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The Schrödinger Group in Molecular Quantum Mechanics:

Beyond the Born-Oppenheimer Approximation

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Abstract

The Galilei transformation invariant form of molecular quantum mechanics is obtained, which is not restricted by the Born-Oppenheimer approximation. The molecular Hamiltonian takes then the form of a linear combination of operators of the Schrödinger group, which define the new space-time molecular symmetry properties (e.g. helicity).

The puzzling homochirality of the hydrogen bonded biomolecular systems appears then as a simple result of the molecular space-time symmetry.

## 1. Introduction

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From the early years of quantum mechanics treatments, of molecular systems and ~~those~~ of of the solid state ~~systems~~ are based on the Born-Oppenheimer approximation, [1], [2] where owing to a big difference between the nuclear and electronic mass, the ratio of nuclear to electronic velocity is considered as negligible. In quantum mechanics, this ratio can be evaluated [3], [4] from the Heisenberg relation where for the electronic energy

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$$\overline{\Delta E} \cong \frac{\hbar}{\Delta t} \quad (1)$$

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$$\overline{v}_e = \frac{D}{\Delta t} = \frac{D \overline{\Delta E}}{\hbar} \quad (2)$$

and by similar expressions for the energy of nuclear vibrations  $\overline{\delta \varepsilon}$ , we have

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$$\kappa = \frac{\overline{v}_n}{\overline{v}_e} = \frac{d}{D} \frac{\overline{\delta \varepsilon}}{\overline{\Delta E}} \quad (3)$$

where D, d are the linear dimensions of the electronic and nuclear distributions.

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For the non-degenerate electronic states

$$\overline{\Delta E} \gg \delta \bar{\epsilon} \quad (4)$$

which justifies the Born-Oppenheimer approximation: an electron adjusts immediately (with no delay) to any momentary nuclear position. In relation (3) the electronic velocity  $\bar{v}_e$

is therefore, considered as very big and we can put  $\kappa=0$  in the Born-Oppenheimer approximation: an electron “sees” the nuclear coordinate but no nuclear velocity.

For the degenerate electronic states, the value of  $\kappa$  – by (3) – is very big (formally infinite) and the Born-Oppenheimer approximation breaks down. In molecular physics, the case of the degenerate electronic states is described in terms of vibronic coupling. For all three well known cases of vibronic coupling (the Jahn-Teller effect [5], [6], the Renner effect [5], [6] and the vibronic coupling in dimers and molecular crystals [7]) in the matrix Hamiltonians for the nuclear wave functions, the off-diagonal terms of the nuclear potential energy are determined and lead only to the purely geometric instabilities for the non-totally symmetric normal coordinates.

The physical situation for the degenerate and non-degenerate electronic molecular states requires, however, somewhat deeper analysis. For the non-degenerate electronic states it is reasonable, by (4), to consider the high frequency electronic states to adjust immediately to the nuclear positions and to neglect in the nuclear Hamiltonian any  $\kappa$  dependent terms.

For the degenerate electronic states, however,

$$\delta \bar{\epsilon} \gg \overline{\Delta E} \quad (5)$$

and it does not make much sense to consider electronic movements as able to adjust immediately to the nuclear positions: they must adjust with a delay, which should be a function of  $\kappa$  and connect both extreme cases (4), (5).

For this purpose, consider a molecular system in the Born-Oppenheimer approximation.

Define the origin of the nuclear reference system by a fixed value of the nuclear coordinate and the origin of the electronic reference system also by its fixed value. The Schrödinger equation for the molecular oscillator equals then

$$i \frac{\partial \Psi}{\partial t} = \frac{1}{2} (p^2 + q^2) \Psi \quad (6)$$

where  $q$  denotes the corresponding nuclear normal coordinate. From (3)  $\kappa$  is then equal to

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$$\kappa = \frac{\bar{v}_e \cdot \bar{v}_n}{|\bar{v}_e|^2} \quad (7)$$

which defines for  $\kappa \neq 0$  two distinct possibilities.

If both electronic and nuclear velocities move in the same direction, then

$$\kappa > 0 \quad (8)$$

but if they move in opposite directions, then

$$\kappa < 0 \quad (9)$$

The physical situation is somewhat similar to that which occurs in the ionic crystals with two atoms in the unit cell. When both ions move in-phase, then an acoustic branch is formed, but when they move out-of-phase, an optical (polar) one is formed. In the acoustic branch, both ions move in phase with the same amplitudes, but in the optical one the amplitudes are inversely proportional to the ionic mass.

To obtain for  $\kappa \neq 0$  the molecular Schrödinger equations, which cover both cases (8) and (9), observe that the Born-Oppenheimer approximation defines (by fixing the normal coordinate as origin) a very special reference system – not a general inertial one. Suppose now that both origins of the reference systems are subject to the following transformation

$$q = q - \kappa p t \quad (10)$$

where  $q$ ,  $p$  are the nuclear coordinate and the linear momentum correspondingly. If we take  $q = 0$  as the origin of the reference system for the molecular oscillator in (6), then  $\dot{q} = 0$  means

$$\frac{q}{t} = \kappa p \quad (11)$$

which (in the Schrödinger picture) is the Galillei transformation. The uniform shift with a constant velocity of both origins is physically equivalent and cannot change the total molecular interaction energy, but now in the space of the relative nuclear-electronic coordinates, any two space-time points are related by the Galillei transformation (10).

