

## QUASI-EXACTLY SOLVABLE MODELS IN QUANTUM CHEMISTRY

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A separable model of  $N$  interacting particles, in which disjoint pairs of particles interact by arbitrary two-particle potentials while the remaining interactions obey the Hooke law, is discussed from a perspective of its applications in quantum chemistry. In particular, properties of three- and four-particle Hookean systems modeling He-like atoms,  $H_2^+$  and  $H_2$  molecules and many exotic systems are analyzed. The energy spectra and the structure of the wave-functions of quasi-exactly solvable Schrödinger equations which result from this analysis are investigated in some detail.

**Keywords:** Schrödinger equation; Quasi-exactly solvable models; Separability; Harmonium; Hookean molecules; Hamiltonian.

Theory of many-electron systems, in particular quantum chemistry, is based on a set of carefully designed approximations. Some of them as, for example, the adiabatic approximation or the one-electron model, impose separability of non-separable multi-dimensional equations. The resulting equations, though much simpler than the original ones, in general are not solvable either analytically or numerically. Therefore the next generation of approximations, usually derived either from the variational principle or from the perturbation theory, is aimed at deriving equations which are solvable. The correctness of the approximations is verified by comparing results of the calculations with experimental data and by checking consistency of results derived from methods based on different approximations. Limitations of this kind of approach stimulate studies on models which may be solved analytically supplying a possibility of very precise tests of flaws and merits of various approximations.

One of the first attempts to find an exactly-solvable model of two particles interacting by Coulomb forces and confined by an external potential

resulted in the construction of the so called Hooke atom or harmonium by Kestner and Sinanoglu<sup>1</sup> in 1962. These authors were satisfied by separability and, not being aware of its quasi-exact solubility, studied the final solutions numerically. The analytical solutions of the Schrödinger equation describing harmonium were originally found by Santos<sup>2</sup> in 1968 but remained unnoticed for several decades and the credit for solving the problem of harmonium has been mostly given to Taut<sup>3</sup> who rediscovered this system in 1993. Afterward, studies on the excited states of harmonium as well on the relations between solutions of the Schrödinger equation for harmonium and of its analog for two particles with the attractive interaction (a model of harmonically confined positronium) were performed<sup>4,5</sup>. A quasi-exactly solvable model with the interaction potential containing, additionally to the Coulombic, also a linear term has been constructed by Samanta and Ghosh<sup>6,7</sup>. Many other quasi-exactly solvable equations are discussed in a mathematically oriented work by Bose and Gupta<sup>8</sup>. Recently a method of construction of quasi-exactly solvable potentials, based on an inverse eigenvalue problem, has been formulated<sup>9</sup>.

It has been noticed very recently that analytically-solvable models of the hydrogen molecule and of its positive ion can also be constructed<sup>10-12</sup>. Models of the so called Hookean molecules may be derived from two simple properties of quadratic forms: (i) a linear combination of quadratic forms is a quadratic form and (ii) a linear transformation of the variables transforms a positive definite quadratic form to the diagonal form with positive coefficients. The Hookean  $H_2^+$  molecule is here considered as a three-particle system with the Hookean interactions between the electron and the protons and the Coulombic potential describing the repulsion of the protons. In a similar way, the Schrödinger equation for harmonium may be derived as an equation describing the relative motion of a pair of particles in a system of three interacting particles rather than an equation for two particles confined in a parabolic potential. It appears that this idea may be generalized to a system of  $N$  particles in which the interactions between disjoint pairs of particles are described by arbitrary two-particle potentials while the remaining interactions obey the Hooke law<sup>13</sup>.

In this paper a unified treatment of several systems relevant in quantum-chemical applications is presented. In particular, properties of three- and four-particle Hookean systems are analyzed. Quasi-exactly solvable equations which result from this analysis are discussed in some detail.

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.

### A SEPARABLE MODEL OF $N$ INTERACTING PARTICLES

Let us consider an  $N$ -particle Hamiltonian

$$H(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i=1}^K H_{2i-1}(\mathbf{r}_{2i-1}, \mathbf{r}_{2i}) + \sum_{i=2}^N \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_{i,j}^N a_{ij} (\mathbf{r}_i - \mathbf{r}_j)^2 \quad (1)$$

with  $a_{ij} = a_{ji}$ ,  $a_{ii} = 0$ , and  $a_{2k-1,2k} = 0$  for  $k = 1, 2, \dots, K$ ,  $K \leq N/2$ ,

$$H_{2i-1}(\mathbf{r}_{2i-1}, \mathbf{r}_{2i}) = \frac{p_{2i-1}^2}{2m_{2i-1}} + \frac{p_{2i}^2}{2m_{2i}} + V(\mathbf{r}_{2i-1,2i}) \quad (2)$$

and  $r_{2i-1,2i} = |\mathbf{r}_{2i-1} - \mathbf{r}_{2i}|$ . The remaining symbols have their usual meaning. The following theorem is valid<sup>13</sup>.

*Theorem:* The  $N$ -particle Hamiltonian (1) may be decoupled to  $N$  one-particle Hamiltonians if certain relations between the masses  $m_i$  of the particles and the coefficients  $a_{ij}$ , the separability conditions, are fulfilled. Out of these equations, one describes the free motion of the center of the mass and  $K$  describe the relative motion of the pairs of particles  $\{1,2\}$ ,  $\{3,4\}$ , ...,  $\{2K-1,2K\}$ , interacting by the potentials  $V(r_{2i-1,2i})$ ,  $i = 1, 2, \dots, K$ . The remaining  $N - K - 1$  equations describe a set of spherical harmonic oscillators in properly constructed normal coordinates.

The special cases of  $N = 3$ ,  $K = 1$  and  $N = 4$ ,  $K = 2$ , are of a particular interest and will be considered in the next two sections.

