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Time-Dependent 4*D* Quantum Harmonic Oscillator and Reacting Hydrogen Atom

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Abstract: With the help of low-dimensional reference equations (ordinary differential equations) and the corresponding coordinate transformations, the non-stationary 4*D* quantum oscillator in an external field is reduced to an autonomous form. The latter, in particular, reflects the existence of a new type of dynamical symmetry that reduces the equation of motion of a non-stationary oscillator to an autonomous form that does not change with time. By imposing an additional constraint on the wave function of the isotropic oscillator, we have obtained the total wave functions of the reacting hydrogen atom in two different cases: (a) when the non-stationary frequency has two asymptotic values and there is no external field; and (b) when, in addition to the non-stationary frequency, an external force acts on the hydrogen atom. The transition *S*-matrix elements of various elementary atomic–molecular processes are constructed. The probabilities of quantum transitions of the hydrogen atom to others, including new bound states, are studied in detail, taking into account the influence of external forces.

Keywords: time-dependent 4*D* quantum oscillator; reference equation method; dynamical symmetry; hydrogen atom in external field; transition *S*-matrix element

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1. Introduction

The hydrogen atom still remains one of the most important systems for research due to its wide application in practice, and it is also a reference problem for testing new theoretical concepts of non-relativistic quantum mechanics. In addition, it is well known that the hydrogen atom is perhaps the most important and rich in hidden symmetries system in quantum physics. Already from Pauli's investigation, the Lie algebra of the symmetry group can be identified as $SO(4)$. However, a reasonable question arises: where does this "accidental" symmetry come from? Fock addressed this question thoroughly in his celebrated work "On the theory of the hydrogen atom" [1] and explained the degeneracy of the energy levels of the Kepler problem (or hydrogen atom) in terms of the dynamical symmetry group $SO(4)$. In particular, he showed that if one makes a stereographic projection in momentum space and rescales momenta with energy eigenvalues, then the problem is equivalent to a geodesic flow on a sphere with unit radius $\mathbb{S}^3$. A dynamical symmetry group isomorphic to $O(4)$ was used by Schwinger [2] to derive the Green's function of the Coulomb field in the momentum representation, but a more complete discussion of the group theory application to the hydrogen atom was given by Bander and Itzykson [3].

As a generalization of Levi–Civita's parabolic coordinates, Kustaanheimo and Stiefel [4] introduced a coordinate transformation as applied to the corresponding classical problem. Boiteux used these coordinate transformations and proved that the bound states of the hy-

drogen atom correspond to the energy states of a $4D$ isotropic oscillator with one additional constraint [5].

The main goal of this work is to construct a mathematically rigorous and consistent representation of the *reacting hydrogen atom* (RHA) using the explicit and hidden symmetries of a $4D$ isotropic harmonic oscillator. Recall that RHA is understood to mean a hydrogen atom that is free in the (in) asymptotic state, while in the (out) asymptotic state, as a result of an elementary atomic–molecular process, it transits to another quantum state, including the possibility of forming a bound state with another atom or molecule (chemical reaction).

To achieve this goal from a mathematical point of view, it is necessary to solve the problem of separating variables in a second-order *partial differential equation* (PDE) of a fairly general form, which in itself is a very complex and important independent mathematical problem. Note that as Miller showed in his monograph [6], the problem of separation of variables in PDE is closely related to one of the most powerful methods of modern mathematics and mathematical physics, namely the theory of Lie algebras.

In this paper, at the first stage, it is shown that with the help of the so-called reference equations, i.e., a system of four ordinary differential equations of small dimension, the original non-stationary Schrödinger equation for an isotropic $4D$ oscillator is reduced to an autonomous form with a constant frequency. At the second stage, using coordinate transformations and imposing an additional constraint on the wave function, the initial equation for the oscillator is reduced to the equation of a hydrogen atom in an external field. In the third stage, we construct the S-matrix elements of the transitions and the probabilities of the corresponding elementary processes involving the hydrogen atom.

In conclusion, the question of the further development of the theory of the reacting hydrogen atom is considered in detail, taking into account its presence in a medium with a finite temperature. The latter can be extremely useful for its wide use in solving many applied problems in physics and chemistry.

2. Statement of the Problem

Let us consider the problem of a $4D$ oscillator with a non-stationary frequency under the action of an external force:

$$i\frac{\partial \Psi}{\partial t} = \hat{\mathrm{H}}(\mathbf{x}, t)\Psi, \qquad \mathbf{x} = (x_1, \ldots, x_4) \in \mathbb{R}^4, \tag{1}$$

where $\mathbb{R}^4$ denotes the $4D$ configuration space and the operator $\hat{\mathrm{H}}(\mathbf{x}, t)$ is the Hamiltonian of the $4D$ *quantum harmonic oscillator* (QHO), which is represented in the following form:

$$\hat{\mathrm{H}}(\mathbf{x}, t) = \sum_{l=1}^{4} \left\{ -\frac{1}{2}\frac{\partial^2}{\partial x_l^2} + \frac{1}{2}\Omega^2(t)x_l^2 - F(t)x_l \right\}, \qquad x_l, t \in (-\infty, +\infty). \tag{2}$$

Mind that Equations (1) and (2) are written in units of $m = \hbar = 1$, where m is the mass of the oscillator and $\hbar$ is the Plank constant.

We suppose that the problem is described by two (in), (at $t \to -\infty$) and (out), (at $t \to +\infty$) asymptotic subspaces. In particular, let the frequency $\Omega(t)$ and the external force $F(t)$ satisfy the following conditions:

$$\lim_{t \to \pm\infty} \Omega(t) = \Omega_{\pm}, \qquad \lim_{t \to \pm\infty} F(t) = 0, \tag{3}$$

where Ω_- and Ω_+ denote constant frequencies in the (in) and (out) asymptotic subspaces, respectively.

