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On the Use of Nonbijective Canonical Transformations in Chemical Physics

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This paper constitutes a contribution to the penetration of nonbijective canonical transformations in the field of theoretical chemistry. We have described in a simple way three quadratic transformations: the Levi-Civita, the Kustaanheimo-Stiefel, and a new transformation. Applications of the Kustaanheimo-Stiefel transformation are reviewed and further developed for the hydrogen atom, the Stark and Zeeman effects in hydrogenlike ions, as well as various potentials entering chemical physics and quantum chemistry.

I. INTRODUCTION

This paper deals with transformations which permit the conversion of Schrödinger equations for some usual quantification cases into Schrödinger equations for isotropic (non)harmonic oscillators accompanied by constraint conditions. Indeed, connections between two famous problems, *viz.*, the hydrogen atom or Kepler problem and the harmonic-oscillator problem have been known for a long time both from a classical[1] and a quantum-mechanical[2–12] viewpoint. In the present paper, we shall devote our attention to the Levi-Civita (LC) transformation and mainly to the Kustaanheimo-Stiefel (KS) transformation, and shall report briefly on a seemingly new transformation.

The LC transformation corresponds to a $R^2 \rightarrow R^2$ surjection and has been used for the restricted three-body problem[13] as well as for problems relative to R^2 and R^3 hydrogen atoms.[14–17] More specifically, the LC transformation has been employed to convert, in a Schrödinger-equation[14,17] and a Feynman-path-integral[16] formulation, the problem of a R^2 hydrogen atom into a R^2 isotropic harmonic oscillator subjected to a constraint; in addition, the LC transformation has been used in the classical approach to the quadratic Zeeman-Hamiltonian for the R^3 hydrogen atom.[15]

The so-called Kustaanheimo-Stiefel (KS) transformation, introduced by Kustaanheimo (cf., Ref. 18) and considered independently by Ikeda and Miyachi[19], corresponds to an $R^4 \rightarrow R^3$ surjection and has been the object of considerable interest in celestial mechanics, theoretical physics, and theoretical chemistry [18–34] during the past twenty years. The KS transformation has been

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originally set up for the regularisation of the Kepler problem.[18] Then, this transformation has been used, in a Schrödinger-equation and a Feynman-path--integral formulation, to show that the quantization of the R^3 hydrogen atom (with Coulomb potential only) is equivalent to the quantization of an R^4 isotropic harmonic oscillator supplemented with a constraint.[19–29] We note in passing that such an equivalence has been also obtained, in a completely different way, by finding and solving a boson realisation of the Lie-like equations for the R^3 hydrogen atom derived by Pauli in the early days of quantum mechanics.[29] The interesting features of the KS transformation has been also pointed out for the problem of a hydrogenlike atom in an electric or magnetic field[30], for the problem of the Hartmann potential of relevance for ring-shaped molecules like benzene[31,32], and for the problem of the Kratzer potential of relevance for vibration-rotation spectroscopy of molecules.[32] Let us finally mention two recent (somewhat exotic from the chemists' point of view) applications of the KS transformation. This transformation has been used in connection with a complete geometrical description of the Wu-Yang monopole (cf., Ref. 33) and a characterisation of a new class of instantons.[34]

Both the KS and LC transformations are nonbijective transformations and correspond, from a quantum-mechanical viewpoint, to nonbijective canonical transformations.[18–20] (They are canonical transformations in the sense that they »conserve« commutation relations of the type $[q, p] = i\hbar$.) In fact, the mathematical framework for the study of such transformations is the one of differential geometry of fiber bundles (cf., Refs. 19, 20, 23, 25, 33, and 34). In this vein, the KS transformation corresponds to the map $S^3 \times R^+ \to S^2 \times R^+$, *i. e.*, an $S^3/S^1 = S^2$ Hopf fibration. We do not adopt this point of view here but rather present, in Sect. II, the LC and KS transformations in a pedestrian way that amalgamates various aspects of the presentations in Refs. 18—20 and 35. We also briefly present in Sect. II a new nonbijective canonical transformation which might be useful in relativistic problems.[36] The reader may consult Refs. 19, 20, and 37 for further nonbijective canonical transformations.

Section III is devoted to a review and an extension of the applications of the KS and, to a less extent, the LC transformations to various quantification cases in the Schrödinger-equation formulation. The case of a hydrogenlike atom is tackled with some details in order to demonstrate how the KS transformation may be applied. Then, the cases of a hydrogenlike atom in electric and magnetic fields are worked out. The next examples concern the cases of the Hartmann[38], Kratzer[39], and Sommerfeld[40] potentials. We end up with an application of the KS transformation to the $-g^2(1-\alpha^2 r^2)/r$ potential which is of relevance in confinement problems and has been used recently[41] for simulating baryonlike quark bound states. Finally, a discussion in Sect. IV rounds up this article.