### THREE PARTICLES

In the case of  $N = 3$  and  $K = 1$ , Hamiltonian (1) may correspond to the Hookean atom (harmonium), to the Hookean  $H_2^+$  molecule, and to many

exotic systems composed of three particles with one pair interacting by a potential  $V(r)$  and two pairs according to the Hooke law. Though taking three different masses does not obstruct the separability<sup>12,13</sup>, we shall assume that  $m_1 = m_2 = m$ , to cover the most interesting cases of harmonium and Hookean  $H_2^+$ . A detailed analysis of mathematical properties of the general problem of three particles may be found in a recent work by Ugalde et al.<sup>12</sup>. Thus, the Hamiltonian may be written as

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{p_3^2}{2m_3} + V(r_{12}) + a^2 (r_{13}^2 + r_{23}^2) \quad (3)$$

where  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$  and  $a$  is a constant.

The transformation  $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ ,

$$\mathbf{R}_0 = \frac{m(\mathbf{r}_1 + \mathbf{r}_2) + m_3\mathbf{r}_3}{2m + m_3}, \quad \mathbf{R}_1 = \mathbf{r}_3 - \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$$

results in

$$H = h_0 + h_1 + h_3 \quad (4)$$

where

$$h_0 = \frac{P(\mathbf{R}_0)^2}{2(2m + m_3)} \quad (5)$$

describes the free motion of the center of the mass,

$$h_1 = \frac{P(\mathbf{r}_{12})^2}{m} + V(r_{12}) + \frac{a^2}{2} r_{12}^2 \quad (6)$$

describes the relative motion of particles 1 and 2, and

$$h_3 = \frac{P(\mathbf{R}_1)^2}{2\mu} + 2a^2 R_1^2 \quad (7)$$

where

$$\mu = \frac{2mm_3}{2m + m_3} \quad (8)$$

describes the relative motion of particle 3 and the mass center of particles {1,2}.

Since we are interested in the relative motion of the particles, it is convenient to set the origin of the coordinate system at the center of the mass, i.e. to set  $\mathbf{R}_0 = 0$ . Then,

$$\mathbf{r}_1 + \mathbf{r}_2 = -\frac{m_3}{m} \mathbf{r}_3 \quad \text{and} \quad \mathbf{R}_1 = t^2 \mathbf{r}_3 \quad (9)$$

where

$$t = \sqrt{\frac{m_3}{\mu}}. \quad (10)$$

Consequently,

$$H = H(\mathbf{r}_{12}, \mathbf{r}_3) = h_1(\mathbf{r}_{12}) + h_3(\mathbf{r}_3) \quad (11)$$

with

$$h_3(\mathbf{r}_3) = \frac{p_3^2}{2m_3 t^2} + 2a^2 t^4 r_3^2. \quad (12)$$

Let us assume that particles 1 and 2 are indistinguishable fermions while the third particle is different. If we choose the wavefunction to be an eigenfunction of the two-fermion spin operators  $S^2$  and  $S_z$ , then the orbital part of the total wavefunction has to be either symmetric (two-particle singlet) or antisymmetric (two-particle triplet) with respect to the transposition  $P_{12}$  of  $\mathbf{r}_1$  and  $\mathbf{r}_2$ . The potentials in both  $h_1(\mathbf{r}_{12})$  and  $h_3(\mathbf{r}_3)$  are spherically symmetric. Therefore, after the elimination of the center of mass, the orbital part of the wavefunction may be written as

$$\Psi(\mathbf{r}_{12}, \mathbf{r}_3)_{nlm_l, v\lambda\mu_\lambda} = \Phi_{nlm_l}(\mathbf{r}_{12}) \Xi_{v\lambda\mu_\lambda}(\mathbf{r}_3) \quad (13)$$

where  $\{n, l, m_l\}$  and  $\{v, \lambda, \mu_\lambda\}$  denote appropriate quantum numbers

$$H\Psi_{nlm_l, v\lambda\mu_\lambda} = E_{nl, v\lambda} \Psi_{nlm_l, v\lambda\mu_\lambda} \quad (14)$$

$$h_1(\mathbf{r}_{12})\Phi_{nlm_l}(\mathbf{r}_{12}) = E_{nl}^{(1)}\Phi_{nlm_l}(\mathbf{r}_{12}), \quad \Phi_{nlm_l}(\mathbf{r}_{12}) = \frac{\phi_{nl}(\mathbf{r}_{12})}{r_{12}} Y_{lm_l}(\hat{\mathbf{r}}_{12}) \quad (15)$$

$$h_3(\mathbf{r}_3)\Xi_{v\lambda\mu_\lambda}(\mathbf{r}_3) = E_{v\lambda}^{(3)}\Xi_{v\lambda\mu_\lambda}(\mathbf{r}_3), \quad \Xi_{v\lambda\mu_\lambda}(\mathbf{r}_3) = \frac{\xi_{v\lambda}(\mathbf{r}_3)}{r_3} Y_{\lambda\mu_\lambda}(\hat{\mathbf{r}}_3) \quad (16)$$

and

$$\bar{E}_{nl, v\lambda} = E_{nl}^{(1)} + E_{v\lambda}^{(3)} \quad (17)$$

where  $Y_{nlm_l}(\hat{\mathbf{r}}_{12})$  and  $Y_{v\lambda\mu_\lambda}(\hat{\mathbf{r}}_3)$  stand for spherical harmonics. Since  $P_{12}\mathbf{r}_{12} = -\mathbf{r}_{12}$ , the wavefunction  $\Psi_{nlm_l, v\lambda\mu_\lambda}$  corresponds to a singlet if  $\Phi_{nlm_l}(-\mathbf{r}_{12}) = \Phi_{nlm_l}(\mathbf{r}_{12})$  and to a triplet if  $\Phi_{nlm_l}(-\mathbf{r}_{12}) = -\Phi_{nlm_l}(\mathbf{r}_{12})$ . But  $\Phi_{nlm_l}(-\mathbf{r}_{12}) = (-1)^l \Phi_{nlm_l}(\mathbf{r}_{12})$ . Therefore, the wavefunctions with even/odd values of  $l$  correspond to two-particle singlets/triplets<sup>14</sup>.

