 2541–2543; *J. Chem. Phys.* **113** (2000) 4203–4205.
7. M. Stanke and L. Adamowicz, *J. Phys. Chem. A* **117** (2013) 10129–10137.
8. X. Lopez, J. M. Ugalde, L. Echevarría, and E. Ludeña, *Phys. Rev. A* **74** (2006) 042504.
9. E. V. Ludeña, X. Lopez, and J. M. Ugalde, *J. Chem. Phys.* **123** (2005) 024102.
10. J. Karwowski, *Int. J. Quantum Chem.* **108** (2008) 2253–2260.
11. C. L. Benavides-Riveros and J. C. Varilly, *Eur. Phys. J. D* **66** (2012) 274–281.
12. U. Müller-Herold, *J. Chem. Phys.* **124** (2006) 014105 (1–5).
13. E. Mátyus, J. Hutter, U. Müller-Herold, and M. Reiher, *Phys. Rev. A* **83** (2011) 052512 (1–5).
14. I. A. Howard, C. Amovilli, N. Gidopoulos, and N. H. March, *J. Math. Chem.* **42** (2007) 603–615.
15. J. Karwowski and K. Szewc, *Collect. Czech. Chem. Commun.* **73** (2008) 1372–1390.
16. J. Karwowski and K. Szewc, *J. Phys. Conf. Series* **213** (2010) 012016 (1–13).
17. B. Sutcliffe, *Advan. Quantum Chem.* **40** (2001) 17–36.
18. M. Moshinsky, *The Harmonic Oscillator in Modern Physics: From Atoms to Quarks*, Gordon and Breach, New York 1969.
19. J.-L. Basdevant and J. Dalibard, *Quantum Mechanics*, p. 228–229, Springer-Verlag, Berlin-Heidelberg 2002.
20. E. Santos, *An. R. Soc. Esp. Fis. Quim.* **64** (1968) 177–193.
21. M. Taut, *Phys. Rev. A* **48** (1993) 3561–3566.