In classical mechanics, the Galillei transformation (10) is a simple shift with constant velocity of the origin of the reference system. In quantum mechanics, however, the Galillei transformation should be considered [8], [9] as the non-relativistic limit of the Lorentz transformation. The last one has the geometrical meaning of a rotation by hyperbolic angles in planes containing the time axis and of a rotation by normal angles in planes containing the space axes. In the continuous transition to the non-relativistic limit

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(contraction) this geometric meaning of the Lorentz transformation should be preserved. In a similar way (by contraction) one can determine the non-relativistic limits of the other operators of the relativistic groups. In particular the Schrödinger group [8], [9] is the non-relativistic limit of the most general relativistic group – the conformal group. The Hamiltonian of a quantum oscillator in (6) is an element of the Schrödinger group [8], [9] and, as will be shown a little later, under the action of the Galillei transformation, leads to a linear combination with the other elements of the Lie algebra of the group, which – like the Lorentz group – is a space-time one. The Hamiltonian of the molecular oscillator in (6) is (for  $\kappa=0$ ) invariant under the space group of the molecular point symmetry one. To extend the validity of molecular quantum mechanics beyond the Born-Oppenheimer approximation we must consider the molecular oscillator (6) in the general inertial reference system (10).

The Born-Oppenheimer approximation acquires now a new physical sense, as an attempt of separating the molecular space and time variables: for  $\kappa \neq 0$  it is no more possible.

In an electronic Hamiltonian, the electronic pairs formed by electrons of opposite spins and equal energy play a similar role to the role of vibrational quanta: the Hamiltonian of an electronic pair under the Galillei transformation leads for  $\kappa \neq 0$  to a linear combination with the other elements of the Lie algebra of the Schrödinger group.

For big values of  $\kappa$ , the space-time group defines a new molecular symmetry element: helicity, which is a projection of the time dependent angular momentum on the linear one.

It will be shown, a little later, that vibrational quanta for  $\kappa \neq 0$  correspond to (8) and have, therefore, a mechanical character, where as molecular electronic pairs correspond to (9) and are therefore, of a polar character, separating the nuclear and electronic charges. Electronic pairs at distances greater than the chemical bonds have a non-vanishing expectation value of helicity and correspond, therefore, to weak, long distance bonds between two electrons, but these bonds have no center or plane of symmetry. Invariance under the Galillei transformation defines the space-time symmetry, which does not contain the space and time inversion: “the left and right glove” are not equivalent.

## 2. Hamiltonian of Nuclear Vibrations in the Inertial Molecular Reference System

Consider the Born-Oppenheimer molecular oscillator (6) in the inertial reference system (10), as

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$$\tilde{q} = UqU^{-1} = q - \kappa pt \quad (12)$$

where

$$U = e^{-\frac{i}{2}p^2\kappa t} \quad (13)$$

then unitary transformation (13) transforms (6) to (Appendix 1)

$$i \frac{\partial \Psi}{\partial t} = \frac{1}{2}(p^2 + \tilde{q}^2)\Psi = \eta \Psi \quad (14)$$

where

$$\eta = \frac{1}{2}(p^2 + q^2) - \frac{1}{2}\kappa t(pq + qp) + \frac{1}{2}\kappa^2 t^2 p^2 \quad (15)$$

The transformed Hamiltonian (15) does not yet have any transparent physical meaning. For

this, purpose introduce the creation and destruction operators  $a^+$ ,  $a$

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$$p = \frac{i}{\sqrt{2}}(a^+ - a), \quad q = \frac{1}{\sqrt{2}}(a^+ + a) \quad (16)$$

with

$$[a^+, a] = 1 \quad (17)$$

and define the following 3 operators

$$\tau_1 = \frac{1}{2}(a^+ a^+ + aa) \quad (18)$$

$$\tau_2 = \frac{i}{2}(a^+ a^+ - aa) \quad (19)$$

$$\tau_3 = \frac{1}{2}(a^+ a + aa^+) = \frac{1}{2}(1 + 2a^+ a) \quad (20)$$

the Hamiltonian (15) takes now the following form

$$\eta = x_0 \tau_3 + x_1 \tau_1 + x_2 \tau_2 \quad (21)$$

and from (15) (Appendix 1)

$$x_0^2 - x_1^2 - x_2^2 = 1 \quad (22)$$

Operators  $\tau_i$  have the following commutation properties

$$[\tau_1, \tau_2] = 2i\tau_3 \quad (23)$$

$$[\tau_2, \tau_3] = -2i\tau_1 \quad (24)$$

$$[\tau_3, \tau_1] = -2i\tau_2 \quad (25)$$

and form the Lie algebra elements of the subgroup (dynamical SU(1,1)) of the Schrödinger group [8], [9]. Operators  $\tau_i$  in (23) – (25) have similar commutation properties to those of the components of the usual angular momentum (except the signs in (24), (25)) and the Galillei transformation (12) has the sense of a rotation of the operator  $\tau_3$