Upon the substitution

$$r^2 = a\sqrt{\frac{m}{2}} r_{12}^2 \quad \text{and} \quad \tilde{r}_3^2 = 2a\sqrt{m_3} t^3 r_3^2 \quad (18)$$

the radial parts of the eigenvalue equations (15) and (16) may be rewritten, respectively, as

$$\left[ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + \frac{\sqrt{2m}}{a} V(r_{12}) + r^2 \right] \phi_{nl}(r) = 2\varepsilon_{nl}^{(1)} \phi_{nl}(r) \quad (19)$$

and

$$\left[ -\frac{d^2}{d\tilde{r}_3^2} + \frac{\lambda(\lambda+1)}{\tilde{r}_3^2} + \tilde{r}_3^2 \right] \xi_{v\lambda}(\tilde{r}_3) = 2\varepsilon_{v\lambda}^{(3)} \xi_{v\lambda}(\tilde{r}_3) \quad (20)$$

where

$$\varepsilon_{nl}^{(1)} = \frac{1}{a} \sqrt{\frac{m}{2}} E_{nl}^{(1)} \quad \text{and} \quad \varepsilon_{v\lambda}^{(3)} = \frac{\sqrt{\mu}}{2a} E_{v\lambda}^{(3)}. \quad (21)$$

The eigenvalues of  $h_3$  may be expressed by the well known solutions of Eq. (20):

$$E_{v\lambda}^{(3)} = \frac{a}{\sqrt{\mu}} \varepsilon_{v\lambda}^{(3)} = a \sqrt{\frac{1}{m_3} + \frac{1}{2m}} \left( 2v + \lambda + \frac{3}{2} \right). \quad (22)$$

Solutions of Eq. (19) depend on the form of  $V$ . In particular, if  $V(r_{12}) = \zeta/r_{12}$  (Coulomb interaction between particles 1 and 2), Eq. (19) reads

$$\left[ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + \frac{\tilde{\zeta}}{r} + r^2 \right] \phi_{nl}(r) = 2\varepsilon_{nl}^{(1)} \phi_{nl}(r) \quad (23)$$

where

$$\tilde{\zeta}^2 = \frac{\zeta^2}{a} \sqrt{2m^3}. \quad (24)$$

Then, the dependence of the solutions of the three-particle problem on the parameters describing the system (masses of the particles and interaction potential parameters  $a$  and  $\zeta$ ) may be effectively reduced to the parameter-dependent scaling of the coordinates and an explicit dependence on only one parameter:  $\tilde{\zeta}$ .

One of interesting aspects of this model is a simple dependence of its solutions on the masses of the particles. First let us consider the dependence on  $m_3$ . The eigenvalue problem of  $h_1$ , i.e. the relative motion of particles 1 and 2, is  $m_3$ -independent. After scaling of  $r_3$ , as given by Eq. (18), the eigenvalue problem of  $h_3$  reduces to the parameter-independent Eq. (20). The scaling parameter,  $q = m_3 \mu^{-3/4} (2a)^{1/2}$ , monotonically increases with increasing  $m_3$  and approaches  $\infty$  if  $m_3 \rightarrow \infty$ . This means that increasing  $m_3$  implies reduction of all dimensions of the system described by  $r_3$  proportionally to  $q$ . In particular, the width of the Gaussian density distribution corresponding to the ground state becomes smaller (the particle is more localized) if  $m_3$  increases, approaching a delta-type distribution if  $m_3 \rightarrow \infty$ . At the limit of  $m_3 \rightarrow \infty$  we get the standard model of two particles in a harmonic confinement interacting by the potential  $V$  and described by  $h_1$ . In particular, if  $V \sim 1/r_{12}$  this model represents harmonium<sup>1-5</sup>. As one can see from Eq. (22), the increase of  $m_3$  to  $\infty$  results in a monotonic decrease of the separation between the neighboring energy levels in the spectrum of  $h_3$  to the limit value  $a/\sqrt{2m}$ .

The dependence on  $m$  is more interesting since both eigenvalue equations, (19) and (20), contain this parameter. In the case of Eq. (20), assuming that  $a$  is  $m$ -independent, for  $m \rightarrow \infty$ , the scaling parameter  $q$  monotonically decreases to the limit value  $m_3^{1/4} (2a)^{1/2}$ . The relative motion of particles 1 and 2 is described by Eq. (19) and, in the special case of the Coulombic interaction, by Eq. (23). If  $a$  is  $m$ -independent then the scaling

parameter is proportional to  $m^{1/4}$  (cf. Eq. (18)). However, if  $a^2 = m\omega^2/2$  then the scaling changes to  $m^{1/2}$ . In both cases increasing  $m$  implies reduction of all dimensions (proportionally either to  $m^{1/4}$  or to  $m^{1/2}$ ). The interaction ( $\zeta \neq 0$ ) modifies this simple rule, but its general character is retained. In Fig. 1 the ground state radial wavefunction  $\phi_{00}(r_{12})$  is plotted versus  $r_{12}$  for several values of  $m$  assuming that  $a^2 = m\omega^2/2$ . As one can see, heavy particles are strongly localized. The degree of this localization may be used as a measure of the validity of the Born–Oppenheimer approximation. In the Born–Oppenheimer limit the nuclei are fully localized, i.e. their density distribution is described by the Dirac delta (note that in Fig. 1 wavefunctions rather than densities are displayed).