Based on the conditions (3), it follows that the quantum system in the asymptotic subspaces (in) and (out) is described by pure states of orthonormal $4D$ bases of an isotropic oscillator.

Below, we will consider two typical cases:

1. When there is no external force acting on the non-stationary oscillator, i.e., $F(t) \equiv 0$ and we have the case of a *quantum parametric oscillator* (QPO), and

2. When an external force acts on the non-stationary oscillator, i.e., $F(t) \neq 0$.

3. Reduction of the 4*D* QHO Equation to the Autonomous Form

Let us consider the classical oscillator problem, which will play a key role in the further constructions. Without taking into account external influence, it satisfies the following homogeneous second-order *ordinary differential equation* (ODE):

$$\ddot{\xi} + \Omega^2(t)\xi = 0, \qquad \dot{\xi} = d\xi/dt. \tag{4}$$

The solution of Equation (4) will be sought in the form:

$$\xi(t) = \sigma(t)e^{i\gamma(t)}, \qquad \sigma(t) = |\xi(t)|, \quad \gamma(t) = \int_{-\infty}^{t} \frac{dt'}{\sigma^2(t')}, \tag{5}$$

where $\sigma(t)$ specifies the length scale at time t, and $\tau = \gamma(t)/\Omega_-$ denotes the corresponding time scale.

It is assumed that the solution $\xi(t)$ satisfies the initial condition:

$$\xi(t) \sim e^{i\Omega_- t}, \quad at \quad t \to -\infty. \tag{6}$$

As a consequence, it is obvious that $\lim_{t\to-\infty} \sigma(t) = 1$.

Now, let us consider the equation of an oscillator that is affected by an external force:

$$\ddot{\eta} + \Omega^2(t)\eta - F(t) = 0, \qquad \eta(-\infty) = \dot{\eta}(-\infty) = 0. \tag{7}$$

Using Green's function method (see for example [7]), we can construct the solution of the inhomogeneous Equation (7) by representing it in terms of the complex solution of the homogeneous Equation (4):

$$\eta(t) = \frac{1}{\sqrt{\Omega_-}}\left\{\xi^*(t)\, d(t) + \xi(t)\, d^*(t)\right\}, \quad d(t) = \frac{i}{\sqrt{\Omega_-}} \int_{-\infty}^{t} \xi(t')F(t')dt'. \tag{8}$$

3.1. The Parametric Quantum Oscillator

Given the representation (5) and the condition (6) (see also [7]), the solution of Equations (1) and (2) can be written as:

$$\Psi(\mathbf{x}, t) = \left(\frac{1}{\sigma^2}\prod_{l=1}^{4} \exp\left\{-\frac{i}{2}\frac{\dot{\sigma}}{\sigma}x_l^2\right\}\right)\Psi_-(\mathbf{y}, \tau), \tag{9}$$

where $\dot{\sigma} = d\sigma/dt$ denotes the derivative with respect to time, and $\Psi_-(\mathbf{y}, \tau)$ is the wave function of a 4*D isotropic harmonic oscillator* (IHO) with constant frequency Ω_-. In addition, $\mathbf{y} = (y_1, \ldots, y_4)$ is the displacement of the quantum oscillator in the 4*D* space, and $y_l = x_l/\sigma(t)$ denotes a new space coordinate.

Substituting the expression (9) into Equations (1) and (2) and taking into account (4), we obtain the following Schrödinger equation:

$$i\frac{\partial}{\partial\tau}\Psi_- = \frac{1}{2}\sum_{l=1}^{4}\left[-\frac{\partial^2}{\partial y_l^2} + \Omega_-^2 y_l^2\right]\Psi_-, \tag{10}$$

where $\{\mathbf{y}, \tau\}$ denotes a new space–time.

It is easy to see that (10) is an autonomous equation that does not change its form during the evolution. In other words, with the help of an ordinary differential Equation (4), which we will call a low-dimensional reference equation, the master Equations (1) and (2) are reduced to an autonomous form. The latter obviously reflects the presence of a hidden dynamical symmetry in the quantum system under consideration. The sequence of mathe-

matical operations that makes it possible to reduce the master equation to an autonomous form will be referred to below as the *reference equation method* (REM).

Let us consider the new coordinate system $(y_1, y_2, y_3, y_4) \mapsto (r, \theta, \phi, \psi)$ first proposed by Kustaanheimo and Stiefel (KS transformation) [4] (see also [8]):

$$\begin{aligned} y_1 &= r\cos\left(\frac{\theta}{2}\right)\cos\left(\frac{\phi+\psi}{2}\right), \qquad y_2 = r\sin\left(\frac{\theta}{2}\right)\cos\left(\frac{\phi-\psi}{2}\right), \\ y_3 &= r\cos\left(\frac{\theta}{2}\right)\sin\left(\frac{\phi+\psi}{2}\right), \qquad y_4 = r\sin\left(\frac{\theta}{2}\right)\sin\left(\frac{\phi-\psi}{2}\right), \end{aligned} \tag{11}$$

where $r = \sqrt{\sum_{l=1}^{4} y_l^2}$, in addition, $\phi \in [0, 2\pi]$ and $\theta, \psi \in [0, +\pi]$.