II. NONBIJECTIVE TRANSFORMATIONS

1. *The Levi-Civita Transformation*

The LC transformation, also known as the conformal transformation, is the $R^2 \to R^2$ surjection defined by

$$\begin{aligned} x_1 &= u_1{}^2 - u_2{}^2 \\ x_2 &= 2\,u_1\,u_2 \end{aligned} \tag{1}$$

The »inverse« transformation

$$\begin{aligned} u_1 &= \pm\, [(x_1 + r)/2]^{1/2} \\ u_2 &= x_2/2\, u_1 \\ r &= (x_1^2 + x_2^2)^{1/2} \end{aligned} \tag{2}$$

giving the parabolic coordinates u_i in terms of the Cartesian coordinates x_i ($i = 1, 2$) is clearly defined modulo the operations of the group C_2. Therefore, the LC transformation corresponds to a 2-to-1 homomorphism of R^2 onto R^2.

By introducing the matrices

$$A = \begin{bmatrix} u_1 & -u_2 \\ u_2 & u_1 \end{bmatrix}, \quad x = \begin{bmatrix} x_1 \\ x_2 \end{bmatrix}, \quad u = \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} \tag{3}$$

Eq. (1) may be rewritten as $x = Au$. We note that

$$\tilde{A}A = A\tilde{A} = (u_1^2 + u_2^2)\, I \tag{4}$$

where I is the 2×2 unit matrix. Consequently, the development of $\tilde{x}x = \tilde{u}\,\tilde{A}\,Au$ immediately leads to

$$r = (x_1^2 + x_2^2)^{1/2} = u_1^2 + u_2^2\,) \tag{5}$$

Equation (1) yields

$$\begin{aligned} dx_1 &= 2\,(u_1\, du_1 - u_2\, du_2) \\ dx_2 &= 2\,(u_2\, du_1 + u_1\, du_2) \end{aligned} \tag{6}$$

which reads $dx = 2Adu$ in matrix form. By developing $d\tilde{x}\, dx = 4\, d\tilde{u}\, \tilde{A}\, A\, du$, we obtain

$$dx_1^2 + dx_2^2 = 4\, r\, (du_1^2 + du_2^2\,) \tag{7}$$

The reader will verify, with calculations as simple as the preceeding ones, that

$$\begin{aligned} \frac{\partial}{\partial u_1} &= 2 \left(u_1 \frac{\partial}{\partial x_1} + u_2 \frac{\partial}{\partial x_2} \right) \\ \frac{\partial}{\partial u_2} &= 2 \left(-u_2 \frac{\partial}{\partial x_1} + u_1 \frac{\partial}{\partial x_2} \right) \end{aligned} \tag{8}$$

or equivalently $\dfrac{\partial}{\partial u} = 2\, \tilde{A}\, \dfrac{\partial}{\partial x}$. Equation (8) can be inverted to give

$$\begin{aligned} \frac{\partial}{\partial x_1} &= \frac{1}{2\, r} \left(u_1 \frac{\partial}{\partial u_1} - u_2 \frac{\partial}{\partial u_2} \right) \\ \frac{\partial}{\partial x_2} &= \frac{1}{2\, r} \left(u_2 \frac{\partial}{\partial u_1} + u_1 \frac{\partial}{\partial u_2} \right) \end{aligned} \tag{9}$$

or $\frac{\partial}{\partial x} = \frac{1}{2r} A \frac{\partial}{\partial u}$ in matrix form. As a consequence of Eq. (9), the Laplacian $\Delta_x = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}$ is given by

$$\Delta_x = (1/4\,r)\,\Delta_u \qquad (10)$$

in term of the Laplacian $\Delta_u = \frac{\partial^2}{\partial u_1^2} + \frac{\partial^2}{\partial u_2^2}$.

2. *The Kustaanheimo-Stiefel Transformation*

We observe that the matrix A defined in the preceding subsection belongs to SO (2) × R$^+$. This provides us with a hint how to generalize the LC transformation: we may look for a matrix A belonging to SO (d) × R$^+$. More specifically, we may look for a d × d real matrix A whose elements are linear and homogeneous functions of $u_\alpha \in R$ $(\alpha = 1, 2, \ldots, d)$ and whose rows and columns are orthogonal and normalised to $\left(\sum_{\alpha=1}^{d} u_\alpha^2 \right)^{1/2}$. According to a theorem by Hurwitz (connected to a theorem by von Neumann on division algebras), the problem of finding A has solutions only for d = 1, 2, 4, and 8. The case d = 2 corresponds to the LC transformation and d = 4 to the KS transformation.

For d = 4, the solution to the just mentioned problem is

$$A = \begin{bmatrix} u_3 & -u_4 & u_1 & -u_2 \\ u_4 & u_3 & u_2 & u_1 \\ u_1 & u_2 & -u_3 & -u_4 \\ u_2 & -u_1 & -u_4 & u_3 \end{bmatrix} \qquad (11)$$

up to row and/or column permutations as well as S$_4$ permutations on the labels u_α $(\alpha = 1, 2, 3, 4)$ with possible changes of sign. (In this respect, our matrix A differs from the one originally introduced by Kustaanheimo and Stiefel.) We now consider the column-matrix

$$2A \begin{bmatrix} du_1 \\ du_2 \\ du_3 \\ du_4 \end{bmatrix} = \begin{bmatrix} 2\,(u_3\,du_1 - u_4\,du_2 + u_1\,du_3 - u_2\,du_4) \\ 2\,(u_4\,du_1 + u_3\,du_2 + u_2\,du_3 + u_1\,du_4) \\ 2\,(u_1\,du_1 + u_2\,du_2 - u_3\,du_3 - u_4\,du_4) \\ 2\,(u_2\,du_1 - u_1\,du_2 - u_4\,du_3 + u_3\,du_4) \end{bmatrix} \qquad (12)$$