At the limit of  $m \rightarrow \infty$  we get the Born–Oppenheimer model of the Hookean  $\text{H}_2^+$  molecule. In this case  $t = 1$  and Eqs (6), (11) and (12) yield

$$H_{\text{BO}}(\mathbf{r}_{12}; \mathbf{r}_3) = \lim_{m \rightarrow \infty} H(\mathbf{r}_{12}, \mathbf{r}_3) = \frac{p_3^2}{2m_3} + 2a^2 r_3^2 + W(r_{12}) \quad (25)$$

where, in this context,  $r_{12}$  is a parameter equal to a fixed separation between the nuclei and

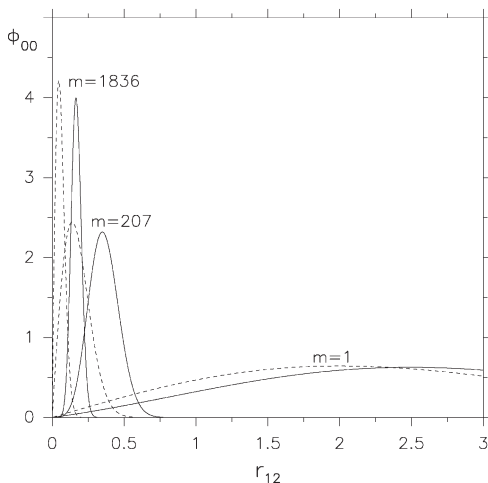


FIG. 1

The ground state radial wavefunction  $\phi_{00}(r_{12})$  plotted versus the interparticle distance  $r_{12}$  for three masses of the particles corresponding to electron ( $m = 1$ ), muon ( $m = 207$ ) and proton ( $m = 1836$ ). In all cases  $a^2 = m/8$ . Solid and dotted lines correspond to  $\zeta = 1$  and 0, respectively



$$W(\mathbf{r}_{12}) = V(\mathbf{r}_{12}) + \frac{a^2}{2} r_{12}^2 \quad (26)$$

is constant. In the eigenvalue problem of  $H_{\text{BO}}$ ,

$$H_{\text{BO}}(\mathbf{r}_{12}; \mathbf{r}_3) \Psi_{\nu\lambda\mu_\lambda}^{\text{BO}}(\mathbf{r}_{12}; \mathbf{r}_3) = E_{\nu\lambda}^{\text{BO}}(\mathbf{r}_{12}) \Psi_{\nu\lambda\mu_\lambda}^{\text{BO}}(\mathbf{r}_{12}; \mathbf{r}_3) \quad (27)$$

$\mathbf{r}_{12}$  appears as a parameter. According to Eqs (16) and (21),

$$E_{\nu\lambda}^{\text{BO}}(\mathbf{r}_{12}) = t^{-1} E_{\nu\lambda}^{(3)} + W(\mathbf{r}_{12}). \quad (28)$$

Since in  $H_{\text{BO}}$  only additive  $\mathbf{r}_{12}$ -dependent terms are present, its eigenfunctions do not depend on  $\mathbf{r}_{12}$ . More precisely,

$$\Psi_{\nu\lambda\mu_\lambda}^{\text{BO}}(\mathbf{r}_{12}; \mathbf{r}_3) = \Phi^{\text{BO}}(\mathbf{r}_{12}) \Xi_{\nu\lambda\mu_\lambda}^{\text{BO}}(\mathbf{r}_3) \quad (29)$$

where  $\Xi_{\nu\lambda\mu_\lambda}^{\text{BO}}(\mathbf{r}_3)$  is an  $\mathbf{r}_{12}$ -independent eigenfunction of  $H_{\text{BO}}$  and  $\Phi^{\text{BO}}(\mathbf{r}_{12})$  is a normalized function of  $\mathbf{r}_{12}$  which may be determined by solving the nuclear motion equation. The eigenvalue equation for the nuclear motion reads

$$\left[ \frac{P(\mathbf{r}_{12})^2}{m} + E_{\nu\lambda}^{\text{BO}}(\mathbf{r}_{12}) \right] \Phi_{nlm_l}^{\text{BO}}(\mathbf{r}_{12}) = E_{nl,\nu\lambda}^{\text{BO}} \Phi_{nlm_l}^{\text{BO}}(\mathbf{r}_{12}). \quad (30)$$

Now, combining Eqs (6), (15), (26), and (28), one can readily get

$$E_{nl,\nu\lambda}^{\text{BO}} = E_{nl}^{(1)} + t^{-1} E_{\nu\lambda}^{(3)} \quad (31)$$

and the wavefunction is given by Eq. (29). By comparing Eqs (30) and (15) we can easily see that

$$\Phi_{nlm_l}(\mathbf{r}_{12}) = \Phi_{nlm_l}^{\text{BO}}(\mathbf{r}_{12}). \quad (32)$$

Similarly, from Eqs (27), (29), (12) and (15) results that

$$\Xi_{\nu\lambda\mu_\lambda}(\mathbf{r}_3) = t^{9/4} \Xi_{\nu\lambda\mu_\lambda}^{\text{BO}}(t^{3/2}\mathbf{r}_3). \quad (33)$$

According to Eq. (29), in the the Hookean molecule the electronic and the nuclear degrees of freedom (described, respectively, by  $\mathbf{r}_3$  and by  $\mathbf{r}_{12}$ ) are decoupled. Therefore, in this case, the model referred to as the adiabatic approximation<sup>15</sup> is exact. However, the motion of the system and its properties depend on the masses of the particles (cf. Fig. 1 and Eq. (33)). In particular, an analysis of the mass density distribution may help to understand how the molecular and the atomic shapes are transformed to each other when the masses of the particles change in an appropriate way<sup>16</sup>. If the mass density operator for particle {3} is defined as

$$\hat{\rho}(\mathbf{z}; \mathbf{r}_3)_{m_3} = m_3 \delta(\mathbf{z} - \mathbf{r}_3) \quad (34)$$

then the density of mass distribution in a state  $\Psi(\mathbf{r}_{12}, \mathbf{r}_3)_{nlm_l, \nu\lambda\mu_\lambda}$  is given by