The length element in these coordinates would be:

$$ds^2 = dr^2 + \frac{r^2}{4}\left(d\theta^2 + d\phi^2 + d\psi^2 + 2\cos\theta d\phi d\psi\right).$$

Rewriting Equation (10) in the new coordinates and replacing $r^2 = \varrho$, we can find the following equation for the $4D$ IHO:

$$\begin{aligned} i\frac{\partial}{\partial\tau}\breve{\Psi}_- = -2\Bigg\{&\frac{1}{\varrho}\frac{\partial}{\partial\varrho}\left(\varrho^2\frac{\partial}{\partial\varrho}\right) + \frac{1}{\varrho}\Bigg[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \\ &\frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2} + \frac{\partial^2}{\partial\psi^2} - 2\cos\theta\frac{\partial^2}{\partial\phi\partial\psi}\right)\Bigg] - \frac{1}{4}\Omega_-^2\varrho\Bigg\}\breve{\Psi}_-. \end{aligned} \tag{12}$$

Recall that $\breve{\Psi}_-(\{\boldsymbol{\varrho}\}, \tau) = \Psi_-(\mathbf{y}, \tau)$ is the wave function of the IHO in the new coordinates; in addition, the following notation is used for the set of new coordinates; $\{\boldsymbol{\varrho}\} = (\varrho, \theta, \phi, \psi) \in \mathbb{R}^4$.

Since Equation (14) has an autonomous form, its solution can be represented as:

$$\breve{\Psi}_-(\{\boldsymbol{\varrho}\}, \tau) = e^{-iE\tau}\Lambda(\{\boldsymbol{\varrho}\}), \tag{13}$$

where E denotes the total energy of the $4D$ IHO in **the** new space–time. Substituting (13) into Equation (14), we obtain:

$$\left\{\frac{1}{\varrho}\frac{\partial}{\partial\varrho}\left(\varrho^2\frac{\partial}{\partial\varrho}\right) + \frac{1}{\varrho}\hat{G}_{(\theta,\phi,\psi)} + \frac{1}{2}E - \frac{1}{4}\Omega_-^2\varrho\right\}\Lambda(\{\boldsymbol{\varrho}\}) = 0. \tag{14}$$

where the angular operator $\tilde{G}_{(\theta,\phi,\psi)}$ has the form:

$$\tilde{G}_{(\theta,\phi,\psi)} = \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2} + \frac{\partial^2}{\partial\psi^2} - 2\cos\theta\frac{\partial^2}{\partial\phi\partial\psi}\right)\right].$$

Representing the wave function $\Lambda(\{\boldsymbol{\varrho}\})$ in the form:

$$\Lambda(\{\boldsymbol{\varrho}\}) = \Lambda^{(0)}(\varrho)\Phi(\theta, \phi, \psi), \tag{15}$$

we can obtain two new equations from Equation (14). In particular, the angular part of the wave function satisfies the following equation:

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2} + \frac{\partial^2}{\partial\psi^2} - 2\cos\theta\frac{\partial^2}{\partial\phi\partial\psi}\right) + \lambda\right]\Phi = 0, \tag{16}$$

where λ is some constant, which will be defined below. The radial part of the wave function satisfies the following second-order ODE:

$$\left\{\frac{1}{\varrho^2}\frac{d}{d\varrho}\left(\varrho^2\frac{d}{d\varrho}\right)+\left[-\frac{\Omega_-^2}{4}+\frac{E}{2\varrho}-\frac{\lambda}{\varrho^2}\right]\right\}\Lambda^{(0)}(\varrho)=0. \tag{17}$$

Concerning Equation (16), as we know, this is the equation of a $3D$ spherical rotator, which has the following solution:

$$\Phi(\theta,\phi,\psi)=\Theta_{JKM}(\theta)e^{i(K\phi+M\psi)}, \tag{18}$$

where

$$\Theta_{JKM}(\theta)=z^{|K-M|/2}(1-z)^{|K+M|/2}F(\alpha,\beta,\gamma;z),\qquad z=\frac{1}{2}(1-\cos\theta),$$

In addition, the following notations are made:

$$\lambda=J(J+1),\qquad J=0,1,\ldots,\qquad M,\,K=J,\,J-1,\ldots,1-J,\,-J.$$

Mind that $F(\alpha,\beta,\gamma;z)$ is a hyper-geometric function, and its parameters are defined as follows:

$$\alpha=-J+|K-M|/2,\qquad \beta=J+|K+M|/2+|K-M|/2,\qquad \gamma=1+|K-M|.$$

As for the equation for the radial wave function (17), it is not difficult to see that it describes the wave function of the hydrogen atom and has an exact solution (see for example [9]):

$$\Lambda^{(0)}_{nJ}(\varrho)=e^{-\rho/2}\rho^J L^{2J+1}_{n-J-1}(\rho),\qquad \rho=2\sqrt{\Omega_-}\varrho,\quad n=1,2,\ldots \tag{19}$$

where $L^m_n(x)$ denotes the associated Laguerre polynomial; in addition, recall that for an isolated hydrogen atom, the energy is $E=-\Omega_-=-1/n^2$.