The first three entries in this matrix are seen to be total differentials so that we put

$$\begin{aligned} x_1 &= 2\,(u_1 u_3 - u_2 u_4) \\ x_2 &= 2\,(u_1 u_4 + u_2 u_3) \qquad (13) \\ x_3 &= u_1^2 + u_2^2 - u_3^3 - u_4^2 \end{aligned}$$

On one other hand, the last entry in the column-matrix (12) is not a total differential. Following Kustaanheimo and Stiefel, we shall take

$$u_2\,du_1 - u_1\,du_2 - u_4\,du_3 + u_3\,du_4 = 0 \qquad (14)$$

The KS transformation is thus the $R^4 \rightarrow R^3$ surjection defined by Eqs. (13) and (14).

By introducing the column-vectors

$$x = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ 0 \end{bmatrix}, \qquad u = \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{bmatrix} \tag{15}$$

we note that Eqs. (12), (13), and (14) can be condensed as $x = Au$ and $dx = 2Adu$. Hence, the development of $\hat{x}\, x = \hat{u}\, \hat{A}\, Au$ and $\hat{dx}\, dx = 4\, \hat{du}\, \hat{A}\, Adu$ yields

$$r = (x_1^2 + x_2^2 + x_3^2)^{1/2} = u_1^2 + u_2^2 + u_3^2 + u_4^2 \tag{16}$$

$$dx_1^2 + dx_2^2 + dx_3^2 = 4\, r\, (du_1^2 + du_2^2 + du_3^2 + du_4^2) \tag{17}$$

It is further possible to prove that

$$\begin{bmatrix} \dfrac{\partial}{\partial x_1} \\ \dfrac{\partial}{\partial x_2} \\ \dfrac{\partial}{\partial x_3} \\ \dfrac{1}{2\, r}\, X \end{bmatrix} = \frac{1}{2\, r}\, A \begin{bmatrix} \dfrac{\partial}{\partial u_1} \\ \dfrac{\partial}{\partial u_2} \\ \dfrac{\partial}{\partial u_3} \\ \dfrac{\partial}{\partial u_4} \end{bmatrix} \tag{18}$$

where the operator X is given by

$$X = u_2 \frac{\partial}{\partial u_1} - u_1 \frac{\partial}{\partial u_2} - u_4 \frac{\partial}{\partial u_3} + u_3 \frac{\partial}{\partial u_4} \tag{19}$$

As a corollary, the three-dimensional Laplacian Δ_x writes

$$\Delta_x = (1/4\, r)\, [\Delta_u - (1/r)\, X^2] \tag{20}$$

in terms of the four-dimensional Laplacian Δ_u and the operator X.

The operator X turns out to be the infinitesimal operator of a group isomorphic to the rotation group $C_{\infty v}$. This may be seen as follows. If $u \in R^4$ has the image $x \in R^3$, then all the points $v \in R^4$ such that

$$\begin{aligned} v_1 &= u_1 \cos \Phi + u_2 \sin \Phi \\ v_2 &= -u_1 \sin \Phi + u_2 \cos \Phi \\ v_3 &= u_3 \cos \Phi - u_4 \sin \Phi \\ v_4 &= u_3 \sin \Phi + u_4 \cos \Phi \end{aligned} \tag{21}$$

admit the image $x \in R^3$ too. Let T_Φ be the transformation which permits the pass from u to v. The set $\{T_\Phi : \Phi \in [0, 2\pi]\}$ generates a one-parameter Lie group, isomorphic to SO(2) or $C_{\infty v}$, whose infinitesimal operator is calculated to be X. This group, of type U(1), is of course a subgroup of the orthogonal group O(4) that leaves $\sum_{\alpha=1}^{4} u_\alpha^2$ invariant. It is to be noted that the operator X is invariant under the symplectic group Sp (2, R) acting on the canonically conjugate coordinates u_α and $\frac{\partial}{\partial u_\alpha}$ for $\alpha = 1, 2, 3, 4$.

The existence of X shows that the points $u \in R^4$ which have a given point $x \in R^3$ as image are defined up to rotations. This can be further understood by searching for the »inverse« transformation of (13). We get
case adapted to $x_3 \geq 0$:

$$\begin{aligned} u_1 &= [(x_3 + r)/2]^{1/2} \cos \varphi \\ u_2 &= [(x_3 + r)/2]^{1/2} \sin \varphi \\ u_3 &= [2 (x_3 + r)]^{-1/2} (x_1 \cos \varphi + x_2 \sin \varphi) \\ u_4 &= [2 (x_3 + r)]^{-1/2} (-x_1 \sin \varphi + x_2 \cos \varphi) \end{aligned} \tag{22}$$

case adapted to $x_3 \leq 0$:

$$\begin{aligned} u_1 &= [2 (-x_3 + r)]^{-1/2} (x_1 \cos \varphi + x_2 \sin \varphi) \\ u_2 &= [2 (-x_3 + r)]^{-1/2} (-x_1 \sin \varphi + x_2 \cos \varphi) \\ u_3 &= [(-x_3 + r)/2]^{1/2} \cos \varphi \\ u_4 &= [(-x_3 + r)/2]^{1/2} \sin \varphi \end{aligned} \tag{23}$$

where φ is an arbitrary angle.