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$$\frac{1}{2}(p^2 + q^2) = \tau_3 \quad (26)$$

in the corresponding two planes, but in the Minkowski space (22). In terms of the  $\tau_i$  operators the transformation U of (13) equals

$$U = e^{-i\frac{1}{2}p^2\kappa t} = \exp\left[-\frac{i}{2}(\tau_3 - \tau_1)\kappa t\right] \quad (27)$$

The dynamical group SU(1,1)  $\approx$  SO(2,1) is the group of the transformations of a real three-dimensional vector space keeping invariant the indefinite form

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$$z_0^2 - z_1^2 - z_2^2 = \text{inv} \quad (28)$$

This group by keeping invariant (22), defines three operators  $\tau_i$  in the space corresponding to the hyperbolic geometry (22).

The coherent states  $\tau_i$  in this group were defined by Barut and Girardello [10] by

$$(\tau_2 + i\tau_1)|z\rangle = z|z\rangle = (\alpha + i\beta)|z\rangle \quad (29)$$

Now, the expectation values of  $\tau_i$  operators

$$\langle z|\tau_1|z\rangle = \bar{\beta} \quad (30)$$

$$\langle z|\tau_2|z\rangle = \bar{\alpha} \quad (31)$$

$$\langle z|\tau_3|z\rangle = \bar{\gamma} \quad (32)$$

can be considered by (21) as components of a vector projected on the axes  $x_0, x_1, x_2$  in the space of the hyperbolic geometry (22), and have, therefore the same metric properties

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$$\bar{\gamma}^2 - \bar{\alpha}^2 - \bar{\beta}^2 = 1 \quad (33)$$

From (21) we have, therefore,

$$i\frac{\partial\Phi}{\partial t} = \bar{\eta}\Phi = (x_0\bar{\gamma} + x_1\bar{\beta} + x_2\bar{\alpha})\Phi \quad (34)$$

where

$$\Psi = |z\rangle\Phi(t) \quad (35)$$



and a rotation of the reference system by a normal angle in the  $\bar{\alpha}, \bar{\beta}$  plane and by a hyperbolic angle in the  $\bar{\gamma}, \bar{\alpha}$  plane reduces (34) to

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$$i \frac{\partial \Phi}{\partial t} = x_0 (1 + \bar{\alpha}^2 + \bar{\beta}^2)^{\frac{1}{2}} \Phi \tag{36}$$

For the expectation values of  $\bar{\alpha}, \bar{\beta}$ , use now the same units as for the coordinates  $x_1, x_2$

$$\bar{\beta} = \beta k^2 \tag{37}$$

$$\bar{\alpha} = \alpha k \tag{38}$$

$$k = \frac{1}{\sqrt{2}} \kappa \tag{39}$$

Then

$$i \frac{\partial \Phi}{\partial T} = \tilde{\Gamma} \Phi \tag{40}$$

where

$$\tilde{\Gamma} = \left[ \left( n + \frac{1}{2} \right)^2 + \alpha^2 k^2 + \beta^2 k^4 \right]^{\frac{1}{2}} \tag{41}$$

$$T = \int_0^t x_0 dt = \frac{1}{k} \operatorname{arctgh}(kt) = \frac{\Theta}{k} \tag{42}$$

The new time coordinate T is determined up to the  $k^2$  terms, therefore, to the same order we may simplify (34) to

$$i \frac{\partial \Phi}{\partial t} = (x_0 \bar{\gamma} + x_1 \bar{\beta}) \Phi \text{ and}$$

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$$x_0^2 - x_2^2 = 1 \tag{44}$$

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$$\bar{\gamma}^2 - \bar{\beta}^2 = 1 \tag{45}$$

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which reduces rotations in (34) to a simple rotation by the hyperbolic angle  $\theta$ . Taking as the zero of energy in (34) its Born-Oppenheimer value, we have finally

$$i \frac{\partial \Phi}{\partial T} = \Gamma \Phi \tag{46}$$

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where

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$$\Gamma = \left[ \left( n + \frac{1}{2} \right)^2 + \alpha^2 k^2 \right]^{\frac{1}{2}} - \left( n + \frac{1}{2} \right) \quad (47)$$

To determine the physical nature of the new term  $\alpha k$  in (47), observe that taking  $\hbar\omega$  as an energy unit we have from (47) for  $|\kappa\alpha| < 1$  an additional term  $\frac{1}{2}(\kappa\alpha)^2$  and for  $|\kappa\alpha| > 1$  a

leading term  $\kappa\alpha$ , which allows to define these terms as correspondingly the kinetic energy and the linear momentum of a vibrational quantum relative to the origin of the electronic reference system.

