Few-particle systems: quasi-exactly solvable models

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Abstract. Several quasi-exactly solvable models of few-particle systems are discussed. In particular, the Hooke atom (also known as harmonium) and its extensions appropriate to a description of non-Born-Oppenheimer one- and two-electron diatomic molecules are presented. Also several methods of construction of quasi-exactly solvable Schrödinger equations are described.

1. Introduction
A model for which all solutions of the pertinent Schrödinger equation may be obtained in the analytic form is referred to as exactly solvable. If only some specific solutions may be expressed analytically then the model is called quasi-exactly solvable. Exactly solvable models play a special role in theory of many-electron systems. Many methods in this theory have been derived in a more or less straightforward way from exactly solvable models such as the hydrogen-like atom or the harmonic oscillator. Besides, exactly solvable models supply opportunities for checking correctness and ranges of applicability of a variety of approximations and give us most important guidelines for the construction of atomic and molecular wavefunctions. In particular, the general form of atomic orbitals as well as the shell structure of atoms have been derived from the basic knowledge of the exact solutions of the Schrödinger equation for the hydrogen-like atom. Last but not least, exactly solvable models are very interesting from the point of view of pure academic curiosity. Though the exactly solvable models have been intensively studied since the outset of quantum mechanics, the importance of the ones which are quasi-exactly solvable has been fully recognized relatively recently.

It is well known that the Schrödinger equation for two unconfined interacting particles may always be reduced to a system of two one-particle equations: One for the relative motion of the particles and another one for the motion of the center of the mass. In general, this separation is impossible if the motion of the particles is confined by an external potential (e.g. two interacting electrons confined by a Coulomb potential modelling a helium-like atom). However, as one can easily see, a parabolic confinement does not obstruct the separability. The resulting system is known as the Hookean atom or harmonium. This system was studied since the sixties of the last century as a base for a better understanding of the electron correlation mechanism [1]. The analytic solutions to the problem were for the first time found by Santos [2]. Then the system was rediscovered several times (see e.g. [3, 4]). A detailed analysis of its spectrum and studies on related systems may be found in references [5, 6]. It appears that only a small fraction of all solutions of the Schrödinger equation describing harmonium may be expressed analytically. Thus, harmonium is an example of a quasi-exactly solvable model. It is also the best known...
example, and probably the most important one, as far as applications in atomic and molecular physics are concerned.

During the last two decades several new quasi-exactly solvable models have been constructed [7–11]. Also the well known Calogero model, formulated in 1971 [12], has been extended [13] and applied in atomic and molecular physics [14, 15].

Two simple properties of quadratic forms: (1) A linear combination of quadratic forms is a quadratic form, and (2) A linear transformation of the variables transforms a positive definite quadratic form to a diagonal form with positive coefficients, imply that also a Hookean molecule can be reduced to a similar, quasi-exactly solvable problem. Recently constructed quasi-exactly solvable models of molecules [16–19] offer a possibility of an analysis of the Born-Oppenheimer approximation from a new perspective.

Among the less known approaches to the problem of exact solubility one should mention the ones based on the properties of the triconfluent Heun equation [20–24]. The resulting Schrödinger equations are quasi-exactly solvable for several potentials with fractional powers of the interparticle distance.

The problem is more difficult in the case of relativistic systems. However, several examples of exactly and quasi-exactly solvable models described by either Dirac or Klein-Gordon equation have recently been discussed [25–30].

Quasi-exact solubility is usually related to symmetry properties of the pertinent system [31]. Some relevant information on these most interesting and important relations may be found in references [32–35].

2. Confinement and separability

A non-relativistic Hamiltonian describing two interacting particles

\[ H_0(r_1, r_2) = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(|r_1 - r_2|), \]

by introducing the center of the mass and the relative coordinates:

\[ R = \frac{m_1}{M} r_1 + \frac{m_2}{M} r_2, \quad r = r_1 - r_2, \]

where \( M = m_1 + m_2 \), may be expressed as

\[ H_0(r_1, r_2) = H_{0R}(R) + H_{0r}(r) = \frac{p_R^2}{2M} + \frac{p_r^2}{2\mu} + V(r), \]

with \( \mu = m_1 m_2 / M \). The resulting Schrödinger equation may be separated to two equations: One for the center of mass and another one for the relative motion. Consequently, the spectrum is composed of two parts: One of the center of mass and one of the relative motion. The relative motion can also be interpreted as a motion of a quasi-particle of mass \( \mu \) confined in an external potential \( V(r) \).