Thus, by combining (9), (13), (15) and (18), we can write the wave function of the reacting $4D$ isotropic quantum oscillator in the explicit form:

$$\breve{\Psi}_{\mathcal{M}}(\{\boldsymbol{\varrho}\},t)=\left(\frac{1}{\sigma^2}\prod_{l=1}^{4}\exp\Big\{-\frac{i}{2}\dot{\sigma}\sigma y_l^2(\{\boldsymbol{\varrho}\})\Big\}\right)\Lambda^{(0)}_{nJ}(\varrho)\Theta_{JKM}(\theta)e^{i(K\phi+M\psi-E\tau)}. \tag{20}$$

where $\mathcal{M}=(n,J,K,M)$ denotes a set of quantum numbers describing the quantum state. However, given that $\sum_{l=1}^{4}y_l^2=\varrho$, the wave function (20) can be rewritten as:

$$\breve{\Psi}_{\mathcal{M}}(\{\boldsymbol{\varrho}\},t)=\frac{1}{\sigma^2}e^{-iE\tau(t)-i\dot{\sigma}\sigma\varrho/2}\Lambda^{(0)}_{nJ}(\varrho)\Theta_{JKM}(\theta)e^{i(K\phi+M\psi)}. \tag{21}$$

Returning to the problem of the hydrogen atom, we note that the wave function of the reacting hydrogen atom is easily found by requiring the following constraint condition $\partial\breve{\Psi}_-/\partial\psi=0$ for the total wave function of the $4D$ IHO. It is easy to check that this condition is equivalent to the case when we put the quantum number $M=0$ in the wave function for the isotropic harmonic oscillator. In other words, we can write the exact expression for the wave function IHO evolving from the asymptotic subspace (in) with frequency Ω_- to the asymptotic subspace (out), where the oscillator frequency is equal to Ω_+:

$$\breve{\Psi}_{\mathcal{M}_0}(\{\boldsymbol{\varrho}_0\},t)=\frac{C_{nJK}}{\sigma^2(t)}e^{-iE\tau(t)-i\dot{\sigma}\sigma\varrho/2}\Lambda^{(0)}_{nJ}(\varrho)\Theta_{JK}(\theta)e^{iK\phi}, \tag{22}$$

where C_{nJK} is some constant to be defined below; in addition, $\mathcal{M}_0=(n,J,K)$ denotes the set of quantum numbers characterizing the hydrogen atom, $\Theta_{JK}(\theta)=\Theta_{JKM}(\theta)\big|_{M=0}$ and

$\{\varrho_0\} = (\varrho, \theta, \phi)$. In the limit $t \to -\infty$ or in the (in) subspace, the total wave function (22) must match with the asymptotic wave function $\breve{\Phi}^{-}_{\mathcal{M}_0}(\{\varrho_0\})$:

$$\breve{\Psi}_{\mathcal{M}_0}(\{\varrho_0\}, t) \quad \xrightarrow[t\to-\infty]{} \quad \breve{\Phi}^{-}_{\mathcal{M}_0}(\{\varrho_0\}) = C_{nJK}\Lambda^{(0)}_{nJ}(\varrho)\Theta_{JK}(\theta)e^{iK\phi}.$$

Note that the constant C_{nJK} can be found from the normalization condition for the wave function of an isolated hydrogen atom. In particular, if this is completed in the $3D$ Euclidean space $\mathbb{R}^3 \ni (\varrho, \theta, \phi)$, then we obtain:

$$C'_{nJK} = \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \left|\Lambda^{(0)}_{nJ}(\varrho)\Theta_{JK}(\theta)\right|^2 \varrho^2 \sin\theta d\varrho d\theta d\phi = \sqrt{\frac{(n-J-1)!}{2n(n+J)!}} \cdot \left(\frac{2}{n}\right)^{\frac{3}{2}}. \tag{23}$$

However, we complete all the construction of the problem in the $4D$ space, so the normalization of the $3D$ wave function (22) must also be performed in the $4D$ space. This new constant C_{nJK} will obviously be different from C'_{nJK} represented by formula (23). Since the coefficient C'_{nJK} does not depend on the quantum number K, in what follows, we will replace C_{nJK} with C_{nJ}.

3.2. Non-Stationary QHO under the Influence of an External Force

Let now consider the case of the non-stationary QHO subjected to an external force, i.e., $F(t) \neq 0$. Our goal now is to reduce the problem to the QPO case.

The wave function of a non-stationary QHO, taking into account the external force action, can be represented as [10]:

$$\bar{\Psi}(\mathbf{x}, t) = \left(\prod_{l=1}^{4} \exp\left\{i[\dot{\eta}(t)\bar{x}_l + \mathtt{S}_l(t)]\right\}\right)\bar{\Psi}_{-}(\bar{\mathbf{x}}, \tau), \qquad \bar{x}_l = x_l - \eta(t), \tag{24}$$

where $\eta(t)$ and $\mathtt{S}_l(t)$ are unknown functions that we define below based on the requirement of reducing Equations (1) and (2) to an autonomous form; in addition, $\bar{\mathbf{x}} = \bar{\mathbf{x}}(\bar{x}_1, \ldots, \bar{x}_4) \in \mathbb{R}^4$ denotes the displacement of the oscillator center of mass in $4D$ Euclidean space. Substituting (24) into Equations (1) and (2), we obtain:

$$\begin{aligned} i\frac{\partial\bar{\Psi}_{-}}{\partial t} = \sum_{l=1}^{4}\Bigg\{ &-\frac{1}{2}\frac{\partial^2}{\partial\bar{x}_l{}^2} + \frac{1}{2}\Omega^2(t)\bar{x}_l^2 + \left[\ddot{\eta} + \Omega^2(t)\eta - F(t)\right]\bar{x}_l \\ &+ \left[\dot{\mathtt{S}}_l(t) - \frac{1}{2}\dot{\eta}^2 + \frac{1}{2}\Omega^2(t)\eta^2 - F(t)\eta\right]\Bigg\}\bar{\Psi}_{-}. \end{aligned} \tag{25}$$

It is easy to see that Equation (25) can be reduced to the case of a parametric oscillator with $F(t) = 0$. In particular, this can be completed if we require that the following inhomogeneous equation holds for the classical oscillator (see also (7)):

$$\ddot{\eta} + \Omega(t)\eta = F(t), \tag{26}$$

and also for the following equalities:

$$\mathtt{L}_l(t) = \dot{\mathtt{S}}_l(t) = \frac{1}{2}\dot{\eta}^2 - \frac{1}{2}\Omega^2(t)\eta^2 + F(t)\eta, \tag{27}$$

where $\mathtt{L}_l(t)$ is the classical Lagrangian of the $1D$ oscillator.