It will be instructive to compare the properties of the molecular oscillator (46) with those of the harmonic oscillator (6) in the Born-Oppenheimer approximation.

It follows from (47) that for big values of  $\kappa\alpha$

$$\Gamma \rightarrow \kappa\alpha > 0 \quad (48)$$

and the physical character of (46) is defined by (8). Nuclear and electronic velocities for  $\kappa \neq 0$  move in  $\pi$  phase, are of the mechanical character and perform periodic movements, which, however, are no more harmonic as in (6). The infrared absorption line shape function of molecular oscillator (46) is the Fourier transform  $\exp[-i\Gamma T]$  (49)

and should present a broad, structured band. The width and structure of this band should be dependent on the isotopic substitution in the reduced mass of the oscillator.

On the other hand the linear structure of the normal coordinates in (6) may – by hyperbolic geometry (22), (33) – appear in (46) as the bent bonds.

### 3. Hamiltonian of Electronic Pairs in the Inertial Molecular Reference System

To describe the electronic states, introduce the creation and destruction operators  $c_n^+, c_n$  defined on the basis of the orthonormal and one-electron solutions of the electronic Hamiltonian in the Born-Oppenheimer approximation which obey the usual anti-commutation rules for fermions

$$\{c_n^+, c_m\} = \delta_{nm} \dots \dots \dots (50)$$

Consider now two fermions  $u, v$

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$$\{u^+, u\} = \{v^+, v\} = 1 \quad \dots \dots \dots (51)$$

$$\{u, u\} = \{v, v\} = \{u, v\} = 0 \quad \dots \dots \dots (52)$$

The Hamiltonian for these two electrons equals

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$$\eta' = \varepsilon_u u^+ u + \varepsilon_v v^+ v = \frac{1}{2}(\varepsilon_u + \varepsilon_v)(1 - \sigma_3) + \frac{1}{2}(\varepsilon_u - \varepsilon_v)(n_u - n_v) \quad \dots \dots \dots (53)$$

where

$$\sigma_3 = 1 - u^+ u - v^+ v = 1 - n_u - n_v \quad \dots \dots \dots (54)$$

For

$$\varepsilon_u = \varepsilon_v = \varepsilon \quad \dots \dots \dots (55)$$

we have, therefore, for the energy eigenvalues

$$i \frac{\partial \Psi'}{\partial t} = (1 - \sigma_3) \Psi' \quad \dots \dots \dots (56)$$

where  $\eta'$  is measured in  $\varepsilon$  units

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Introduce now the operators  $\sigma_i$

$$\sigma_3 = 1 - u^+ u - v^+ v = 1 - n_u - n_v \quad \dots \dots \dots (57)$$

$$\sigma_2 = u^+ v^+ - v u \quad \dots \dots \dots (58)$$

$$\sigma_1 = i(u^+ v^+ + v u) \quad \dots \dots \dots (59)$$

which obey the commutation rules

$$[\sigma_1, \sigma_2] = 2i\sigma_3 \quad \dots \dots \dots (60)$$

$$[\sigma_2, \sigma_3] = -2i\sigma_1 \quad \dots \dots \dots (61)$$

$$[\sigma_3, \sigma_1] = -2i\sigma_2 \quad \dots \dots \dots (62)$$

which are identical with those of (23) – (25) and for any  $i, k$

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$$[\tau_i, \sigma_k] = 0 \quad \dots \dots \dots (63)$$

In terms of  $\sigma_i$  operators the Galillei transformation  $U$  in (27) takes the form of  $V$ , where

$$V = \exp\left[-\frac{i}{2}(\sigma_3 - \sigma_1)kt\right] \dots\dots\dots (64)$$

and (56) transforms to

$$i\frac{\partial\psi'}{\partial t} = (1 + x_0'\sigma_3 + x_1'\sigma_1 + x_2'\sigma_2)\psi' \dots\dots\dots (65)$$

where

$$x_0'^2 - x_1'^2 - x_2'^2 = 1 \dots\dots\dots (66)$$

and

$$x_0' = -x_0 \dots\dots\dots (67)$$

$$x_1' = -x_1 \dots\dots\dots (68)$$

$$x_2' = -x_2 \dots\dots\dots (69)$$

Introduce, as in (29), the coherent states in the  $SU(1,1)$  group

$$(\sigma_2 + i\sigma_1)|z'\rangle = (\alpha' + i\beta')|z'\rangle \dots\dots\dots (70)$$

where

$$\psi' = |z'\rangle\Phi'(t)$$

and

$$\langle z'|\sigma_3|z'\rangle = \bar{\gamma}' \dots\dots\dots (71)$$

$$\langle z'|\sigma_2|z'\rangle = \bar{\alpha}' \dots\dots\dots (72)$$

$$\langle z'|\sigma_1|z'\rangle = \bar{\beta}' \dots\dots\dots (73)$$

and

$$\bar{\gamma}'^2 - \bar{\alpha}'^2 - \bar{\beta}'^2 = 1 \dots\dots\dots (74)$$

In the same units as in (37), (38)

$$\bar{\beta}' = k^2\beta' \dots\dots\dots (75)$$

$$\bar{\alpha}' = k\alpha' \dots\dots\dots (76)$$

and up to the  $k^2$  terms, we may simplify (65) to

$$i\frac{\partial\Phi'}{\partial t} = -\Gamma'\Phi' \dots\dots\dots (77)$$

where

$$\Gamma' = \left[ \varepsilon^2 + \alpha'^2 k^2 \right]^{\frac{1}{2}} - \varepsilon \quad (78)$$

