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Elementary solutions of the quantum planar two-center problem

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Abstract – The quantum problem of an electron moving in a plane under the field created by two Coulombian centers admits simple analytical solutions for some particular intercenter distances. These elementary eigenfunctions, akin to those found by Demkov for the analogous three-dimensional problem, are calculated using the framework of quasi-exactly solvability of a pair of entangled ODE’s descendants from the Heun equation. A different but interesting situation arises when the two centers have the same strength. In this case completely elementary solutions do not exist.

Introduction. – The quantum spectral problem of a charged particle moving in the field created by two fixed Coulomb centers appears in a natural way in the study of diatomic molecular ions, in the Born-Oppenheimer approximation. Although the three-dimensional case has been profusely studied from different points of view: computational, see, e.g., [1], analytical, see [2,3], as far as we know the search for elementary solutions has been reduced to the work of Demkov [4] in the two-center problem in three dimensions.

In this letter, the existence of elementary solutions for the planar problem is studied. The underlying idea is similar to the Demkov approach [4] to the three-dimensional case, and thus we search for the eigenfunctions of the system that can be written essentially as polynomials. Unlike the three-dimensional problem, the planar system admits elementary solutions not only of hydrogenoid type, i.e., eigenfunctions with energy coinciding with the energy levels of an hydrogenoid atom, but also of a new type that we shall term as “quasi”-hydrogenoid. These new type of elementary solutions does not arise in the three-dimensional problem, its existence in the plane is reminiscent of the particular topology subjacent to the 2D problem.

The Schrödinger equation for the planar problem is separable in Euler elliptic coordinates. After the separation process the PDE wave equation reduces to two ODE’s, namely a Razavy and a Whittaker-Hill equation, linked by the two invariants of the system. In his original article [5] Razavy showed that, for certain values of parameters, a finite part of the spectrum was calculable in closed form. Later, in [6,7], it was proved that these exact computable eigenfunctions for Razavy equation could be obtained in terms of four polynomial sets. Finkel et al. [8] showed that the Schrödinger equation associated to the Razavy potential is quasi-exactly solvable (QES), the mentioned sets of polynomials was nothing but instances of the associated weakly orthogonal polynomial family [9], which allow to find these special eigenfunctions. Finally, these results were also extended to the Whittaker-Hill equation in [8].

In this work we will follow a slightly different approach treating the two equations as particular descendants of the Confluent Heun equation (CHEq), and, thus, considering that it is possible to obtain polynomial solutions when the parameters of the problem render these two versions of CHEq simultaneously QES [10].

The separability properties and the study of the general potentials that admit exact and quasi-exact solvability for a broad family of physical problems associated to the 3D two-center problem have been recently analyzed thoroughly in ref. [11].

When the two centers are of equal strength, contrary to expectations, the problem is more involved. The Whittaker-Hill equation descends to the Mathieu equation which is never QES. Thus, there are not completely elementary eigenfunctions in this situation, although interesting wave functions may be derived for certain intercenter distances determined from the Mathieu characteristic values.

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The planar quantum problem posed by two Coulombian centers. – The stationary Schrödinger equation governing the quantum dynamics of a charged particle moving in the potential of two fixed Coulombian centers (nuclei, ions, etc) in the plane reads:

\[
\left(-\frac{1}{2} \Delta - \frac{Z_1}{r_1} - \frac{Z_2}{r_2}\right) \Psi = E \Psi, \tag{1}
\]

where \( \Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \), and atomic units are used: \( \hbar = m_e = e = a_0 = 1 \), \( a_0 \) being the Bohr radius. \( Z_1 \) and \( Z_2 \) are the atomic numbers of the two nuclei, and \( r_1 \) and \( r_2 \) are the distances from the electron to the nuclei:

\[
r_1 = \sqrt{(x - R/2)^2 + x_1^2}, \quad r_2 = \sqrt{(x + R/2)^2 + x_2^2},
\]

while \( R \) is the internuclear distance. Equation (1) admits separation of variables using Euler elliptic coordinates \((\xi, \eta), \xi = (r_1 + r_2)/R \in (1, +\infty) \) and \( \eta = (r_2 - r_1)/R \in (-1, 1) \). Search for separated wave functions \( \Psi(\xi, \eta) = F(\xi)G(\eta) \) converts eq. (1) into two ODEs: one