Thus, we were able to determine the unknown functions $\eta_l(t)$ and $\mathtt{S}_l(t)$ and, what is very important, reduce the problem to the case of the QPO. Combining (9), (24) and (27) for

the wave function of a non-stationary QHO that is subjected to an external force, we can write the following expression:

$$\breve{\Psi}_{\mathcal{M}}(\{\bar{\varrho}\},t)=\frac{1}{\sigma^2(t)}e^{-iE\tau-i\dot{\sigma}\sigma\bar{\varrho}/2}\Lambda^{(0)}_{nJ}(\bar{\varrho})\left(\prod_{l=1}^{4}e^{i\left[\dot{\eta}\sigma\bar{y}_l(\{\bar{\varrho}\})+\mathbb{S}_l(t)\right]}\right)\Theta_{JKM}(\theta)e^{i(K\phi+M\psi)}, \quad (28)$$

where $\bar{y}_l=\bar{x}_l/\sigma$ denotes the scaled coordinate shift; in addition, $\bar{\varrho}=\sum_{l=1}^{4}\bar{y}_l^2$ is the radius; $\{\bar{\boldsymbol{\varrho}}\}=(\bar{\varrho},\theta,\phi,\psi)\in\mathbb{R}^4$ denotes a set of coordinates, and finally, $\mathbb{S}_l(t)=\int_{-\infty}^{t}L_l(t')dt'$ is the action of the $1D$ classical oscillator. If we now set $M=0$, then the wave function (28) will describe the reacting hydrogen atom, taking into account the external fields' influence.

In the end, we note that the wave function (28) must be normalized in a $4D$ space before using it in some other constructions, such as calculating the matrix elements of quantum transitions, for example.

4. Transition Probabilities between (*in*) and (*out*) Asymptotic Quantum States

In this section, we construct the transition probabilities between two asymptotic states (in) and (out) for the QPO. Particular attention will be paid to the case when the quantum number $M=0$, i.e., the problem of the hydrogen atom under the influence of external fields, which leads to a change in the frequency.

Taking into account the condition (3) for the external force, we can claim that in (in) and (out) asymptotic subspaces, the QPO will be described by purely quantum states:

$$\breve{\Phi}^{\mp}_{\mathcal{M}}(\{\boldsymbol{\varrho}\})=\Lambda^{(0)\mp}_{nJ}(\varrho)\Theta_{JKM}(\theta)e^{i(K\phi+M\psi)}, \quad (29)$$

where $\Lambda^{(0)\mp}_{nJ}(\varrho)=e^{-\rho_{\mp}/2}(\rho_{\mp})^J L^{2J+1}_{n-J-1}(\rho_{\mp})$ and $\rho_{\mp}=2\Omega_{\mp}\varrho$ denote the radial parts of the wave functions of the hydrogen atom in the corresponding asymptotic subspaces. In other words, our task will be to calculate the probability of transitions between asymptotic states $\breve{\Phi}^{-}_{\mathcal{M}}(\{\boldsymbol{\varrho}\})$ and $\breve{\Phi}^{+}_{\mathcal{M}'}(\{\boldsymbol{\varrho}\})$. In particular, if we assume that in the (in) asymptotic subspace the QPO was in a pure quantum state $\breve{\Phi}_{\mathcal{M}}(\{\boldsymbol{\varrho}\})$, then the evolving total wave function of the oscillator $\breve{\Psi}^{-}_{\mathcal{M}}(\{\boldsymbol{\varrho}\},t)$ can be represented in the form:

$$\breve{\Psi}_{\mathcal{M}}(\{\boldsymbol{\varrho}\},t)=\sum_{\mathcal{M}'}S_{\mathcal{M}'\mathcal{M}}(t)\breve{\Phi}^{+}_{\mathcal{M}'}(\{\boldsymbol{\varrho}\}). \quad (30)$$

Calculating the expansion coefficient of the sum $S_{\mathcal{M}\mathcal{M}'}(t)$, we obtain:

$$S_{\mathcal{M};\mathcal{M}'}(t)=\int_{\mathbb{R}^4}\breve{\Psi}_{\mathcal{M}}(\{\boldsymbol{\varrho}\},t)\overline{\breve{\Phi}^{+}_{\mathcal{M}'}(\{\boldsymbol{\varrho}\})}d^4V(\{\mathbf{y}\}), \quad (31)$$

where the infinitesimal volume in the new coordinates is defined as follows:

$$d^4V(\{\mathbf{y}\})=\left|\frac{\partial(x_1,x_2,x_3,x_4)}{\partial(\varrho,\ \vartheta,\ \phi,\ \psi)}\right|d\varrho d\vartheta d\phi d\psi=\sigma^4(t)\left|\frac{\partial(y_1,y_2,y_3,y_4)}{\partial(\varrho,\ \vartheta,\ \phi,\ \psi)}\right|d\varrho d\vartheta d\phi d\psi,$$

in addition, in expression (31), the symbol $\overline{\{\cdot\}}$ denotes the complex conjugate function. As for the determinant of coordinate transformations in the integral (31), we can calculate it explicitly using expressions (11):