It follows from (77), (78) that for big values of  $|k\alpha'|$

$$-\Gamma' \rightarrow -k\alpha' \quad (79)$$

Therefore the physical character of (78) is determined by (9). Electronic pairs in (77) describe the out-of-phase, polar movements of nuclear and electronic velocities, separating the nuclear and electronic charges.

It follows from (77) that an electronic pair has, by (78), a lower energy than it has in the Born-Oppenheimer case (56), forming, therefore, some attractive interaction – a kind of a two-electron bond. This bonding – by (78) – is dependent on the ratio of velocities (3) and (in contrast to any Coulombic interaction) depends on the reduced mass of the quantum oscillator. It can be described as an electron-electron attraction by a virtual exchange of a vibrational quantum.

Observe now that the expectation values of the  $\tau_i$  operators are determined on one branch of the hyperbola (for the positive values of  $x_i$ ), where as those of the  $\sigma_i$  ones are determined on the other branch, (of the negative  $x_i$ ) by (67) – (68). A continuous change of  $\kappa$  in the Galillei transformation is a rotation. Space for  $\kappa \neq 0$  where vibrational quanta and electronic pairs are determined, cannot contain these discrete operations of space and time reversal.

An electronic pair described by (77), (78) cannot have, therefore, a symmetry center or a plane of symmetry perpendicular to the bond.

#### 4. Molecular Space-Time Symmetry Properties

Consider now equations (46), (77) for different values of

$$\tilde{q} = q - kpt \quad (80)$$

For

$$|q| > |kpt| \quad (81)$$

we have

$$\left[ \left( n + \frac{1}{2} \right)^2 + k^2 \alpha'^2 \right]^{\frac{1}{2}} \rightarrow n + \frac{1}{2} \quad (82)$$

$$T \rightarrow t \quad (83)$$

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and then (82) reduces to the energy of a standard harmonic oscillator and the normal coordinate  $q$  has the space symmetry determined by the irreducible representations of the molecular point symmetry group.

If, however, for the electronic pair, in (80)

$$|kpt| > |q| \quad (84)$$

therefore, for an electronic pair located at a distance greater than the linear dimension of the nuclear distribution or greater than the corresponding chemical bond in the molecular quantum oscillator, we have from (77)

$$-\left[\varepsilon^2 + k^2\alpha^2\right]^{\frac{1}{2}} \rightarrow -k\alpha \quad (85)$$

and

$$T = \frac{\Theta}{k} = \frac{1}{k} \operatorname{arctgh}(kt) \quad (86)$$

It follows from (84) that the molecular point symmetry group of  $q$  can no more be used for defining the symmetry of the time dependent operator

$$kpt \quad (87)$$

which has the symmetry of a pseudoscalar - even in the time reversal and odd in the space reversal.

The time dependent equation for the electronic pair in (77) equals now

$$ki \frac{\partial \Phi'}{\partial \Theta} = kM\Phi' = -k\alpha' \Phi' \quad (88)$$

and defines helicity [3].

As  $M$  is an operator of rotation by an angle  $\Theta$ , (88) is equivalent to

$$\langle \Psi' | Mkp | \Psi' \rangle = -k\alpha' \quad (89)$$

or

$$\chi = \frac{\langle \Psi' | Mkp | \Psi' \rangle}{|k\alpha'|} = -1 \quad (90)$$

and (90) defines the helicity [3]: projection of the angular momentum on the linear one, which is a pseudoscalar.

From (88) the wave function  $\Phi'$  equals

$$\Phi' = \exp[-ik\alpha'T] \quad (91)$$

In the limit (85) the wave function of an electronic pair takes, therefore, a form which is that of a mass-less particle with a helicity equal  $\chi = -1$ .

For the values of  $|k\alpha'|$  smaller than the limiting case (85), only the expectation values of the helicity can be determined. For the group velocity from (77), (78)

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$$-\frac{\partial(\Gamma')}{\partial(k\alpha')} = -\frac{k\alpha'}{[\varepsilon^2 + k^2\alpha'^2]^{\frac{1}{2}}} = -\overline{k\alpha'} \dots\dots\dots (92)$$

and then the helicity expectation value  $\bar{\chi}$  equals: for the Born-Oppenheimer case

$$\bar{\chi} = 0 \dots\dots\dots (93)$$

and for (84)

$$\bar{\chi} = -1 \dots\dots\dots (94)$$

and (92) takes values between (93), (94) otherwise.