\[
(\xi^2 - 1) \frac{d^2 F(\xi)}{d\xi^2} + \xi \frac{d F(\xi)}{d\xi} + \left(\frac{ER^2}{2} - \frac{\lambda}{\xi} + \frac{2}{\xi} R(Z_1 + Z_2) \xi + \lambda\right) F(\xi) = 0 \tag{2}
\]

in the “radial” coordinate \( \xi \in (1, \infty) \), the other

\[
(1 - \eta^2) \frac{d^2 G(\eta)}{d\eta^2} - \eta \frac{d G(\eta)}{d\eta} - \left(\frac{ER^2}{2} \eta^2 - \frac{\lambda}{\eta} + \frac{2}{\eta} R(-Z_1 + Z_2) \eta + \lambda\right) G(\eta) = 0 \tag{3}
\]

in the “angular” \( \eta \in (-1, 1) \) coordinate. \( \lambda \) is the separation constant.

Equations (2) and (3) are nothing but the algebraic form of Razavy and Whittaker-Hill equations, respectively, see, e.g., [12]. The wave functions of our problem are given by the product of solutions of (2) and (3) for identical values of \( \xi \) and \( \eta \), respectively, see [12]. The wave functions of our problem are given by the product of solutions of (2) and (3) for identical values of \( \xi \) and \( \eta \).

The connection with the Confluent Heun equation. Both (2) and (3) are reduced to CHEq [13,14]:

\[
\begin{align*}
(z^2 - 1) u''(z) + \left(\frac{\epsilon}{2} (z^2 - 1) + \gamma (z - 1) + \delta (z + 1)\right) u'(z) &+ \left(\frac{\alpha}{2} (z + 1) - q\right) u(z) = 0, \tag{4}
\end{align*}
\]

via the changes of variable:

\[
\begin{align*}
F(\xi) &= (\xi + 1)^{\frac{\delta - 1}{2}} (\xi - 1)^{\frac{\delta - 1}{2}} e^{\xi - \frac{q}{2}} u(\xi), \tag{5}
G(\eta) &= (1 + \eta)^{\frac{\alpha - 1}{2}} (1 - \eta)^{\frac{\alpha - 1}{2}} e^{\frac{q}{2}} u(\eta), \tag{6}
\end{align*}
\]

that are compatible with the form of Razavy and Whittaker-Hill equations only in the four following cases:

\[
\begin{align*}
a) \delta &= \gamma = 1/2, & b) \delta &= \gamma = 3/2, & c) \delta &= 1/2, \gamma = 3/2, & d) \delta &= 3/2, \gamma = 1/2. \tag{7}
\end{align*}
\]

The rest of CHEq constants are related to the physical parameters of eqs. (2) and (3) by the identities: \( \epsilon^2 = -8ER^2 \), and

\[
\lambda = \frac{\epsilon^2}{16} + \frac{\epsilon(\gamma - \delta)}{4} - \frac{(\gamma + \delta)(\gamma + \delta - 2)}{4} + \frac{2\alpha - 1}{4} - q
\]

together with \( \alpha = \frac{\epsilon}{4} (\delta + \gamma) = R(Z_1 + Z_2) \)

in the radial equation, and

\[
\alpha = \frac{\epsilon}{4} (\delta + \gamma) = R(Z_2 - Z_1)
\]

in the angular one.

If we interpret CHEq as a spectral problem \( Du(z) = qu(z) \), it is not difficult to show, see [10], that the differential operator \( D \) can be written as a quadratic combination of the generators of the Lie algebra sl(2, \( R \)) if and only if \( \alpha = -\pi \epsilon \), being \( \pi \) a non-negative integer, and consequently CHEq represents a quasi-exactly solvable spectral problem [15–17] for this special combination of parameters. In this situation it is possible to find an invariant module of polynomial solutions of (4) associated with each arbitrary value of \( n \). Following the standard procedure [9,18] we search for Frobenius solutions of the form:

\[
u(z) = \sum_{k=0}^{\infty} \frac{(-1)^k P_k(q)(\gamma + 1)}{2^k k! (\gamma)_k} (z + 1)^k, \tag{8}
\]

where \( (\gamma)_k = \gamma(\gamma + 1)\ldots(\gamma + k - 1) \) and \( P_0(q) = 1 \), which leads to the following three-term recurrence between the polynomials \( P_k(q) \) for \( k \ge 1 \):

\[
P_{k+1}(q) = (q - k(\delta + \gamma - \epsilon + k - 1)) P_k(q) - k\epsilon(n - k + 1)(\gamma + k - 1) P_{k-1}(q). \tag{9}
\]