$$\left|\frac{\partial(\cdot)}{\partial(\cdot)}\right|=\begin{vmatrix}\frac{1}{2\sqrt{\varrho}}\cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2} & -\frac{\sqrt{\varrho}}{2}\sin\frac{\theta}{2}\cos\frac{\phi+\psi}{2} & -\frac{\sqrt{\varrho}}{2}\cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2} & -\frac{\sqrt{\varrho}}{2}\cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2}\\ \frac{1}{2\sqrt{\varrho}}\cos\frac{\theta}{2}\sin\frac{\phi-\psi}{2} & \frac{\sqrt{\varrho}}{2}\sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2} & -\frac{\sqrt{\varrho}}{2}\cos\frac{\theta}{2}\cos\frac{\phi-\psi}{2} & \frac{\sqrt{\varrho}}{2}\cos\frac{\theta}{2}\cos\frac{\phi-\psi}{2}\\ \frac{1}{2\sqrt{\varrho}}\cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2} & -\frac{\sqrt{\varrho}}{2}\sin\frac{\theta}{2}\sin\frac{\phi+\psi}{2} & \frac{\sqrt{\varrho}}{2}\cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2} & \frac{\sqrt{\varrho}}{2}\cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2}\\ \frac{1}{2\sqrt{\varrho}}\sin\frac{\theta}{2}\sin\frac{\phi-\psi}{2} & \frac{\sqrt{\varrho}}{2}\cos\frac{\theta}{2}\sin\frac{\phi-\psi}{2} & \frac{\sqrt{\varrho}}{2}\sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2} & -\frac{\sqrt{\varrho}}{2}\sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2}\end{vmatrix}.$$

Recall that the calculation shows that the value of the determinant is $\left|\frac{\partial(\cdot)}{\partial(\cdot)}\right|=\frac{\varrho\sin\theta}{16}$.

The transition S-matrix element can be obtained from the expression (31) in the limit $t \to +\infty$, the square of the modulus of which will denote the transition probability between $\breve{\Phi}^{-}_{\mathcal{M}}(\{\varrho\})$ and $\breve{\Phi}^{+}_{\mathcal{M}'}(\{\varrho\})$ quantum states:

$$W_{\mathcal{M};\mathcal{M}'} = \lim_{t\to+\infty} |S_{\mathcal{M};\mathcal{M}'}(t)|^2. \tag{32}$$

For definiteness, below, we are going to study quantum transitions involving the hydrogen atom in more detail. We are going to consider two asymptotic states described by the following wave functions:

$$\breve{\Phi}^{-}_{\mathcal{M}_0}(\{\varrho_0\}) = e^{-\rho/2}\rho^J L^{2J+1}_{n-J-1}(\rho), \qquad \breve{\Phi}^{+}_{\mathcal{M}'_0}(\{\varrho_0\}) = e^{-\nu\varrho/2}(\nu\rho)^{J'} L^{2J'+1}_{n'-J'-1}(\nu\rho), \tag{33}$$

where $\rho = \rho_- = 2\Omega_-\varrho$ and $\nu = \Omega_+/\Omega_-$.

Note that if we assume that the wave function $\breve{\Phi}^{-}_{\mathcal{M}_0}(\{\varrho_0\})$ describes an isolated hydrogen atom, then the wave function $\breve{\Phi}^{+}_{\mathcal{M}'_0}(\{\varrho_0\})$ that includes the frequency $\Omega_+ \neq \Omega_-$ will describe the conditionally bonded hydrogen atom. Our task will be to calculate the probability of transition between these two quantum states $W_{\mathcal{M}_0\mathcal{M}'_0}$. Taking into account that the elementary atomic–molecular process occurs in the $4D$ Euclidean space $\mathbb{R}^4 \ni (\varrho, \theta, \phi, \psi)$, the transition S-matrix element can be written as:

$$S_{\mathcal{M}_0;\mathcal{M}'_0}(t) = \frac{\sigma^4(t)}{16}\int_0^\infty\int_0^\pi\int_0^\pi\int_0^{2\pi} \breve{\Psi}_{\mathcal{M}_0}(\{\varrho_0\},t)\overline{\breve{\Phi}^{+}_{\mathcal{M}'_0}(\{\varrho_0\})}\varrho\sin\theta d\varrho d\theta d\phi d\psi, \tag{34}$$

where $\mathcal{M}_0 = (n, J, K)$ and $\mathcal{M}'_0 = (n', J', K')$ denote the sets of quantum numbers of the hydrogen atom, respectively, in (in) and (out) asymptotic states.

Before proceeding to the calculation of the S-matrix element by the formula (34), it is necessary to normalize both the total and the asymptotic wave functions. In particular, for the full wave function, this normalization constant will have the form:

$$C_{nJK}(t) = \frac{4}{\sigma^2(t)}\left(\int_0^\infty\int_0^\pi\int_0^\pi\int_0^{2\pi} \left|\breve{\Psi}_{\mathcal{M}_0}(\{\varrho_0\},t)\right|^2\varrho\sin\theta d\varrho d\theta d\phi d\psi\right)^{-1/2}. \tag{35}$$

Substituting the expression for the hydrogen wave function (22) into (35), we find:

$$C_{nJ}(t) = \frac{4}{\sigma^2(t)}\left(\int_0^\infty \rho^{2J+1}e^{-\rho}\left[L^{2J+1}_{n-J-1}(\rho)\right]^2 d\varrho\right)^{-1/2}. \tag{36}$$