$$\begin{aligned} \rho(\mathbf{z})_{m_3} &= m_3 \langle \Psi(\mathbf{r}_{12}, \mathbf{r}_3) | \hat{\rho}(\mathbf{z}; \mathbf{r}_3)_{m_3} | \Psi(\mathbf{r}_{12}, \mathbf{r}_3) \rangle = \\ &= m_3 \int_{\Omega_r} |\Phi(\mathbf{r}_{12})|^2 |\Xi(\mathbf{z})|^2 d^3r_{12} = m_3 |\Xi(\mathbf{z})|^2 \end{aligned} \quad (35)$$

where, for simplicity, the quantum numbers have been omitted. In the case of particles {1,2}

$$\hat{\rho}(\mathbf{z}; \mathbf{r}_1, \mathbf{r}_2)_m = m[\delta(\mathbf{z} - \mathbf{r}_1) + \delta(\mathbf{z} - \mathbf{r}_2)]. \quad (36)$$

According to Eq. (9)

$$\mathbf{r}_1 = \frac{1}{2}\mathbf{r}_{12} - \frac{m_3}{2m}\mathbf{r}_3, \quad \mathbf{r}_2 = -\frac{1}{2}\mathbf{r}_{12} - \frac{m_3}{2m}\mathbf{r}_3. \quad (37)$$

Consequently, the distribution of the density of mass of the {1,2} pair is given by a convolution of  $|\Phi|^2$  and  $|\Xi|^2$ :

$$\rho(\mathbf{z})_m = 16m \int_{\Omega_{r_3}} \left| \Phi \left( 2\mathbf{z} + \frac{m_3}{m} \mathbf{r}_3 \right) \right|^2 |\Xi(\mathbf{r}_3)|^2 d^3 r_3 . \quad (38)$$

If  $m \rightarrow \infty$  then

$$\rho(\mathbf{z})_m \rightarrow 16m |\Phi(2\mathbf{z})|^2 . \quad (39)$$

As one can easily check using Eqs (38) and (39),

$$\int_{\Omega_r} \rho(\mathbf{z})_m d^3 z = 2m .$$

The mass dependence in three-particle Hookean systems has also been discussed in refs<sup>10-12,16</sup>.

#### FOUR PARTICLES

In general, the case of  $N = 4$ ,  $K = 2$  is similar to the one discussed in the preceding section. The four-particle Hamiltonian with  $m_1 = m_2 = m_a$  and  $m_3 = m_4 = m_b$  is decoupled by the following transformation of coordinates<sup>11-13</sup>:

$$\mathbf{R}_0 = \frac{m_a \mathbf{r}_a + m_b \mathbf{r}_b}{m_a + m_b}, \quad \mathbf{r}_{2i-1,2i} = \mathbf{r}_{2i-1} - \mathbf{r}_{2i}, \quad i = 1, 2, \quad \mathbf{R}_1 = \mathbf{r}_a - \mathbf{r}_b \quad (40)$$

where

$$\mathbf{r}_a = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2), \quad \mathbf{r}_b = \frac{1}{2}(\mathbf{r}_3 + \mathbf{r}_4) .$$

The resulting one-particle Hamiltonians read

$$h_0 = \frac{P(\mathbf{R}_0)^2}{4(m_a + m_b)} \quad (41)$$

$$h_i = \frac{P(\mathbf{r}_{2i-1,2i})^2}{m(i)} + V(r_{2i-1,2i}) + a^2 r_{2i-1,2i}^2 \quad (42)$$

$$i = 1, 2, \quad m(1) = m_a, \quad m(2) = m_b$$

$$h_3 = \frac{P(\mathbf{R}_1)^2}{4\mu} + 4a^2 R_1^2 \quad (43)$$

with  $\mu = m_a m_b / (m_a + m_b)$ . Here  $h_0$  corresponds to the motion of the center of the mass,  $h_i$ ,  $i = 1, 2$  describe the relative motion of two pairs of particles interacting by potentials  $V_i(r_{2i-1,2i})$  and  $h_3$  describes the relative motion of the centers of mass of the pairs  $\{1,2\}$  and  $\{3,4\}$ . If one of the pairs, say  $\{3,4\}$ , describes heavy particles (nuclei) then we can apply the Born–Oppenheimer approximation, i.e. fix coordinates of these particles. However, this does not affect the relative motion of two remaining particles since the relative motions of the two pairs of particles are separated. Consequently, similarly as in the three-particle case, the adiabatic description is, effectively, exact.

### ONE-PARTICLE EQUATIONS

All eigenvalue equations of the one-particle Hamiltonians derived from the models discussed in the preceding sections are spherically symmetric. Then, the angular parts are separable from the radial ones and the angular eigenfunctions are equal to the spherical harmonics in appropriate angular coordinates. The radial equations corresponding to  $h_0$  (Eqs (5) and (41)) describe the free motion of the center of the mass. The ones corresponding to  $h_3$  (Eqs (7) and (43)) describe harmonic motion related to the Hooke force. Both equations are analytically solvable and their solution is a textbook exercise. The analytical solubility of equations describing the relative motion of particles  $\{1,2\}$  and, in the case of  $N = 4$ , also  $\{3,4\}$  (one-particle Hamiltonians  $h_1$  and  $h_2$ , as defined in Eqs (6) and (42)) depends on the form of  $V$ . The equations are exactly (analytically) solvable if  $V(r_{12}) \sim r_{12}^{-2}$  (Calogero model<sup>17</sup>) or  $V(r_{12}) \sim r_{12}^2$  (Moshinsky model<sup>18</sup>). In many other cases only some eigenfunctions (and eigenvalues) may be expressed analytically (the best known example is harmonium). These cases are referred to as quasi-exactly solvable.