An electronic pair with a helicity corresponding to (84) cannot have a center or a plane of symmetry. Indeed, the wave function of a quantum system with a center or plane of symmetry can be classified as even or odd with respect to these operators, therefore

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$$\langle \psi_i | M_{kp} | \psi_i \rangle = \sum_i \langle \psi_i | M | \psi_i \rangle \langle \psi_i | kp | \psi_i \rangle \quad (95)$$

which can never be different from zero. This confirms the conclusion obtained by a different argument at the end of section 3.

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Conditions (85), (86), which by (84) define the physical situation beyond the Born-Oppenheimer approximation lead, therefore, to a new type of the two-electron bonding interaction. It appears that at a distance greater than a valence chemical bond an electronic pair has a pseudoscalar character with some expectation value, of the helicity and that the pair has no center or plane of symmetry. The nature of this interaction results from the physical sense of  $\kappa$  in (10) as a measure of retardation of electrons in following the nuclear movements. The increasing of the mass of the vibrating nucleus will by (3) diminish  $\kappa$  and (in contrast to any Coulombic interaction) diminish the electron-electron bonding.

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One can expect such a weak, long range two-electron bonding interaction to occur between the electrons that are not localized in the primary chemical bonds – like non bonding

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1  
2 | electrons, [the](#)  $\pi$ -type electrons delocalized in aromatic molecules, or [in](#) graphite or [the](#)  
3  
4 | electrons near the Fermi level in metals.

### 5. Hydrogen Bond: Quantum Oscillator and the Retarded Electronic Pair

9 | In a hydrogen bond, the lightest nucleus has at its both sides the non-bonding electrons  
10 | which can be easily displaced by the vibrating proton and are shielded from the direct  
11 | Coulombic repulsion.

14 | A quantum oscillator and an electronic pair of the non-bonding electrons in the Born-  
15 | Oppenheimer approximation can serve as a good starting model for studying the hydrogen  
16 | bond properties.

$$19 \quad i \frac{\partial \Psi}{\partial t} = [\hbar \omega \tau_3 + \varepsilon(1 - \sigma_3)] \Psi \dots\dots\dots (96)$$

22 | The Gallilei transformation invariant form of (96) extends its validity beyond the Born-  
23 | Oppenheimer approximation and leads to equations (46), (77) for [the](#) description of the  
24 | vibrational and electronic properties.

27 | It was shown in a recent paper [3] that [the](#) main results concerning the experimental infrared  
28 | spectra of the hydrogen bond are well reproduced by a perturbation treatment of equation  
29 | (46).

32 | The properties of the electronic pair in (77), which result from our analysis in the  
33 | present paper, are:

- 34 | a. it follows from (84) that [the](#) distance in the [electronic](#) pair should be [greater, than the](#)  
35 | length of the chemical bond in [the](#) quantum oscillator
- 36 | b. it follows from (95) and the discussion in Section 3 that the electronic pair cannot have  
37 | a center or a plane of the space symmetry
- 38 | c. it follows from (78) and (3) that [the](#) substitution of proton by deuterium in the  
39 | hydrogen bond should diminish [the](#) attraction between the electrons (in contrast to any  
40 | Coulombic interaction) and, therefore, make the bond longer.
- 41 | d. infrared absorption beyond the Born-Oppenheimer approximation is defined by  
42 |  $\langle 0 | \tilde{q} | 1 \rangle$  of (10) and (in contrast to [the](#) harmonic oscillator of (6)) is accompanied by [the](#)  
43 | change of  $k\alpha'$  in (77) and determines the nuclear – electronic charge separation. This

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should lead to a big change of the dipole moment in absorption and its dependence on the isotopic substitution in the hydrogen bond.

All [the](#) above [conclusions](#), deduced from our treatment in this paper, are well known as very characteristic properties of the hydrogen bond [11], [12], [13], [14].

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## 6. Enhancement of Homochirality in the Hydrogen Bonded Biomolecular Systems

Consider a molecular model system composed of a linear polymer of identical molecules interconnected by the hydrogen bonds. [The](#) electronic Hamiltonian of the hydrogen bonds in the Born-Oppenheimer approximation equals

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$$H = \sum_i \varepsilon_i (1 - \sigma_3^{(i)}) \quad (97)$$

and for

$$E_0 = \sum_i \varepsilon_i, \quad \varepsilon_i = \varepsilon \quad (98)$$

$$S_3 = \sum_i \sigma_3^{(i)} \dots\dots\dots (99)$$

[we](#) have [therefore](#)