Following Ikeda and Miyachi, we note that the (Cayley-Klein) parametrisation of R^4

$$\begin{aligned} u_1 &= \sqrt{r} \cos \frac{\Theta}{2} \cos \frac{\varphi + \psi}{2} \\ u_2 &= \sqrt{r} \cos \frac{\Theta}{2} \sin \frac{\varphi + \psi}{2} \\ u_3 &= \sqrt{r} \sin \frac{\Theta}{2} \cos \frac{\varphi - \psi}{2} \\ u_4 &= \sqrt{r} \sin \frac{\Theta}{2} \sin \frac{\varphi - \psi}{2} \end{aligned} \tag{24}$$

used in conjunction with Eq. (13) produces

$$\begin{aligned} x_1 &= r \sin \Theta \cos \varphi \\ x_2 &= r \sin \Theta \sin \varphi \\ x_3 &= r \cos \Theta \end{aligned} \tag{25}$$

3. *A New Transformation*

At this stage, we may wonder if the KS transformation is really a generalisation of the LC transformation especially in view of the fact that the kernel of the LC transformation is discrete while the one of the KS transformation is continuous. The LC transformation corresponds to the $R^2 \rightarrow R^2$ surjection associated with the conformal transformation $x_1 + i\, x_2 = (u_1 + i\, u_2)^p$ with $p = 2$. Therefore, we may think to extend this conformal transformation from complex numbers to quaternionic (and even octonionic) numbers. In the case of quaternions, this idea leads to the transformation

$$x_1 + i\, x_2 + j\, x_3 + k\, x_4 = (u_1 + i\, u_2 + j\, u_3 + k\, u_4)^p \tag{26}$$

which for $p = 2$ corresponds to the $R^4 \rightarrow R^4$ surjection defined by

$$\begin{aligned} x_1 &= u_1^2 - u_2^2 - u_3^2 - u_4^2 \\ x_2 &= 2\, u_1\, u_2 \\ x_3 &= 2\, u_1\, u_3 \\ x_4 &= 2\, u_1\, u_4 \end{aligned} \tag{27}$$

The kernel of the transformation (27) is discrete since the »inverse« transformation writes

$$\begin{aligned} u_1 &= \pm\, [(x_1 + r)/2]^{1/2} \\ u_2 &= x_2/2\, u_1 \\ u_3 &= x_3/2\, u_1 \\ u_4 &= x_4/2\, u_1 \end{aligned} \tag{28}$$

where

$$r = (x_1^2 + x_2^2 + x_3^2 + x_4^2)^{1/2} = u_1^2 + u_2^2 + u_3^2 + u_4^2 \tag{29}$$

We note that

$$\begin{aligned} d\, x_1^2 + d\, x_2^2 + d\, x_3^2 + d\, x_4^2 &= 4\, [(u_1^2 + u_2^2 + u_3^2 + u_4^2)\, d\, u_1^2 + \\ &+ (u_1^2 + u_2^2)\, d\, u_2^2 + (u_1^2 + u_3^2)\, d\, u_3^2 + (u_1^2 + u_4^2)\, d\, u_4^2 + \\ &+ 2\, (u_2\, u_3\, d\, u_2\, d\, u_3 + u_3\, u_4\, d\, u_3\, d\, u_4 + u_4\, u_2\, d\, u_4\, d\, u_2)] \end{aligned} \tag{30}$$

Therefore, the transformation defined by Eq. (27) appears to be a little bit more difficult to manipulate than the KS transformation and therefore we stop the investigation of this transformation at this point reserving its complete study for future applications to (relativistic) quantum-mechanical problems

III. APPLICATIONS TO NONRELATIVISTIC SYSTEMS

1. *The Coulomb Potential*

Let us consider the case of a hydrogenlike atom of nucleus charge Ze and reduced mass μ. The Schrödinger equation for such a system reads

$$[(-\hbar^2/2\, \mu)\, \Delta_x - Z\, e^2/r]\, \psi = E\, \psi \tag{31}$$

We may use Eqs. (16) and (20) relative to the KS transformation to bring this R^3 partial differential equation into an R^4 partial differential equation. Since the KS transformation is nonbijective, we require that $X\psi = 0$ in order to ensure that $\psi = \psi(x_i(u_\alpha))$ be an univalued wavefunction for all the points $u \in R^4$ having the same image $x \in R^3$. Consequently, the R^4 partial differential equation breaks into the system

$$\begin{gathered}[-(\hbar^2/2\mu)\,\Delta_u - 4E(u_1^2+u_2^2+u_3^2+u_4^2)]\,\psi = 4Ze^2\psi \\ X\psi = 0\end{gathered} \tag{32}$$