Now, using a simple formula [11]:

$$\int_0^\infty z^\lambda e^{-z} L^\lambda_m(z) L^\lambda_n(z) dz = \frac{\Gamma(n+\lambda+1)}{n!}\delta_{mn}, \qquad \mathtt{Re}(\lambda) > -1,$$

we can calculate the integral (36) for the normalization constant:

$$C_{nJ}(t) = \frac{4}{\sigma^2(t)}\sqrt{\frac{(n-J-1)!}{\Gamma(n+J+1)}}. \tag{37}$$

Given (37), the wave function of the reacting hydrogen atom $\breve{\Psi}_{\mathcal{M}_0}(\{\varrho_0\},t)$ normalized in $4D$ space can be written as:

$$\breve{\Psi}_{\mathcal{M}_0}(\{\varrho_0\},t) = C_{nJ}(t)\breve{\Psi}_{\mathcal{M}_0}(\{\varrho_0\},t). \tag{38}$$

Note that the normalized wave function for an isolated hydrogen atom $\breve{\underline{\Phi}}^{-}_{\mathcal{M}_0}(\{\varrho_0\})$ can be obtained from (38) in the $t \to -\infty$ limit, when $\sigma(t) \to 1$ and $C_{nJ}(t) \to C^0_{nJ} = 4\sqrt{\frac{(n-J-1)!}{\Gamma(n+J+1)}}$. We normalize the asymptotic wave function $\breve{\underline{\Phi}}^{+}_{\mathcal{M}'_0}(\{\varrho_0\})$ in a similar way.

Now, given that the following more general integral can be computed exactly [11]:

$$\int_0^\infty z^{\alpha-1}e^{-pz}L^\lambda_m(az)L^\beta_n(bz)dz = \frac{\Gamma(\alpha)(\lambda+1)_m(\beta+1)_n}{m!n!p^\alpha}\sum_{j=0}^{m}\frac{(-m)_j(\alpha)_j}{(\lambda+1)_j j!}\left(\frac{a}{p}\right)^j \times \sum_{k=0}^{n}\frac{(-n)_k(j+\alpha)_k}{(\beta+1)_k k!}\left(\frac{b}{p}\right)^k, \qquad \mathtt{Re}(\alpha) > 0,\ \mathtt{Re}(p) > 0,\ m,n \in \mathbb{N}, \tag{39}$$

we can proceed to the calculation of the S-matrix element (34).

Taking into account that the deformation of the wave function of the reacting hydrogen occurs only along the radial coordinate and substituting (22), (37), (38) and (33) into the expression (34), we can find:

$$\begin{aligned} S_{\mathcal{M}_0;\mathcal{M}'_0}(t) &= \delta_{JJ'}\delta_{KK'}\int_0^\infty e^{-i\dot{\sigma}\sigma\varrho/2}e^{-\rho/2}\rho^J L^{2J+1}_{n-J-1}(\rho)e^{-\nu\varrho/2}(\nu\rho)^{J'}L^{2J'+1}_{n'-J'-1}(\nu\rho)\rho d\rho \\ &= B^0_{nJK}B^0_{n'J'K'}\delta_{JJ'}\delta_{KK'}\nu^{J'}\int_0^\infty e^{-q(t)\rho}\rho^{J+J'+1}L^{2J+1}_{n-J-1}(\rho)L^{2J'+1}_{n'-J'-1}(\nu\rho)d\rho, \end{aligned} \tag{40}$$

where $q(t) = \left(i\dot{\sigma}(t)\sigma(t) + 1 + \nu\right)/2$ and $B^0_{nJ} = C^0_{nJ}/4$. The integral (40) can be simplified by writing it in the form:

$$S_{nJ;n'J}(t) = A_{nJ;n'J}\int_0^\infty \rho^{2J+1}e^{-q(t)\rho}L^{2J+1}_{n-J-1}(\rho)L^{2J+1}_{n'-J-1}(\nu\rho)d\rho,$$

where $A_{nJ;n'J} = \nu^J\sqrt{\frac{(n-J-1)!(n'-J-1)!}{\Gamma(n+J+1)\Gamma(n'+J+1)}}$.
Continuing the calculations taking into account (39), we find:

$$S_{nJ;n'J}(t) = A_{nJ;n'J}\frac{1}{q^{2(J+1)}(t)}\frac{\Gamma(2J+2)(2J+1)_{n-J-1}(2J+1)_{n'-J-1}}{(n-J-1)!(n'-J-1)!} \times \sum_{j=0}^{n-J-1}\frac{(J-n+1)_j(2J+2)_j}{(2J+1)_j j!q^j(t)}\sum_{k=0}^{n'-J-1}\frac{(J-n'+1)_k(j+2J+2)_k}{(2J+2)_k k!}\left[\frac{\nu}{q(t)}\right]^k \tag{41}$$

With the help of (39), we can explicitly write the first two elements of the S-matrix:

$$S_{10;10}(t) = \frac{4}{[1+\nu+i\dot{\sigma}(t)\sigma(t)]^2}, \qquad S_{21;21}(t) = \frac{16\nu}{[1+\nu+i\dot{\sigma}(t)\sigma(t)]^4}. \tag{42}$$

As we can easily see, there are strict selection rules for quantum transitions. Only those transitions are possible that can be represented in the form $S_{n(n-1);n(n-1)}$; $n \in \mathtt{N}$. Returning to the transition probability issue, we note that in this case, it is very important to study the S-matrix elements' behaviour in the $t \to +\infty$ limit, when the frequency $\Omega(t)$ tends to a constant value Ω_+. To carry out the necessary research, we need to turn to the classical oscillator problem (4), since the modulus of its solution determines the function $\sigma(t) = |\xi(t)|$.