Let us consider a particle of mass  $m$  in an effective spherically-symmetric potential

$$V_{\text{eff}}(r) = \frac{I(I+1)}{2mr^2} + V(r) \quad (44)$$

composed of the centrifugal term and of an external potential  $V(r)$ . The corresponding radial Schrödinger equation reads

$$\left[ -\frac{1}{2m} \frac{d^2}{dr^2} + V_{\text{eff}}(r) - E_{nl} \right] \phi_{nl}(r) = 0 \quad (45)$$

where  $\phi_{nl}(r)$  is the radial part of the wavefunction

$$\Phi_{nlm_l}(\mathbf{r}) = \frac{\phi_{nlm_l}(r)}{r} Y_{lm_l}(\hat{\mathbf{r}}). \quad (46)$$

If the external potential supports bound states, Eq. (45) may be solved numerically using standard procedures. In some cases (an extensive set of examples has been discussed by Bose and Gupta<sup>8</sup>) the equation may be solved analytically. In this context the external potential

$$V(r) = \delta \frac{\zeta}{r} + \frac{m\omega^2}{2} (r - \delta r_e)^2 \quad (47)$$

where  $m > 0$ ,  $\omega \geq 0$ ,  $\zeta \geq 0$ ,  $\delta = \pm 1$ , is of a particular interest. It corresponds to one of equations discussed by Bose and Gupta<sup>8</sup> and was analyzed by Ghosh and Samantha<sup>6,7</sup>. Special cases of this potential describe a large set of important model systems. In particular,  $\omega = 0$ ,  $\delta = -1$  correspond to a H-like atom,  $\zeta = r_e = 0$  to the harmonic oscillator,  $\zeta = 0$  to the nuclear motion of a diatomic molecule in the harmonic approximation. If  $r_e = 0$  then  $V(r)$  corresponds to harmonium (if  $\delta = 1$ ) or to positronium confined in a parabolic potential (if  $\delta = -1$ ). The shapes of the potential in these two cases and the corresponding energy levels are shown in Fig. 2.

If we set  $r = r_{12}$  then Eq. (45) is equivalent to the radial part of the eigenvalue equation of  $h_1$  (6) (and also of  $h_1$  or  $h_2$  defined in Eq. (42)), with properly selected  $V$  and recalibrated constants. Then, Eq. (45) also describes the relative motion of particles interacting by a two-particle potential  $V(r_{12})$  in the model systems discussed in preceding sections.

Eq. (45), with the external potential (47), depends on four parameters:  $m$ ,  $\omega$ ,  $\zeta$  and  $r_e$ . For all values of these parameters, with the only restriction  $\omega > 0$  and  $m > 0$ , its square-integrable solutions may be expressed as

$$\phi_{nl}(r) \sim r^{l+1} e^{-m\omega(r-r_e)^2/2} P_{nl}^\delta(r) \quad (48)$$

where  $P_{nl}^\delta(r)$  is a function which does not influence the asymptotic behavior for both  $r \rightarrow 0$  and  $r \rightarrow \infty$ . The set of eigenfunctions is complete and the

energy spectrum is discrete<sup>19</sup>. In general the energy depends on the choice of  $\delta$ . Therefore we set  $E_{nl} = E_{nl}^{\delta}$ . However, in the analytically solvable cases<sup>4,9</sup>  $E_{nl}^{+} = E_{nl}^{-}$ . Besides, in the analytically solvable cases  $P_{nl}^{\delta}(r)$  is a polynomial. Since the transformation  $\delta \rightarrow -\delta$  is equivalent to the transformation  $r \rightarrow -r$  (cf. Eqs (45) and (47)), the polynomial may be expressed as