The next step is to look for a solution of type

$$\psi = f(u_1, u_2)\, g(u_3, u_4) \tag{33}$$

Then, the system (32) may be separated as

$$-(\hbar^2/2\mu)\,\Delta_{12} f - 4E(u_1^2+u_2^2) f = 4Z_1 e^2 f \tag{34a}$$

$$-(\hbar^2/2\mu)\,\Delta_{34} g - 4E(u_3^2+u_4^2) g = 4Z_2 e^2 g \tag{34b}$$

$$\Delta_{\alpha\beta} = \frac{\partial^2}{\partial u_\alpha^2} + \frac{\partial^2}{\partial u_\beta^2} \tag{34c}$$

$$Z_1 + Z_2 = Z_3 \tag{34d}$$

$$u_1\frac{\partial f}{\partial u_2} - u_2\frac{\partial f}{\partial u_1} = Z_3 f \tag{34e}$$

$$u_3\frac{\partial g}{\partial u_4} - u_4\frac{\partial g}{\partial u_3} = Z_3 g \tag{34f}$$

where Z_1, Z_2, and Z_3 are separation constants. To go further on, it is necessary to separately consider three cases: $E = 0$ (the zero-energy case), $E > 0$ (the continuous spectrum case), and $E < 0$ (the discrete spectrum case). This leads to the three following results.

Result 1. — The Schrödinger equation for the zero-energy point of an R^3 hydrogenlike atom is equivalent to the set comprising (i) the Schrödinger equations for a pair of R^2 free-particle systems [Eqs. (34a) and (34b) with $E = 0$] coupled by Eq. (34d) and (ii) a coupled pair of constraint conditions [Eqs. (34e) and (34f)].

Result 2. — The Schrödinger equation for the continuous spectrum of an R^3 hydrogenlike atom is equivalent to the set comprising (i) the Schrödinger equations for a pair of R^2 isotropic harmonic oscillators with repulsive potentials $-4E(u_1^2+u_2^2) < 0$ and $-4E(u_3^2+u_4^2) < 0$ [Eqs. (34a) and (34b) with $E > 0$] coupled by Eq. (34d) and (ii) a coupled pair of constraint conditions [Eqs. (34e) and (34f)].

Result 3. — The Schrödinger equation for the discrete spectrum of an R^3 hydrogenlike atom is equivalent to the set comprising (i) the Schrödinger equations for a pair of R^2 isotropic harmonic oscillators with attractive potentials $-4E(u_1^2 + u_2^2) > 0$ and $-4E(u_3^2 + u_4^2) > 0$ [Eqs. (34a) and (34b) with $E < 0$] coupled by Eq. (34d) and (ii) a coupled pair of constraint conditions [Eqs. (34e) and (34f)].

At this point we restrict our attention to the discussion of Result 3 and demonstrate how it makes it possible to recover the Balmer-Bohr formula in a straightforward way. The frequency $\nu = \omega/2\pi$ of the two oscillators under consideration is clearly given by

$$-4E = (1/2)\,\mu\,\omega^2 \tag{35}$$

and their energies by

$$\begin{gathered} 4Z_1 e^2 = [n_1 + n_2 + 2(1/2)]\,\hbar\,\omega \\ 4Z_2 e^2 = [n_3 + n_4 + 2(1/2)]\,\hbar\,\omega \\ n_\alpha = 0, 1, 2, \ldots \text{ for } \alpha = 1, 2, 3, 4 \end{gathered} \tag{36}$$

By combining Eqs. (34d), (35), and (36), we obtain

$$E = -2\,\mu\,Z^2 e^4/\hbar^2 (n_1 + n_2 + n_3 + n_4 + 2)^2 \tag{37}$$

We now use the constraint conditions [Eqs. (34e) and (34f)] in order to obtain a relationship between n_1, n_2, n_3, and n_4. In fact, it is enough to look for solutions of the type

$$\begin{aligned} f &= \sum_{n_1 n_2} C_{n_1 n_2}\,\varphi_{n_1}(u_1)\,\varphi_{n_2}(u_2) \\ g &= \sum_{n_3 n_4} C_{n_3 n_4}\,\varphi_{n_3}(u_3)\,\varphi_{n_4}(u_4) \end{aligned} \tag{38}$$

where $\varphi_{n_\alpha}(u_\alpha)$ stands for an eigenfunction of a one-dimensional isotropic harmonic oscillator and $C_{n_\alpha n_\beta}$ denotes an expansion coefficient. The introduction of Eq. (38) into Eqs. (34e) and (34f) yields the two recurrence relations

$$\begin{aligned} C_{n_1-1,\,n_2+1}[n_1(n_2+1)]^{1/2} - C_{n_1+1,\,n_2-1}[(n_1+1)n_2]^{1/2} &= Z_3 C_{n_1 n_2} \\ C_{n_3-1,\,n_4+1}[n_3(n_4+1)]^{1/2} - C_{n_3+1,\,n_4-1}[(n_3+1)n_4]^{1/2} &= Z_3 C_{n_3 n_4} \end{aligned} \tag{39}$$

which may be proved to admit solutions for $n_1 + n_2 + n_3 + n_4 =$ even integer. Hence, Eq. (37) reduces to the famous Balmer-Bohr formula

$$E = -\mu Z^2 e^4/2\hbar^2 n^2 \tag{40}$$

where $n = (n_1 + n_2 + n_3 + n_4 + 2)/2 = 1, 2, 3, \ldots$ stands for the principal quantum number. We may verify that this approach leads to the correct degeneracy for the discrete spectrum of the hydrogen atom. The degeneracy degree of the level $E \sim -1/n^2$ is found to be the well-known Stone number n^2 (cf., Ref. 26).