In general, the Hamiltonian of two confined particles,

\[ H(r_1, r_2) = H_0(r_1, r_2) + W(r_1, r_2) \]

is not separable. A particular confinement which retains the separability is the harmonic one

\[ W = a_1^2 r_1^2 + a_2^2 r_2^2 \]

with

\[ \frac{a_1^2}{a_2^2} = \frac{m_1}{m_2}. \]
Relation (6) is known as the *separability condition*. Thus, if
\[ a_1^2 = \frac{1}{2} m_1 \omega^2, \quad \text{and} \quad a_2^2 = \frac{1}{2} m_2 \omega^2 \] then, under transformation (2),
\[ H(r_1, r_2) = H_R(R) + H_r(r), \]
with
\[ H_R(R) = \frac{p_R^2}{2M} + \frac{M \omega^2}{2} R^2 \]
and
\[ H_r(r) = \frac{p_r^2}{2\mu} + V(r) + \frac{\mu \omega^2}{2} r^2. \]
In this case the center of mass equation corresponds to a spherical harmonic oscillator. Consequently, its energy is discrete and transforms to continuum at the limit of \( \omega = 0 \). The relative motion equation is also spherically-symmetric. Its radial part reads
\[ \left[ -\frac{1}{2\mu} \frac{d^2}{dr^2} + \frac{l(l+1)}{2\mu r^2} + V(r) + \frac{\mu \omega^2}{2} r^2 \right] \phi_{nl}(r) = E_{nl} \phi_{nl}(r). \]
This equation may model a large number of systems, as e.g. pairs of identical particles (electrons, protons), pairs of different particles (electron-positron, electron-proton, etc), a charged particle and a neutral or ionized atom, two atoms, two quarks, etc. Depending on the case, the interaction potential may be either of a Coulomb type or of any other form.

A Born-Oppenheimer atom or molecule may be interpreted as a number of electrons confined in a potential \( W \) generated by one or several, properly distributed, point charges. In the case of a Coulomb interaction potential
\[ V = \frac{\zeta}{|r_1 - r_2|} = \frac{\zeta}{r}, \]
a helium-like atom is modelled by the confinement
\[ W = -\frac{Z}{r_1} - \frac{Z}{r_2} \]
and a hydrogen molecule – by
\[ W = \sum_{j=1}^{2} \left[ \frac{1}{|r_j - D/2|} + \frac{1}{|r_j + D/2|} \right], \]
where \( D \) is the distance between the two point charges, i.e. the bong length. The harmonic confinement
\[ W = k \left( r_1^2 + r_2^2 \right) \]
generates a quasi-exactly solvable Hooke atom (harmonium). The so called Hookean hydrogen molecule is defined by
\[ W = \sum_{j=1}^{2} k \left[ (r_j - D/2)^2 + (r_j + D/2)^2 \right] = 2k \left( r_1^2 + r_2^2 \right) + kD^2 \]
Then, a Born-Oppenheimer Hookean \( H_2 \) molecule is equivalent to harmonium.
3. Harmonium and related systems

Let us consider two particles of the same mass with either the same or with the opposite electric charges, e.g. two electrons or an electron-positron pair respectively, interacting by the Coulomb force. If we set, for simplicity, \(m_1 = m_2 = 1\) then, \(\mu = 1/2\) and the radial equation describing the relative motion of the particles reads

\[
\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + \frac{\omega^2}{4} r^2 + \frac{\zeta}{r}\right] \phi_{nl}(r) = E_{nl} \phi_{nl}(r),
\]

where \(\zeta\) is the product of the electric charges of the particles, i.e. \(\zeta > 0\) corresponds to a repulsive and \(\zeta < 0\) to an attractive potential. These two cases are usually referred to, respectively, as harmonium and as confined positronium [6]. An asymptotically correct solution may be written as

\[
\phi_{nl}(r) = i^{l+1} e^{-\omega r^2/4} P^{(p)}_{nl}(r).
\]

The substitution

\[
P^{(p)}_{nl}(r) = \sum_{i=0}^{p} a_i r^i
\]

leads to [4]

\[
A_i a_i + B_{i+1} a_{i+1} + C_{i+2} a_{i+2} = 0,
\]

with

\[
A_i = E - \omega(i + l + 3/2), \quad B_i = -\zeta, \quad C_i = i(i + 2l + 1).
\]