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$$H = (1 - S_3) \quad (100)$$

in units of  $E_0$

Introduce now the unitary transformations

$$V = V_1 \cdot V_2 \dots \quad (101)$$

where

$$V_i = \exp \left[ -\frac{i}{2} (\sigma_3^{(i)} - \sigma_1^{(i)}) kt \right] \quad (102)$$

then (100) transforms to

$$\tilde{H} = 1 + x_0 S_3 + x_2 S_2 \quad (103)$$

where

$$S_2 = \sum_i \sigma_2^{(i)} \quad (104)$$

and where

$$x_0'^2 - x_2'^2 = 1 \quad (105)$$

Introduce now the coherent states in  $SU(1,1)$  group by

$$\sigma_2^{(i)} |z_i\rangle = \alpha_i |z_i\rangle \quad (106)$$

$$|z\rangle = |z_1\rangle |z_2\rangle \dots \quad (107)$$

then, putting the Born-Oppenheimer energy  $E_0$  at zero,

$$\Gamma = -\left[ E_0^2 + k^2 \left( \sum \alpha_i \right)^2 \right]^{\frac{1}{2}} + E_0 \quad (108)$$

energy value in (108) is lowered below its Born-Oppenheimer value if

$$k^2 \sum_i \alpha_i^2 + k^2 \sum_{i \neq 1} \alpha_i \alpha_1 > 0 \quad (109)$$

Therefore,  $\alpha_i \alpha_1$  must be of the same sign and by the same reason as in (79)

$$k \alpha_i < 0 \quad (110)$$

to have, however,

$$\sum_{i \neq 1} \alpha_i \alpha_1 > 0 \quad (111)$$

the symmetry of the space separating two electrons of different hydrogen bonds should be the same as all  $\alpha_i \alpha_1$ , and therefore, the space should have the symmetry of the pseudoscalar. The molecules separating the hydrogen bonds should be, therefore, chiral and of the same negative sign as the helicity in hydrogen bond in (77).

The chirality of molecules, considered in older chemical literature as a purely static space property ("left and right glove") is now, understood [15], [16], [17], [18] as a dynamic property, which allows to differentiate between the true and false chirality. The modern definition of molecular chirality is determined by its pseudoscalar property: even in the time reversal and odd in the parity reversal – corresponding to the helicity

The puzzling homochirality in biomolecular systems seems, therefore, to be the result of the space-time molecular symmetry.

## 7. Molecular Quantum Mechanics and Molecular Quantum Field Theory.

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4 The classical papers [1], [2] in which the quantum mechanical foundations of molecular  
5 and solid state physics were introduced, contain implicitly a serious drawback: the separation  
6 of the center of mass movement from the Hamiltonian in the relative nuclear electronic  
7 coordinates was not obtained. Deleted: the

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10 There is no doubt that after separation of the nuclear and electronic motion, proper  
11 elimination of the center of mass motion is, as pointed by Mankhorst [19], of central  
12 importance to a dynamic theory of molecules.

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15 For atoms a proper linear combination of coordinates (the Jacobi ones) allows for a  
16 simple elimination of the center of mass movement. Any attempts along this line of reasoning  
17 applied to the molecular systems lead to the linear combination of the electronic and nuclear  
18 coordinates resulting in an awkward dependence of the Hamiltonian on these coordinates  
19 which eliminates any effective treatment [20], [21]. The only way of avoiding these  
20 difficulties seems to be the introduction of an independent set of coordinates [22], [23]  
21 relative to some nuclear coordinate  $q_N$  (e.g. of the most heavy atom). Molecular properties,  
22 however, cannot depend on an arbitrary choice of a particular nucleus as the origin of a  
23 reference system. Deleted: the  
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26 Any general reconciliation of a separation of nuclear and electronic motions introduced in the  
27 classical papers [1], [2], with an effective elimination of the center of the mass motion seems,  
28 however, still inaccessible. Deleted: [19],  
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31 For an atom a linear combination of only the space coordinates (Jacobi ones) is  
32 sufficient to eliminate the uniform movement with a constant velocity of a single point (the  
33 center of mass). Deleted: We must admit that a  
molecular Hamiltonian in the relative  
nuclear-electronic coordinates is still  
inaccessible. ¶

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36 For a molecular system (in the Born-Oppenheimer approximation), a quantum oscillator  
37 determines the time unit and the linear combination of the space and time coordinates (the  
38 Gallilei transformation) is necessary to define, in the inertial reference system, the  
39 Hamiltonian in the relative space-time coordinates. Deleted: the

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42 This approach requires, however, the reformulation of the molecular quantum  
43 mechanics in the spirit of a molecular quantum field theory.

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46 The energy eigenvalues of a quantum oscillator and an electronic pair in (6), (56) are  
47 determined in the corresponding reference systems located in the usual Euclidean space, for

fixed values of the origins. Inversion of the space coordinates in the reference systems cannot change the eigenvalues in (6), (56) as the Euclidean space is uniform.

How the vibrational quanta and electronic pairs move in the relative time and space remains yet undetermined: the Born-Oppenheimer separation is formulated in the time independent Schrödinger equation and contains no relative nuclear-electronic velocity as  $\kappa=0$  in (6), (56).

The Gallilei transformation invariant equations with the new relative coordinate  $T$  define the vibrational quanta and electron pairs on the opposite branches (44), (66) of a two dimensional space-time hyperbola. In this non-Euclidean space, the left and right directions are no more equivalent: the parity operator does not commute with the corresponding Hamiltonians. Energy expectation values for electronic pairs and vibrational quanta are, for  $k \neq 0$  and the same time  $T$ , separated by an energy gap. This energy gap results from the hyperbolic geometry in which move now vibrational quanta and electronic pairs: for a sufficiently big gap, the electronic pair by (91) can move as a mass-less particle in the Euclidean space.