At this point, we understand that it is possible to derive all the results concerning the spectrum of a hydrogenlike atom from the spectra of isotropic harmonic oscillators subjected to constraints. Indeed, it is also possible to obtain the well-known dynamical symmetry group SO(4, 2) of the hydrogen atom from the above three results. As a point of fact, we know from theoretical physics that the eigth canonically conjugate coordinates u_α and $\frac{\partial}{\partial u_\alpha}$ ($\alpha = 1, 2, 3, 4$) span the Lie algebra of the symplectic group Sp (8, R). Thus, we may ask what happens when we introduce the constraint condition $X = 0$ into the Lie algebra of Sp (8, R). This leads to the pending result.

Result 4. — The introduction of the constraint condition $X = 0$ into the Lie algebra of Sp (8, R) produces an *under constraint* Lie algebra isomorphic to the Lie algebra of SO (4, 2), thus establishing the relevance of SO (4, 2) for the hydrogen atom.

2. *The Hydrogen Atom in an Electric Field*

The Schrödinger equation for a hydrogenlike atom in an electrostatic field pointing in the positive 3-direction writes

$$[-(\hbar^2/2\,\mu)\,\Delta_x - Z\,e^2/r + e\,F\,x_3]\,\psi = E\,\psi \tag{41}$$

where F characterizes the strength of the field. The use of Eqs. (13), (16), and (20) relative to the KS transformation allows us to transform Eq. (40) into an R^4 partial differential equation. By using $X\,\psi = 0$ and the method of separation of variables [cf., Eq. (33)], we end up with the following result.

Result 5. — The Schrödinger equation for a R^3 hydrogenlike atom in an electric field is equivalent to the set comprising (i) the Schrödinger equations

$$\begin{aligned} &-(\hbar^2/2\,\mu)\,\Delta_{12}\,f - 4\,E\,(u_1^2 + u_2^2)\,f + 4\,e\,F\,(u_1^2 + u_2^2)^2\,f = 4\,Z_1\,e^2\,f \\ &-(\hbar^2/2\,\mu)\,\Delta_{34}\,g - 4\,E\,(u_3^2 + u_4^2)\,g - 4\,e\,F\,(u_3^2 + u_4^2)^2\,g = 4\,Z_2\,e^2\,g \end{aligned} \tag{42}$$

for a pair of R^2 isotropic anharmonic oscillators with quartic anharmonicity coupled by Eq. (34d) and (ii) a coupled pair of constraint conditions [Eqs. (34e) and (34f)].

3. *The Hydrogen Atom in a Magnetic Field*

By ignoring spin-dependent contributions, the Schrödinger equation for a hydrogenlike atom in the presence of a magnetostatic field pointing along the 3-axis is amenable to the form

$$[(-\hbar^2/2\,\mu)\,\Delta_x - Z\,e^2/r + (e/2\,\mu\,c)\,HL_3 + (e^2/8\,\mu\,c^2)\,H^2\,(x_1^2 + x_2^2)]\,\psi = E\psi \tag{43}$$

where H/c represents the intensity of the field, and the third and fourth terms the paramagnetic and diamagnetic contributions, respectively. The use of Eqs. (13), (16), (18), and (20) relative to the KS transformation and $X\,\psi = 0$ lead to the nonseparable system

$$\begin{aligned} &-(\hbar^2/2\,\mu)\,\Delta_u\,\psi - 4\,E\,(u_1^2 + u_2^2 + u_3^2 + u_4^2)\,\psi + \\ &+ (2\,e\,\hbar/i\,\mu\,c)\,H\,[(u_1^2 + u_2^2)\,(u_3\frac{\partial\psi}{\partial u_4} - u_4\frac{\partial\psi}{\partial u_3}) + (u_3^2 + u_4^2)\,(u_1\frac{\partial\psi}{\partial u_2} - u_2\frac{\partial\psi}{\partial u_1})] + \\ &+ (2\,e^2/\mu\,c^2)\,H^2\,(u_1^2 + u_2^2 + u_3^2 + u_4^2)\,(u_1^2 + u_2^2)\,(u_3^2 + u_4^2)\,\psi = 4\,Z\,e^2\,\psi \end{aligned} \tag{44}$$

$$u_2\frac{\partial\psi}{\partial u_1} - u_1\frac{\partial\psi}{\partial u_2} - u_4\frac{\partial\psi}{\partial u_3} + u_3\frac{\partial\psi}{\partial u_4} = 0 \tag{45}$$

In the special case of a strong field (*i. e.*, a field for which the linear magnetic contribution may be neglected with respect to the quadratic magnetic contribution), we have the following result.