Thus, given a concrete value of \( n \), and fixing \( q \) as one of the \( n + 1 \) roots of \( P_{n+1}(q) \), \( q_j, j = 1, \ldots, n + 1 \), solutions (7) truncate to polynomials of degree \( n \),

\[
u_{n,j}(z) = \sum_{k=0}^{n} \frac{(-1)^k P_k(q_j)(\gamma + 1)}{2^k k! (\gamma)_k} (z + 1)^k \tag{10}
\]

and consequently a \((n + 1)\)-dimensional module of polynomial eigenfunctions of (4) can be determined algebraically. The polynomials \( P_k(q) \) constitute the weakly orthogonal polynomial family [9] associated to the QES property for CHEq [10]. It is interesting to remark that the particularization of this family to the Razavy and Whittaker-Hill parameters corresponds with the first polynomial family found in [8] for these equations.
Elementary solutions of Razavy equation. — Translating the QES condition of (4) to the Razavy equation (2): $\alpha = -n^r \epsilon$, $n^r \in \mathbb{N}$, a quantization condition in the expression of $\epsilon$ appears,

$$\frac{\alpha}{2} - \frac{\epsilon}{4}(\gamma + \delta) = R(Z_1 + Z_2) \implies \epsilon = -\frac{4R(Z_1 + Z_2)}{(2n^r + \gamma + \delta)}$$

and, consequently, in the energy eigenvalues,

$$E = -\frac{\epsilon^2}{8R^2} \implies E_{n^r} = -\frac{2(Z_1 + Z_2)^2}{(2n^r + \gamma + \delta)^2}.$$  

(11)

Meanwhile, the separation constant is characterized by $n^r$ but also by $j = 1, \ldots, n^r + 1$, because the explicit dependence in the $q_j$ parameter:

$$\lambda_{n^r,j} = \frac{R^2(Z_1 + Z_2)^2}{(2n^r + \gamma + \delta)^2} + \frac{(2n^r - \gamma + \delta)R(Z_1 + Z_2)}{(2n^r + \gamma + \delta)^2} - \frac{(\gamma + \delta)(\gamma + \delta - 2)}{4} - \frac{1}{4} - q_j.$$

(12)

As was mentioned above, the compatibility between Razavy and CHEq is only possible in four concrete choices of constants $\delta$ and $\gamma$. Thus we find the following expressions for energies, separation constants and eigenfunctions:

**Type a.** $\delta = \gamma = \frac{1}{2}$.

$$E_{n^r} = -\frac{2(Z_1 + Z_2)^2}{(2n^r + 1)^2},$$

$$\lambda_{n^r,j} = -\frac{R^2E_{n^r}}{2} + \frac{2n^rR(Z_1 + Z_2)}{2n^r + 1} - q_j,$$

$$F_{n^r,j}(\xi) = e^{-\frac{\eta(x_1 + x_2)\xi}{2n^r + 1}} \eta_{n^r,j}(\xi).$$

**Type b.** $\delta = \gamma = \frac{3}{2}$.

$$E_{n^r} = -\frac{2(Z_1 + Z_2)^2}{(2n^r + 1)^2},$$

$$\lambda_{n^r,j} = -\frac{R^2E_{n^r}}{2} + \frac{2n^rR(Z_1 + Z_2)}{2n^r + 1} - q_j - 1,$$

$$F_{n^r,j}(\xi) = \sqrt{\xi + 1} e^{-\frac{\eta(x_1 + x_2)\xi}{2n^r + 1}} \eta_{n^r,j}(\xi).$$

In the cases c) and d) the energies do not correspond to the planar hydrogenoid atoms, because the even character of the denominator, $2n^r + 2$. Recall that the spectrum of the planar hydrogen problem [12] is $E = \frac{2}{(2n + 1)^2}$. Nevertheless, there exist interesting elementary solutions of Types c) and d) which are reminiscent of the lemniscatic orbits of the classical problem and we shall refer to as “quasi”-hydrogenoid.