In order to terminate the recurrence and to determine the coefficients of the polynomial (19) we need two conditions: One for the energy and one for either \(\omega\) or \(\zeta\). Note, that in the case of exactly solvable systems (e.g. the hydrogen atom) we have a two-step recurrence: \(\tilde{A}_i \tilde{a}_i + \tilde{B}_{i+1} \tilde{a}_{i+1} = 0\). The recursion terminates at \(a_p\) if

\[
E = \omega(p + l + 3/2),
\]

i.e. if \(A_i = \omega(p - i)\). The non-trivial solutions \(a_0, a_1, \ldots, a_p\) exist if

\[
\begin{vmatrix}
-\zeta & 1(2l+2) & 0 & \cdots & 0 & 0 & 0 \\
p \omega & -\zeta & 2(2l+3) & \cdots & 0 & 0 & 0 \\
0 & (p-1) \omega & -\zeta & \cdots & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & \cdots & 2 \omega & -\zeta & p(2l+p+1) \\
0 & 0 & 0 & \cdots & 0 & \omega & -\zeta
\end{vmatrix} = 0.
\]

Consequently, \(\omega = \omega(\zeta, l, p)\).

If \(p = 0\) then the analytic solution exists for \(\zeta = 0\) only (non-interacting particles in a parabolic confinement). The value of \(\omega\) is arbitrary and \(E = \omega(l + 3/2)\). If \(p = 1\) then

\[
\omega = \frac{\zeta^2}{2(l+1)} , \quad E = \frac{\zeta^2}{4(l+1)} 2l + 5.\]

If \(p = 2\) then

\[
\omega = \frac{\zeta^2}{2(4l+5)} , \quad E = \frac{\zeta^2}{4(4l+5)} 2l + 7.\]
Figure 1. Excitation energies (relative to the ground state) in the spectrum of $H_r$ with $V(r) = 1/r$ and $\mu = 1/2$, versus $\ln \omega$. Left panel: The energies scaled by $\omega^{-1}$; each energy level, at the large $\omega$ limit, is labelled by quantum numbers $(n, l)$. Right panel: The energies corresponding to $n = 0$ scaled by $\omega^{-4/3}$.

$$\phi \sim r^{l+1} \left(1 + \frac{\zeta r}{2(l+1)} + \frac{(\zeta r)^2}{4(l+1)(4l+5)} \right) \exp \left[ -\frac{(\zeta r)^2}{8(4l+5)} \right].$$

(27)

As we see, for $\zeta > 0$ the wavefunctions (25) and (27) are nodeless and both correspond to the ground state. For $\zeta < 0$ the case of $p = 1$ corresponds to the first and the case of $p = 2$ to the second excited state.

Only a very small fraction of solutions of equation (17) may be expressed analytically. It is interesting to note that a solution is analytic if and only if the energy of harmonium is the same as one of the energies of the confined positronium [11]. The energies of all solutions of harmonium, corresponding to 16 lowest energy states are plotted, versus $\ln \omega$, in the left panel of figure 1. One can see an interesting correlation pattern between the large $\omega$ (asymptotically corresponding to a spherical harmonic oscillator) and the small $\omega$ limit, in which all energy levels corresponding to a given quantum number $n$ are quasi-degenerate. For small $\omega$ the energy may be expressed as

$$E_{nl} = E_{00} + \omega \left[ \sqrt{3} n + (\omega/2)^{1/3} l(l+1) + \cdots \right].$$

(28)

A plot of small $\omega$ limit of the ground state area, scaled by $\omega^{-4/3}$, is shown in the right panel of figure 1 [6].

Hookean molecules form another very interesting class of quasi-exactly solvable systems. The corresponding models have been constructed very recently by Lopez, Ludeña and Ugalde [16–19]. The positive ion of the hydrogen molecule is modelled by the Hamiltonian

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \frac{p_3^2}{2m_3} + V(r_{12}) + \frac{m_1 \omega_1^2}{2} r_{13}^2 + \frac{m_2 \omega_2^2}{2} r_{23}^2. \quad (29)$$

Under the separability condition $\omega_1 = \omega_2 = \omega$, transformation (2) supplemented by

$$Q = \frac{m_1 r_1 + m_2 r_2 + m_3 r_3}{m_1 + m_2 + m_3} \quad \text{and} \quad q = R - r_3 \quad (30)$$

results in

$$H = H_0(Q) + H_i(r) + H_q(q). \quad (31)$$
with $H_0(Q) = P^2/2M$ describing the free motion of the centre of the mass,

$$H_0(r) = \frac{P^2}{2\mu} + V(r) + \frac{\mu \omega^2}{2} r^2$$

(32)

describing the relative motion of particles 1 and 2, and

$$H_1(q) = \frac{P_q^2}{2\mu_t} + \frac{M \omega^2}{2} q^2,$$

(33)

with $M = m_1 + m_2$, $M = \mathfrak{m} + m_3$, $\mu_t = \mathfrak{m} m_3 / M$, describing the motion of the centre of the mass of particles 1 and 2 in the harmonic oscillator potential associated with particle 3. As we see, if $V$ is a Coulomb potential then equation (32) corresponds to a harmonium. Equation (33) describes a spherical harmonic oscillator.