In the (out) subspace, i.e., in the $t \to +\infty$ limit, Equation (4) is simplified and, accordingly, its solution can be formally represented as a combination of the incident and reflected waves [7]:

$$\xi(t) = c_1 e^{i\Omega_+ t} - c_2 e^{-i\Omega_+ t}, \qquad |c_1|^2 - |c_2|^2 = \frac{\Omega_-}{\Omega_+}, \tag{43}$$

where c_1 and c_2 are some complex constants that can be found after solving Equation (4) over the entire time interval $-\infty < t < +\infty$.

Given (43) for the $\sigma(t)$ function, it is easy to find the following expression:

$$\sigma(t) = \sqrt{\bar{c}_1^2 + \bar{c}_2^2 + 2\bar{c}_1\bar{c}_2\cos(\delta_1 - \delta_2 - 2\Omega_+ t)}, \tag{44}$$

where $\bar{c}_j = |c_j|$ and $\delta_j = \arg(c_j)$, $j = 1, 2$.

Continuing the calculations and taking into account (44), we find that:

$$\dot{\sigma}(t)\sigma(t) = -2\bar{c}_1\bar{c}_2\Omega_+ \sin(\delta_1 - \delta_2 - 2\Omega_+ t), \tag{45}$$

and accordingly, the S-matrix elements will be:

$$S_{10;10}(t) = \frac{4}{\chi^2(t)}, \qquad S_{21;21}(t) = \frac{16\nu}{\chi^4(t)}, \tag{46}$$

where $\chi(t) = [1 + \nu - i2\bar{c}_1\bar{c}_2\Omega_+ \sin(\delta_1 - \delta_2 - 2\Omega_+ t)]$.

From (46), it becomes obvious that in the limit of $t \to +\infty$, the elements of the S-matrix do not converge to constant limits but perform periodic oscillations. Based on this, it is necessary to additionally integrate the elements of the S-matrix over the oscillation period:

$$\bar{S}_{nJ;n'J} = \frac{\Omega_+}{\pi}\int_0^{\pi/\Omega_+} S_{nJ;n'J}(t)dt,$$

Accordingly, the transition probability per unit time will be determined as follows:

$$W_{nJ;n'J} = |\bar{S}_{nJ;n'J}|^2.$$

The analysis shows that quantum transitions can be calculated in a similar way also for the model of a reacting hydrogen atom when it is affected by an external force. However, in this case, there is no special selection law, and quantum transitions between any states are possible.

5. Conclusions

In addition to the obvious relevance of the results obtained for the theory of atomic–molecular collisions and reactions, where the importance of exact results cannot be overestimated, the developed approach is also of great importance for the theory of fundamental processes. The fact is that from the moment of the first attempts to construct a field theory to obtain fundamental solutions, the main approach was to reduce the dimension of the problem. However, after Fock's fundamental work [1], it became obvious to everyone that the problem can also be simplified by increasing its dimension and bringing it to a form in which the symmetry of the problem is realized in a natural way and most completely. Recall that Fock used the dynamic symmetry group $SO(4)$ to explain the degenerate energy levels of the hydrogen atom. In addition, which is very important, he proved the equivalence of the considered problem to the propagation of a geodesic flow on the surface of $3D$ sphere of unit radius.

The point becomes much more complicated when we consider an arbitrarily moving non-stationary $4D$ quantum oscillator, which, logically, should break the hidden symmetries of a quantum system. Moreover, one would expect that the connection between the problem of an isotropic harmonic oscillator in a real $4D$ space and the Kepler problem in an ordinary $3D$ space would also be broken [5,12,13]. However, as we showed in this paper using the example of a non-stationary $4D$-isotropic oscillator, by the low-dimensional reference equation method, the initial Schrödinger equation reduces to an autonomous form. However, as we have shown in this article, using the low-dimensional reference Equation (4), the original Schrödinger Equations (1) and (2) for the non-stationary $4D$ isotropic oscillator is reduced to an autonomous form (10). In other words, we have proved

the existence of a new type of dynamical symmetry that preserves the invariant form of the master equation with respect to time in which the reference equation plays a key role. Note that the Schrödinger equation also reduces to an autonomous form for the case when an external force acts on the oscillator. After reducing the equation to an autonomous form, the coordinate transformation KS (11) is used, which makes it possible to reduce the problem to the Kepler problem and solve it exactly both for the wave function of the oscillator (see expressions (21) and (28)) and for the hydrogen atom (see (22) and (28), substituting in it $M = 0$).

An important result is the calculation of the explicit expressions of transition S-matrix elements for a reacting hydrogen atom in the absence of an external field (41) and (42). This problem is basic for calculating rearrangement processes in the theory of atomic–molecular collisions, so that in the near future, we can expect a revision of many results for three- and many-particle reactive collisions and an increase in the efficiency of their calculations. On the other hand, in view of the special role of the hydrogen atom in the theory of fundamental processes, it seems to us that the performed calculations make it possible to shed new light on some approaches to the formulation of the theory of elementary particles, especially in terms of the influence of hidden symmetries on the selection rules.

Finally, note that the method can be easily generalized to the case when the oscillator is immersed in a thermostat with a finite temperature (see [14] and also [15]). This, in particular, will make it possible to construct the thermodynamics of the reacting hydrogen atom in various media from the first principles of quantum mechanics, which will be very instructive both from the point of view of the foundations of quantum physics and for solving many important applied problems of physics and chemistry.

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Abbreviations

RHO	reacting harmonic oscillator
PDE	partial differential equation
QHO	quantum harmonic oscillator
IHO	isotropic harmonic oscillator
REM	reference equation method
ODE	ordinary differential equation
QPO	quantum parametric oscillator

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