**Elementary solutions of Whittaker-Hill equation.** — An equivalent analysis can be performed for the angular equation (3) simply changing the relative sign of the charge $Z_1$ and the range of variation for the angular coordinate. Thus, the condition: $\alpha = -n^a \epsilon$, $n^a \in \mathbb{N}$, leads to the following structure of solutions:

**Type a.** $\delta = \gamma = \frac{1}{2}$.

$$E_{n^a} = -\frac{2(-Z_1 + Z_2)^2}{(2n^a + 1)^2},$$

$$\lambda_{n^a,j} = -\frac{R^2E_{n^a}}{2} + \frac{2n^aR(-Z_1 + Z_2)}{2n^a + 1} - q_j,$$

$$G_{n^a,j}(\eta) = \sqrt{1 - \eta^2} e^{-\frac{\mu(x_1 + x_2)\eta}{2n^a + 1}} \eta_{n^a,j}(\eta).$$

**Type b.** $\delta = \gamma = \frac{3}{2}$.

$$E_{n^a} = -\frac{2(-Z_1 + Z_2)^2}{(2n^a + 1)^2},$$

$$\lambda_{n^a,j} = -\frac{R^2E_{n^a}}{2} + \frac{2n^aR(-Z_1 + Z_2)}{2n^a + 1} - q_j - 1,$$

$$G_{n^a,j}(\eta) = \sqrt{1 - \eta^2} e^{-\frac{\mu(x_1 + x_2)\eta}{2n^a + 1}} \eta_{n^a,j}(\eta).$$

**Type c.** $\delta = \frac{1}{2}, \gamma = \frac{3}{2}$.

$$E_{n^a} = -\frac{2(-Z_1 + Z_2)^2}{(2n^a + 1)^2},$$

$$\lambda_{n^a,j} = -\frac{R^2E_{n^a}}{2} + \frac{(2n^a - 1)R(-Z_1 + Z_2)}{2n^a + 2} - q_j - 1,$$

$$G_{n^a,j}(\eta) = \sqrt{1 - \eta^2} e^{-\frac{\mu(x_1 + x_2)\eta}{2n^a + 2}} \eta_{n^a,j}(\eta).$$

**Type d.** $\delta = \frac{3}{2}, \gamma = \frac{1}{2}$.

$$E_{n^a} = -\frac{2(-Z_1 + Z_2)^2}{(2n^a + 1)^2},$$

$$\lambda_{n^a,j} = -\frac{R^2E_{n^a}}{2} + \frac{(2n^a + 1)R(-Z_1 + Z_2)}{2n^a + 2} - q_j - 1,$$

$$G_{n^a,j}(\eta) = \sqrt{1 - \eta^2} e^{-\frac{\mu(x_1 + x_2)\eta}{2n^a + 2}} \eta_{n^a,j}(\eta).$$

**Elementary solutions of the Schrödinger equation.** — The simultaneous existence of elementary solutions in both radial and angular equations, for fixed values of $Z_1$ and $Z_2$, is obviously possible only if the parameters $E$ and $\lambda$ determined in the resolution process are the same for both equations.

Thus, there exist elementary solutions of the Schrödinger equation only for those values of $\eta_1 \in \mathbb{N}$ and
as illustrative examples, we present several elementary solutions for two pairs of charges: Z₁ = 5, Z₂ = 1, and Z₁ = 2, Z₂ = 1.