A hydrogen molecule and other systems composed of four interacting particles may be modelled by the Hamiltonian

$$H = \left[ \frac{p_1^2}{2M} + \frac{p_2^2}{2M} + \frac{ZM^2}{r_{12}} \right] + \left[ \frac{p_3^2}{2m} + \frac{p_4^2}{2m} + \frac{Zm^2}{r_{34}} \right] + \frac{\omega^2}{2} \left[ r_{13}^2 + r_{14}^2 + r_{23}^2 + r_{24}^2 \right].$$

(34)

The transformation

$$\rho = r_1 - r_2, \quad P = \frac{M(r_1 + r_2) + m(r_3 + r_4)}{2(m + M)},$$

$$r = r_3 - r_4, \quad q = \frac{1}{2}(r_1 + r_2 - r_3 - r_4)$$

(35)

decouples the Hamiltonian to four one-particle Hamiltonians:

$$H_r = \frac{p_r^2}{m} + \frac{\omega^2 r^2}{2} + \frac{Z_m^2}{r}, \quad H_\rho = \frac{p_\rho^2}{M} + \frac{\omega^2 \rho^2}{2} + \frac{Z_M^2}{\rho},$$

(36)

$$H_q = \frac{p_q^2}{4\mu} + 2\omega^2 q^2, \quad H_P = \frac{p_P^2}{4(m + M)},$$

(37)

where $\mu = mM/(m + M)$. Again, the problem has been reduced to harmonium. More precisely, to two decoupled pairs of Coulomb-interacting particles in a harmonic confinement.

**4. Searching for quasi-exactly solvable equations**

The relative motion radial equation (17) may be rewritten as

$$V(r) + \frac{\omega^2 r^2}{4} - E = \frac{1}{\phi} \frac{d^2 \phi}{dr^2} - \frac{l(l+1)}{r^2}$$

(38)

Let us assume that the ground-state wavefunction can be expressed in the form:

$$\phi(r) \sim r^{l+1}(1 + r/b) e^{Q(r)}, \quad b > 0.$$ 

(39)

Then

$$V(r) + \frac{\omega^2 r^2}{4} - E_0 = Q'' + Q' \left[ Q' + \frac{2(l+1)}{r} + \frac{2}{b + r} \right] + \frac{2(l+1)}{r(b+r)}.$$ 

(40)

Using equation (40) one can generate potentials corresponding to arbitrarily chosen $Q$. In particular, this equation may be used as a starting point for the construction of quasi-exactly solvable models. Here are several examples and many more can be easily generated:
One of remarkable theorems concerning this equation says that if
\[ Q = -\frac{\omega r^2}{4} \Rightarrow V(r) = \frac{\zeta}{r} - \frac{\zeta - b\omega}{b + r}, \quad \zeta = \frac{2(l + 1)}{b}. \]
In a special case of \( b\omega = \zeta \) we get \( V = \zeta/r \), i.e. harmonium or confined positronium, depending on the sign of \( \zeta \).

\[ Q = -\frac{\omega (r - r_c)^2}{4} \Rightarrow V(r) = \frac{\zeta}{r} + a r \text{ and } V(r) \sim (r - r_c)^2 \text{ – correspond to the Ghosh and Samantha model [3] as well as to the harmonic approximation of the ro-vibronic motion of a diatomic molecule} \]

\[ Q = -\frac{A r^{q+1}}{q+1} \Rightarrow V = A^2 r^{2q} - A(q + 2l + 2)r^{q-1} - \omega^2 r^2/4 \text{ – yields a family of anharmonic oscillators.} \]

In the case of excited states we may assume that \( \phi(r) \sim r^\gamma P(r) e^{Q(r)} \) with \( P(r) = \sum_{i=0}^{p} a_i r^i \). Then equation (38) yields
\[ r P'' + 2P' \left( \gamma + r Q' \right) + r P(T + E) = 0, \tag{41} \]
where
\[ T = Q'' + Q' \left( Q' + \frac{2\gamma}{r} \right) - V - a r^2. \tag{42} \]