Result 6. — The Schrödinger equation for an R^3 hydrogenlike atom in a strong magnetic field is equivalent to the set comprising (i) the Schrödinger equation

$$\begin{aligned} &-(\hbar^2/2\,\mu)\,\Delta_u\,\psi - 4\,E\,(u_1^2+u_2^2+u_3^2+u_4^2)\,\psi + \\ &+ (2\,e^2/\mu\,c^2)\,H^2\,(u_1^2+u_2^2+u_3^2+u_4^2)\,(u_1^2+u_2^2)\,(u_3^2+u_4^2)\,\psi = 4\,Z\,e^2\,\psi \end{aligned} \tag{46}$$

for a R^4 isotropic anharmonic oscillator with sextic anharmonicity and (ii) a constraint condition [Eq. (44)].

4. *The Hartmann Potential*

We consider the three-dimensional potential (energy)

$$V_q = \eta\,\sigma^2\,(2\,a_0/r - q\eta\,a_0^2/r^2\,\sin^2\Theta)\,\varepsilon_0 \tag{47}$$

which is a function of the polar coordinates r and Θ. The quantities a_0 and ε_0 in Eq. (47) denote the radius of the first Bohr orbit and the energy of the ground level of the hydrogen atom, respectively. Furthermore, η and σ are two positive real (dimensionless) parameters taking values between 1 up to 10 in problems of interest for theoretical chemistry. Finally, q is a (dimensionless) parameter. For $q = 1$ Eq. (47) gives the Hartmann potential, while for $q = 0$ and $\eta\,\sigma^2 = Z$ Eq. (47) gives the potential of a hydrogenlike atom.

The KS transformation allows us to transform the Schrödinger equation for the (generally nonspherical) potential V_q into a coupled pair of Schrödinger equations for two R^2 isotropic nonharmonic oscillators. More precisely, by using Eqs. (13), (16), (20), and (25), the Schrödinger equation for the potential V_q may be converted into an R^4 partial differential equation. Moreover, the use of $X\,\psi = 0$ and the method of separation of variables [cf., Eq. (33)] leads to the following result.

Result 7. — The Schrödinger equation for the potential V_q is equivalent to the set comprising (i) the Schrödinger equations

$$\begin{aligned} &-(\hbar^2/2\,\mu)\,\Delta_{12}\,f - 4\,E\,(u_1^2+u_2^2)\,f - q\,\eta^2\,\sigma^2\,a_0^2\,\varepsilon_0\,(u_1^2+u_2^2)^{-1}\,f = \alpha\,f \\ &-(\hbar^2/2\,\mu)\,\Delta_{34}\,g - 4\,E\,(u_3^2+u_4^2)\,g - q\,\eta^2\,\sigma^2\,a_0^2\,\varepsilon_0\,(u_3^2+u_4^2)^{-1}\,g = \beta\,g \end{aligned} \tag{48}$$

for a pair of R^2 isotropic nonharmonic oscillators with inverse-square potentials coupled by

$$\alpha + \beta = -8\,\eta\,\sigma^2\,a_0\,\varepsilon_0 \tag{49}$$

and (ii) a coupled pair of constraint conditions [Eqs. (34e) and (34f)].

The system constituted by Eqs. (34e), (34f), (48), and (49) may be solved easily for $E < 0$ and $q > 0$. As a net result, we have the discrete eigenvalues where N is a q-dependent parameter defined via

$$N = (m^2 + q\,\eta^2\,\sigma^2)^{1/2} + n_r + n_r' + 1$$
$$m = 0,\ \pm 1,\ \pm 2, \ldots \tag{51}$$
$$n_r = 0,\ 1,\ 2, \ldots$$
$$n_r' = 0,\ 1,\ 2, \ldots$$

We note that for N and $|m|$ fixed, *i. e.*, for a fixed value of

$$n = N - (m^2 + q\,\eta^2\,\sigma^2)^{1/2} + |m| \tag{52}$$

the number of corresponding wave functions is equal to the number of values taken by n_r and n_r' with the restriction that $n_r + n_r'$ has a fixed value. From ordinary combinatorics, this number is seen to be $n - |m|$.

In the particular case $q = 1$, Eqs. (50) and (51) give the known eigenvalues for the Hartmann potential while in the case $q = 0$ and $\eta\,\sigma^2 = Z$, Eqs. (50)—(52) gives back

$$E = (Z^2/n^2)\,\varepsilon_0 \qquad (n = 1,\ 2,\ 3, \ldots) \tag{53}$$

in agreement with Eq. (40)

5. *The Kratzer and Sommerfeld Potentials*

We now consider the three-dimensional potential (energy)

$$W_q = -2\,a\,D\,(1/r - q\,a/2\,r^2) \tag{54}$$

The case $q = 1$ corresponds to the Kratzer potential, the case $2\,a\,D = Z\,e^2$ and $q\,a^2\,D > 0$ to the Sommerfeld potential, and the case $q = 0$ and $2\,a\,D = Z\,e^2$ to the Coulomb potential. The use of Eqs. (16) and (20) relative to the KS transformation as well as the condition $X\,\psi = 0$ enables us to reach the following result.