**Charges Z₁ = 5, Z₂ = 1:** The elementary eigenfunction of minimum energy corresponds to the n₁ = 3 and n₂ = 2 solution of (13): E = –8. This solution appears considering Type b) in Razavy equation with n² = 0 and Type d) in Whittaker-Hill equation with n² = 0. The compatible value of λ is –7/16 that is obtained for R = 3/8. Thus, we have the eigenfunction (see fig. 1):

\[ \Psi(\xi, \eta) = \sqrt{\xi^2 - 1 - \eta} e^{-\frac{1}{2}(\xi - \eta)}. \]  

The next energy level where elementary solutions are found is E = –2. These solutions are obtained for n₁ = 6 and n₂ = 4 in (13), in four different combinations of Types c) and d):

- **Type d)** in both equations. The values of the constants are: λ = –583/256 and R = 3/16 and the wave function reads (fig. 2)

\[ \Psi(\xi, \eta) = \sqrt{\xi^2 - 1 - \eta} \left( \eta + \frac{1}{3} \right) \times \left( \xi^2 - 10\xi - 7 \right) e^{-\frac{1}{2}(\xi - \eta)}. \]  

- **Type d)** in Razavy equation and Type c) in Whittaker-Hill equation. λ = –2.247, R = 0.435,

\[ \Psi(\xi, \eta) = \sqrt{\xi^2 - 1 - \eta} (\eta - 0.713) \times \left( \xi^2 - 3.889\xi - 3.538 \right) e^{-0.435(\xi - \eta)}. \]

- **Type c) and d)**, respectively. λ = –3.111, R = 1.643,

\[ \Psi(\xi, \eta) = \sqrt{\xi + 1} \left( \eta + 3.203 \right) \times \left( \xi^2 - 10.555\xi + 16.819 \right) e^{-1.643(\xi - \eta)}. \]

- **Type c) and d)** again. λ = –0.587, R = 0.292,

\[ \Psi(\xi, \eta) = \sqrt{\xi + 1} \left( \eta + 3.203 \right) \times \left( \xi^2 - 10.555\xi + 16.819 \right) e^{-1.643(\xi - \eta)}. \]
In order to facilitate the presentation we have written some of the numbers rounded to three significant decimal digits, although all these elementary eigenfunctions have been obtained using exact analytic expressions. There exist also elementary solutions containing polynomials of higher orders, that have to be calculated using numerical approximations because the determination of the roots of the radial equation (2) is still a Razavy equation, but the an-

tions only for Razavy equation and to determine the solutions of Mathieu equation corresponding to the values of $E\nu^n$ and $\lambda_{\nu^n,j}$, (11), (12). Each elementary Razavy solution is associated with a Mathieu equation (17) with the parameters:

$$a_{n,j} = -\lambda_{n,j} = \frac{E\nu^n R^2}{4}, \quad p_{n,j} = \frac{E\nu^n R^2}{8}. $$

There exist solutions of Mathieu equation (17) with different periodicity or quasi-periodicity properties, and they are applicable to a physical problem depending on its special characteristics, see for instance [21]. In the two-center problem, the physically admissible eigenfunctions of the Schrödinger equation must be univalued and thus it is necessary to consider only the $2\pi$-periodic solutions of (17), the proper Mathieu functions: $Ce_n(p,z)$ and $Se_n(p,z)$ [19,20]. The Mathieu cosine $Ce_n(p,z)$, $n = 0, 1, \ldots$, and sine $Se_n(p,z)$, $n = 1, 2, \ldots$, are solutions of (17) only if the parameter $a$ takes the Mathieu characteristic values $a_n(p)$ and $b_n(p)$, respectively.

An elementary Razavy solution determined by $E\nu^n$ and $\lambda_{\nu^n,j}$ is compatible only with values of $R$ such that the Mathieu parameter $a_{\nu^n,j}$ coincides with a characteristic value of the Mathieu cosine or sine functions, i.e.

$$-\lambda_{\nu^n,j} = \frac{E\nu^n R^2}{4} = a_n \left(\frac{E\nu^n R^2}{8}\right)$$

Fig. 3: (Colour online) Graphical representation of $\rho(x_1, x_2)$ for (20) and several level curves of $\rho(x_1, x_2)$.

Mathieu equation (17) does not admit polynomial solutions [20], this fact can be easily checked because the quasi-exact solvability condition for CHEq is not compatible with the form of Mathieu equation (16). Complete elementary solutions, products of two polynomials, for the planar two-center problem in the symmetric case do not exist.