The resulting potentials leading to quasi-exactly solvable Schrödinger equations include:

| V | Q | \( \gamma \) |
|---|---|---|
| \( ar^b + br^a + cr \) | \( Ar^a + Br^b \) | \( l + 1 \) |
| \( ar^2 + br + \frac{\zeta}{r} \) | \( Ar^2 + Br \) | \( l + 1 \) |
| \( ar^2 + \frac{br^2}{1 + \gamma} \) | \( Ar^2 \) | \( l + 1 \) |
| \( a \frac{r}{r} + \frac{b}{c + \gamma} \) | \( Ar \) | \( l + 1 \) |
| \( \frac{a}{r} + \frac{b}{r^2} + \frac{c}{r^3} + \frac{d}{r^4} \) | \( A s + \frac{B}{r^4} \) | \( 3 - \frac{c}{2\sqrt{3}} \) |
| \( a + \frac{b}{r^2} + \frac{c}{r^3} + \frac{d}{r^4} \) | \( Ar + \frac{B}{r} \) | \( 1 + \frac{c}{2\sqrt{3}} \) |

Several quasi-exactly solvable equations with potentials containing fractional powers may be derived from the triconfluent Heun equation [20, 21]
\[ F''(r) + \left( a - \frac{b^2}{4} + 3nr - \frac{3b}{2}r^2 - \frac{9}{4}r^4 \right) F(r) = 0, \quad n = 1, 2, 3, \ldots \tag{43} \]

One of remarkable theorems concerning this equation says that if
\[ D_n = \begin{vmatrix} a & -b & 2 \cdot 1 & \cdots & \cdots & 0 \\ 3(n-1) & a & -2b & \cdots & \cdots & 0 \\ 0 & 3(n-2) & a & \cdots & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & 3 \cdot 2 & a & -(n-1)b \\ 0 & 0 & \cdots & \cdots & 3 \cdot 1 & a \end{vmatrix} = 0, \tag{44} \]
then the Heun equation (43) has a solution
\[ F(r) \sim e^{-(r^3 + br)/2} P_{n-1}(r) \tag{45} \]
and the coefficients of the polynomial \( P \) are equal to the components of the eigenvector of \( D \).

One can easily see that the transformation
\[ \rho = (r/\alpha)^{1/\lambda}, \quad F(r) \sim \rho^{(\lambda - 1)/2} \Psi(\rho) \tag{46} \]
leads to a Schrödinger-like equation for $\Psi$:

$$\Psi'' + \left( \frac{1 - \lambda^2}{4\rho^2} + (\alpha\lambda)^2 W \right) \Psi = 0 \quad (47)$$

with

$$W = \left[ a - b^2/4 + 3\alpha\rho^\lambda - 3\alpha^2b\rho^{2\lambda} - \frac{9}{2}\alpha^4\rho^{4\lambda} \right] \rho^{2\lambda-2} \quad (48)$$

The equation for $\Psi$ transforms to a Schrödinger equation if one of the powers in $W$ vanishes. Then $W$ may be expressed as $E - V$. Hence, there are four different potentials derived from the Heun equation and giving quasi-exactly solvable Schrödinger equations:

| $\lambda$ | powers of $\rho$ |
|-----------|------------------|
| $1$       | $0$ $1$ $2$ $3$  |
| $\frac{1}{2}$ | $-\frac{2}{3}$ $0$ $\frac{2}{3}$ $2$ |
| $\frac{1}{2}$ | $-1$ $-\frac{1}{2}$ $0$ $1$ |
| $\frac{1}{2}$ | $-\frac{4}{3}$ $-1$ $-\frac{2}{3}$ $0$ |

5. Final remarks

- Harmonium is a fascinating model for studying properties of interacting systems. It may be a starting point for the construction of many-particle models and opens a possibility of a precise analysis of models derived from the approximate separability of the Schrödinger equation, as the one-electron model, the Born-Oppenheimer approximation, etc.

- Harmonium is also a prototype for a class of quasi-exactly solvable Schrödinger equations in which the analytic solutions are of the form $\Psi = P(r) \exp[Q(r)]$, where $P$ and $Q$ are polynomials and $Q$ is the same for all analytic solutions. Coefficients of $P$ are determined by a three-step recurrence. The termination of the recurrence and the secular equation define constraints on both energy and the parameters of the potential.

- The analytic solutions exist only for a specific set of the coupling constants defining the Hamiltonian and only a subset of all solutions corresponding to these coupling constants is expressible in an analytic form. The analytic solutions exhibit specific properties by which they differ in an essential way from the other solutions. These properties reflect a hidden dynamical symmetry responsible for the existence of the analytic solutions.

- Among less known equations of a particular interest is the Heun equation. It leads to a Schrödinger equation in which quasi-exact solubility is based on a four-term recurrence. More systems of this kind are still to be looked for.

- Relativistic generalizations are interesting but still very little has been done

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