Result 8. — The Schrödinger equation for the spherical potential W_q is equivalent to the set comprising (i) the Schrödinger equation

$$-(\hbar^2/2\,\mu)\,\Delta_u\,\psi - 4\,E\,(u_1^2 + u_2^2 + u_3^2 + u_4^2)\,\psi +$$
$$+ q\,a^2\,D\,(u_1^2 + u_2^2 + u_3^2 + u_4^2)^{-1}\,\psi = -8\,a\,D\,\psi \tag{55}$$

for an R^4 nonharmonic oscillator with inverse-square potential and (ii) a constraint condition [Eq. (44)].

At this stage, it is perhaps interesting to point out the formal analogy between Eqs. (48) and (55), although Eq. (48) is concerned with a motion in a two-dimensional space and Eq. (55) with a motion in a four-dimensional space. With regard to this, we may employ the LC transformation to derive the following result.

Result 9. — The Schrödinger equation for a two-dimensional potential of type W_q is equivalent to the set comprising (i) the Schrödinger equation for a R^2 isotropic nonharmonic oscillator with inverse-square potential [the form of which equation is similar to the one of Eq. (48)] and (ii) the constraint condition $\psi(x_i(u_i)) = \psi(x_i(-u_i))$ with $i = 1, 2$.

6. *The* $-g^2(1-q^2r^2)/r$ *Potential*

We shall close this study with the three-dimensional potential (energy)

$$X_q = -g^2(1-q^2r^2)/r \tag{56}$$

which identifies with the potential for a hydrogenlike atom for $q = 0$ and $g^2 = Ze^2$. By using Eqs. (16) and (20) relative to the KS transformation as well as the condition $X\psi = 0$, we come to the last result.

Result 10. — The Schrödinger equation for the spherical potential X_q is equivalent to the set comprising (i) the Schrödinger equation

$$-(\hbar^2/2\mu)\,\Delta_u\psi - 4E(u_1^2+u_2^2+u_3^2+u_4^2)\psi + \\ +(2gq)^2(u_1^2+u_2^2+u_3^2+u_4^2)^2\psi = 4g^2\psi \tag{57}$$

for a R^4 isotropic anharmonic oscillator with quartic anharmonicity and (ii) a constraint condition [Eq. (44)].

IV. DISCUSSION

Let us first discuss Results 1 to 4. The connection between the R^3 hydrogen atom and a R^4 isotropic harmonic oscillator under constraint was obtained from the KS transformation first by Ikeda and Miyachi[19] and independently by Boiteux[20] while special attention was paid to the bound states of the hydrogen atom. This result has been rediscovered on various occasions and extended to the scattering states and the zero-energy point.[21,24,29] Results 1, 2, and 3 throw new light on these matters since they indicate that the R^4 oscillator under constraint breaks into a coupled pair of R^2 isotropic harmonic oscillators. Furthermore, as a group-theoretical pending part of Results 1, 2, and 3, Result 4 shows the relevance of the Lie algebra of the group SO(4, 2) for the hydrogen atom in a way distant from the original derivations.[42] With regard to this, let us mention that so(4, 2) was described by Kleinert[42] as arising from an extension of so(4,1), while here so(4,2) is obtained from a constraint on sp(8, R). It should be noted that Result 4 was originally derived by finding and solving a boson realisation of the Pauli equations for the R^3 hydrogen atom.[29]

Results 5 and 6 are indeed preliminary results which demand further investigations in order to tackle the obtained Schrödinger equations. It should be noted that Result 6 establishes a link between two presently unsolved problems of applied quantum mechanics, *viz.*, the problem of the R^3 hydrogen atom in a (strong) magnetic field and the problem of anharmonic oscillators. In recent years, numerous studies have focused on both problems, and it is hoped that any progress in one problem will have repercussions on the other thanks to Result 6.

Result 7 provides us with a good illustration of what can be expected of the application of the KS transformation to another problem of interest to chemical physics. The Schrödinger equation for a slightly modified form (V_q) of the Hartmann potential has been transformed into a system involving nonharmonic oscillators, the solution of which may be readily found. Let us however mention that our study of the V_q potential problem is far from being complete since we leave open questions on the dynamical symmetry group for this problem (cf., Ref. 32). Similar remarks apply to Results 8 and 9 that concern the Kratzer and Sommerfeld potentials as well as to Result 10 concerning a potential used in confinement problems.

At this point, it is worth to mention briefly a connection between the approach via nonbijective canonical transformations and the method of homogeneous canonical transformations developed by Dirac[43]. We note that the constraint condition $X\psi = 0$, which has been overlooked by several people dealing with the KS transformation, corresponds to a primary first-class constraint ($X = 0$) in the sense of Dirac. This point should be further investigated, especially in conjunction with the so-called nonbijectivity or ambiguity group[20,37], and the reader is referred to Ref. 26 and to a forthcoming paper (cf., Ref. 28) for more details.

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SAŽETAK

Primjena nonbijektivnih kanonskih transformacija u kemijskoj fizici

Maurice Kibler i Tidjani Négadi

Razmotrena je primjena nonbijektivnih kanonskih transformacija u teorijskoj kemiji. Opisane su tri jednostavne kvadratne transformacije: Levi-Civita, Kustaanheimo-Stiefel i nova, izvorna transformacija. Posebna pažnja poklonjena je primjeni Kustaanheimo-Stiefelove transformacije na Starkov i Zeemanov efekt u atomu vodika kao i u ionima sličnima vodiku.