Nevertheless, it is possible to consider elementary solutions only for Razavy equation and to determine the solutions of Mathieu equation corresponding to the values of $E\nu^n$ and $\lambda_{\nu^n,j}$, (11), (12). Each elementary Razavy solution is associated with a Mathieu equation (17) with the parameters:

$$a_{n,j} = -\lambda_{n,j} = \frac{E\nu^n R^2}{4}, \quad p_{n,j} = \frac{E\nu^n R^2}{8}. $$

There exist solutions of Mathieu equation (17) with different periodicity or quasi-periodicity properties, and they are applicable to a physical problem depending on its special characteristics, see for instance [21]. In the two-center problem, the physically admissible eigenfunctions of the Schrödinger equation must be univalued and thus it is necessary to consider only the $2\pi$-periodic solutions of (17), the proper Mathieu functions: $Ce_n(p,z)$ and $Se_n(p,z)$ [19,20]. The Mathieu cosine $Ce_n(p,z)$, $n = 0, 1, \ldots$, and sine $Se_n(p,z)$, $n = 1, 2, \ldots$, are solutions of (17) only if the parameter $a$ takes the Mathieu characteristic values $a_n(p)$ and $b_n(p)$, respectively.

An elementary Razavy solution determined by $E\nu^n$ and $\lambda_{\nu^n,j}$ is compatible only with values of $R$ such that the Mathieu parameter $a_{\nu^n,j}$ coincides with a characteristic value of the Mathieu cosine or sine functions, i.e.

$$-\lambda_{\nu^n,j} = \frac{E\nu^n R^2}{4} = a_n \left(\frac{E\nu^n R^2}{8}\right)$$

Fig. 4: (Colour online) Graphical representation of $\rho(x_1, x_2)$ for (21) and several level curves of $\rho(x_1, x_2)$.
for some \( n = 0, 1, 2, \ldots \), or
\[
-\lambda_{n', j} - \frac{E_{n'}R^2}{4} = b_n \left( \frac{E_{n'}R^2}{4} \right)
\]  
for some \( n = 1, 2, \ldots \).

As examples, several eigenfunctions of this type are presented:

**Charges** \( Z_1 = Z_2 = 3 \): We illustrate the process with the simplest example: Choosing the energy \( E = -8 \), obtained for \( n' = 1 \) in the Type a) of Razavy equation, there are two allowable values for the separation constant: \( \lambda_{1,1} \) and \( \lambda_{1,2} \).

The associated Mathieu equations have parameters: \( a_{1,1} \) and \( a_{1,2} \), respectively, and \( p_1 = -R^2 \). There exists only one possibility for \( R \) that leads \( a_{1,1} \) and/or \( a_{1,2} \) to be a characteristic value of the Mathieu equation: if \( R = 1.335 \), then \( a_{1,2} = b_1(p_1) = 2.298 \), \( \lambda_{1,2} = 1.268 \). For these values, the transcendent equation (19) is satisfied. Thus, the eigenfunction is (fig. 3)
\[
\Psi(\xi, \nu) = e^{-2.6714\xi}(\xi + 0.911)Se_1(-1.783, \nu).
\] (20)

Other examples are
\[
\begin{align*}
- \quad & E = -18, \quad \lambda = -0.264, \quad R = 0.329, \quad a_1(p_0) = 0.750, \\
\Psi(\xi, \nu) &= e^{-0.986\xi}\sqrt{\xi + 1}Ce_1(-0.243, \nu), \text{ see fig. 4}; \\
- \quad & E = -\frac{9}{2}, \quad \lambda = -3.133, \quad R = 0.870, \quad b_2(p_1) = 3.985, \\
\Psi(\xi, \nu) &= e^{-1.305\xi}\sqrt{\xi + 1}(\xi + 0.491)Ce_2(-0.426, \nu); \\
- \quad & E = -\frac{72}{25}, \quad \lambda = 6.412, \quad R = 4.491, \quad a_2(p_2) = 8.111, \\
\Psi(\xi, \nu) &= e^{-5.389\xi}(\xi^2 + 1.729\xi + 0.735) \\
& \quad \quad \times Ce_2(-7.262, \nu).
\end{align*}
\] (21)

For aesthetic reasons, the characteristic values and the other quantities involved in (20), (21) and the rest of the equations, are presented using only three significant decimal digits, although obviously an arbitrary precision can be obtained.

It is possible to find a plethora of solutions of this mixed type with specific values of \( R \) physically meaningful in the atomic/molecular range.

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