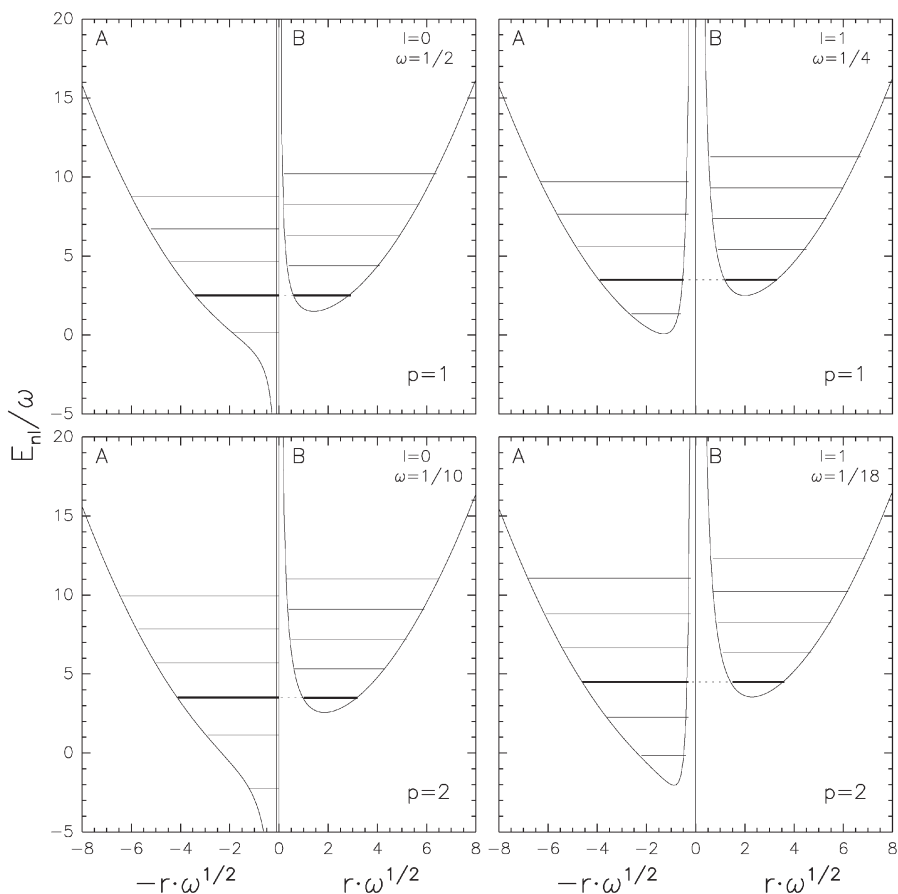


FIG. 2

Shapes of the effective potential  $V_{\text{eff}}(r)$  versus  $r\omega^{1/2}$  and the energy levels of confined positronium (panels A) and of harmonium (panels B). The plots correspond to the eigenvalues of Eq. (45), with the external potential (47), scaled by  $1/\omega$ , with  $m = 1/2$ ,  $r_e = 0$ ,  $\zeta = 1$  and  $\delta = -1$  (panels A),  $\delta = +1$  (panels B). The values of  $\omega$  correspond to analytically solvable cases with  $l = 0, 1$  and  $p = 1, 2$ . The analytical energies, marked by the thick lines, in the case of harmonium are the same as the ones in the case of the confined positronium

$$P_{nl}^{\delta}(r) = \sum_{i=0}^p a_i^{(nl)} (\delta r)^i. \quad (49)$$

Consequently, in the analytically solvable cases, Eq. (45) with potential (47) may be rewritten as

$$\left[ -\frac{1}{2m} \frac{d^2}{dx^2} + \frac{l(l+1)}{2mx^2} + \frac{\zeta}{x} + \frac{m\omega^2}{2} (x-r_e)^2 - E_{nl} \right] \phi_{nl}(x) = 0 \quad (50)$$

where  $x = \pm r \in (-\infty, \infty)$  and due to the boundary conditions at  $r = 0$ ,  $\phi_{nl}(0) = 0$ . The resulting wavefunction,  $\phi_{nl}(x)$ , corresponds to a system with repulsive/attractive Coulomb interaction if  $x > 0/x < 0$ . In particular, if  $r_e = 0$  and  $\zeta = 1$  then the part of  $\phi_{nl}(x)$  with  $x \in (-\infty, 0)$  describes confined positronium and the part with  $x \in (0, \infty)$  describes harmonium.

The coefficients of the polynomial (49) may be determined using the standard method of Sommerfeld. In this case the substitution of Eqs (48) and (49) to Eq. (50) leads to the following set of recurrence relations:

$$\begin{aligned} B_0 a_0 + C_1 a_1 &= 0 \\ A_0 a_0 + B_1 a_1 + C_2 a_2 &= 0 \\ A_1 a_1 + B_2 a_2 + C_3 a_3 &= 0 \\ A_2 a_2 + B_3 a_3 + C_4 a_4 &= 0 \\ A_3 a_3 + B_4 a_4 + C_5 a_5 &= 0 \\ \dots \quad \dots \quad \dots & \end{aligned} \quad (51)$$

with

$$\begin{aligned} A_i &= 2m[E - \omega(i+1+3/2)] \\ B_i &= 2m\delta[\omega r_e (i+1) - \zeta] \\ C_i &= i(i+2l+1) \end{aligned} \quad (52)$$

where the indices  $nl$  have been, for simplicity, omitted. As one can see, if  $A_p = 0$ , i.e. if

$$E = \omega(p + l + 3/2) \quad (53)$$

then  $a_{p+1} = a_{p+2} = \dots = 0$  while  $a_i$  with  $i \leq p$  fulfill the appropriate set of homogeneous linear equations.

First let us consider the case of a spherical harmonic oscillator, i.e. the case of  $\zeta = r_e = 0$ . The recurrence relations (51) split to two independent sets: One set for  $i = 2j + 1$  and the other one for  $i = 2j$ , with  $j = 0, 1, 2, \dots$ . Since  $C_i \neq 0$ , the only solution of the first set:  $C_1 a_1 = 0$ ,  $A_1 a_1 + C_3 a_3 = 0$ ,  $A_3 a_3 + C_5 a_5 = 0, \dots$ , is  $a_1 = a_3 = a_5 = \dots = 0$ . The second set of the recurrence relations reads:

$$A_{2j} a_{2j} + C_{2j+2} a_{2j+2} = 0. \quad (54)$$

If  $A_p \equiv A_{2n} = 0$ , i.e. if

$$E = \omega(2n + l + 3/2) \quad (55)$$

then the recursion terminates with  $a_{2n+2} = a_{2n+4} = \dots = 0$  and

$$\frac{a_{2j}}{a_{2j+2}} = -\frac{C_{2j+2}}{A_{2j}} = -\frac{(j+1)(j+l+3/2)}{m\omega(n-j)}, \quad j = 0, 1, \dots, n-1. \quad (56)$$

In this case the condition which determines energies of the stationary states, i.e. Eq. (55), is sufficient to determine the coefficients of the polynomial (49) and, consequently, all solutions of the radial Schrödinger equation.

The case of  $B_i \neq 0$  is essentially different. Though setting  $A_p = 0$  terminates the recurrence, it is not enough to determine the coefficients of  $P_{nl}(r)$ . Indeed, let us take  $p = 0$ . Setting  $A_0 = 0$  implies  $E = \omega(l + 3/2)$ ,  $a_1 = a_2 = \dots = 0$  and  $B_0 a_0 = 0$ . Then,  $a_0 \neq 0$  if  $B_0 = 0$ , i.e. if

$$\zeta = \omega r_e (l + 1). \quad (57)$$

The corresponding wavefunction

$$\phi_{0l}^{(p=0)}(r) \sim r^{l+1} e^{-m\omega(r-r_e)^2/2} \quad (58)$$



is nodeless, i.e. it corresponds to the ground state ( $n = 0$ ). For  $p = 1$ ,  $A_1 = 0$  implies  $E = \omega(l + 5/2)$  and  $a_2 = a_3 = \dots = 0$ . Coefficients  $a_0$  and  $a_1$  fulfill the following set of equations:

$$\begin{pmatrix} m\delta(\omega r_e(l+1) - \zeta) & l+1 \\ \omega & \delta(\omega r_e(l+2) - \zeta) \end{pmatrix} \begin{pmatrix} a_0 \\ a_1 \end{pmatrix} = 0. \quad (59)$$

Non-zero solutions exist if

$$\omega(l+1) = m[\omega r_e(l+1) - \zeta][\omega r_e(l+2) - \zeta] \quad (60)$$

i.e. if the parameters of the radial equation are related in a specific way. The corresponding wavefunction reads

$$\phi_{nl}^{(p=1)}(r) \sim (1 + br)r^{l+1} e^{-m\omega(r-r_e)^2/2} \quad (61)$$

where  $b = a_1/a_0 = \delta\omega/[\zeta - \omega r_e(l+2)]$  and  $n = 0$  if  $b > 0$  (nodeless function) or  $n = 1$  if  $b < 0$ . Similar, but more complicated analytical solutions may be derived for  $p = 2, 3, \dots$ .

The case of  $r_e = 0$ , corresponding to a pair of particles interacting by Coulomb forces and confined in a harmonic oscillator potential, deserves a special attention. As one can see from Eq. (57), if  $r_e = 0$  then the analytical solutions for  $p = 0$  exist only if  $\zeta = 0$ . These solutions exist for an arbitrary  $\omega$  and correspond to a spherical harmonic oscillator. For  $p = 1$  instead of condition (60) we have

$$\omega = \frac{m\zeta^2}{(l+1)} \quad (62)$$

and  $b = \delta m\zeta/(l+1)$ . Thus, if the Coulomb interaction is repulsive (as it is in harmonium) then  $b > 0$  and the wavefunction (61) is nodeless. Thus, it describes the ground state. If it is attractive (as it is in the confined positronium) then  $b < 0$  and the wavefunction has a node at  $r = -1/b$ . Thus, it describes the first excited state. Explicitly, the radial wavefunction for  $p = 1$  is given by

$$\phi(r) \sim r^{l+1} \left[ 1 + \frac{\delta m\zeta}{(l+1)} r \right] e^{-[m^2\zeta^2/2(l+1)]r^2}. \quad (63)$$

If we remember that in the case of three- and four-particle systems  $r$  has to be replaced by the interparticle distance  $r_{12}$ , Eq. (63) gives the exact  $r_{12}$ -

dependence of the wavefunction. In particular, by setting  $\zeta = 1$ ,  $l = 0$  and  $m = 1/2$  (the reduced mass of two particles of unit mass) one can easily extract from Eq. (63) the celebrated  $1 + r_{12}/2$  term of Kato<sup>20</sup>. Another interesting feature of the Hooke atoms is an interplay between the effects of the electron correlation and the effects of spacial confinement, i.e. between the influence of  $\omega$  and  $\zeta$  on the form of the wavefunction and on the structure of the spectrum. A detailed analysis<sup>5</sup> leads to the conclusion that, in harmonium, there are two different regimes: Low correlation (if  $\omega > \zeta$ ) and high correlation (if  $\omega \ll \zeta$ ). Plots of the ground state densities for different values of the interaction parameters are shown in Fig. 3. As one can see, with increasing correlation the maximum of the density is shifted towards larger values of  $r$ , i.e. towards larger distances between the particles.

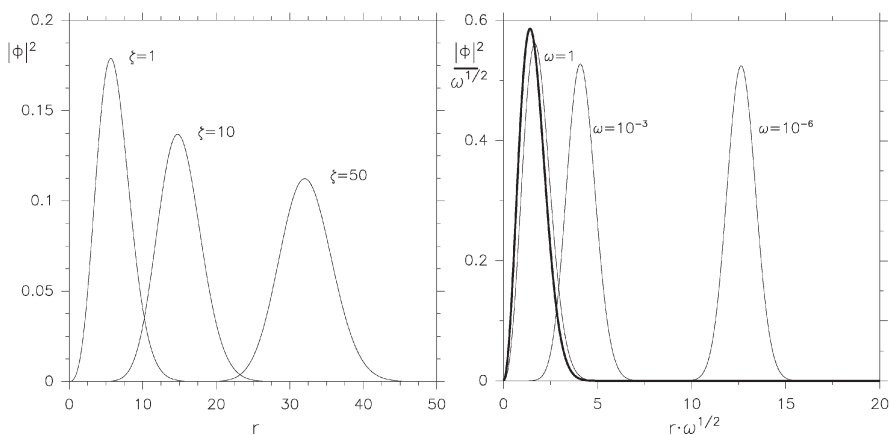


FIG. 3

The dependence of the radial density distribution in the ground state ( $n = l = 0$ ) on the parameters of the Hamiltonian in Eq. (45). In all cases  $r_e = 0$ . Left panel:  $m = 1/2$ ,  $\omega = 2$ . Right panel:  $m = 1/2$ ,  $\zeta = 0$  (thick line – in this case the same curve corresponds to all values of  $\omega$ ) and  $\zeta = 1$  (thin lines); three values of  $\omega$  correspond to high, medium and low correlation regime of harmonium

### FINAL REMARKS

The Schrödinger equation for a systems of particles in which disjoint pairs interact by arbitrary two-particle potentials while the remaining interactions are described by harmonic oscillator potentials proved to be separable. Among special examples of this model the ones known as the Hooke atoms and the Hookean molecules are particularly interesting in the context of quantum-chemical applications. As a result of the separation of the

pertinent many-particle Schrödinger equations all these cases are reduced to a set of spherically-symmetric one-particle eigenvalue equations. For a large set of physically interesting interaction potentials the corresponding radial equations are either exactly or quasi-exactly solvable. Their analysis, apart of the academic curiosity, supplies interesting data on the nature of various schemes of separability. In particular, it allows for an analysis of the electron correlation problems and of the nature of the Born–Oppenheimer approximation from a new perspective.

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