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#### 8. Space –Time Symmetry Elements in Molecular Quantum Mechanics

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We have started our considerations by choosing a molecular system composed of a quantum oscillator and an electronic pair (with opposite spins and the same energy) defined in the reference systems with fixed origins ( Born-Oppenheimer approach).

$$i \frac{\partial \Psi}{\partial t} = [\tau_3 + (1 - \sigma_3)] \Psi \dots\dots\dots (112)$$

The interaction energy between the nuclear and electronic subsystems cannot be changed, if both origins are subject to the Gallilei transformation  $\tilde{q} = q - \kappa pt$  \dots\dots\dots (113)

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and therefore, the total energy in

$$i \frac{\partial \tilde{\Psi}}{\partial t} = (\eta + \eta') \tilde{\Psi} \dots\dots\dots (114)$$

is, by (46), (77) the same as in (112).

The physical sense of (112) and (114) is, however, much different.

The vibrational quanta and electronic pairs move now, by (114), in a space where any two space-time points are related by the Gallilei transformation (113). This transformation can be written in an equivalent form

$$\tilde{q} = q - \frac{\kappa}{c} p c t \quad (115)$$

where  $c$  is the light velocity. At the range

$$c t = \lambda > q \quad (116)$$

where  $\lambda$  is the wave length of the virtual transition in quantum oscillator – the dynamic

operator of the linear momentum is changed by the scaling factor  $\frac{\kappa}{c}$

$$p' = \frac{\kappa}{c} p \quad (117)$$

In the molecular and solid state physics  $\kappa$  can be very big (formally infinite for the degenerate electronic states) and may lead to important relative velocity dependent interactions.

In (112), the space, in which the electronic and nuclear coordinates are defined, is, of course, Euclidean. This is not the case for vibrational quanta and electronic pairs in (114).

The coordinates  $x_i$  in (21) or  $x'_i$  in (65) appearing in the one-to-one correspondence with operators  $\tau_i$  or  $\sigma_i$  satisfy the condition

$$x_0^2 - x_1^2 - x_2^2 = 1 \quad (118)$$

which defines a space-time hyperbola.

Relation (118) is equivalent (for  $\text{inv} = 1$ ) to the condition (28) defining the dynamical group SU (11) to which belong  $\tau_i$  and  $\sigma_i$ . The expectation values of these operators follow by (33), (66) the same geometry.

In (114), the new time coordinate

$$T = \frac{1}{k} \text{arctanh}(k t) \quad (119)$$

is the same for vibrational quanta and electronic pairs but energy expectation values for the vibrational and electronic quanta are separated by an energy gap.

A linear normal coordinate of a quantum oscillator in (112) may appear in (114) as a bent bond owing to the effective hyperbolic geometry.

The Gallilei transformation (12) can also be considered as a unitary transformation introducing in the Schrödinger equation the dilatation of the time coordinate

$$t' = \kappa t \dots\dots\dots (120)$$

which, therefore leads to the change of scale of the dynamic operator like (117).

Neither the Born-Oppenheimer treatment [1] nor the Born one [2] can describe the molecular systems for  $\kappa \neq 0$ . The simplest molecular invariant of the Gallilei transformation allows this description for any  $\kappa$ , but in terms of a space-time group: the Schrödinger group.

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Appendix 1.

In transforming  $i \frac{\partial}{\partial t}$  operator in (6), (56), the time independent term  $\frac{1}{2} \kappa p^2$  must be put equal to zero, as for  $\kappa t \rightarrow 0$ ,  $\tilde{q} \rightarrow q$  and (15), (65) must reduce to (6), (56). The Born-Oppenheimer Hamiltonians in (6), (56) are, therefore, the initial values of transformed ones (15), (65).

In (21) the explicit forms of  $x_i$  are equal to

$$x_0 = 1 + \frac{1}{2} \kappa^2 t^2 \quad (A1)$$

$$x_1 = -\frac{1}{2} \kappa^2 t^2 \quad (A2)$$

$$x_2 = -\kappa t \quad (A3)$$

and

$$x_0^2 - x_1^2 - x_2^2 = 1 \quad (A4)$$

The metric properties (A4) are valid for any value of the time coordinate  $t$ . Therefore, (A4) can be considered as equivalent to

$$\bar{x}_0^2 - \bar{x}_1^2 - \bar{x}_2^2 = 1 \quad (A5)$$

where  $\bar{x}_1, \bar{x}_2$  are two independent space coordinates subject to relation (A5).

Appendix 2

The relativistic wave equation for the massive particles is invariant under the operators of the conformal group. Therefore, as should be, the non relativistic limit of this wave equation is invariant under the non-relativistic limits of the conformal group operators.

The non-relativistic limit of this wave equation is the Schrödinger operator [8], [9]

$$S = 2mi \frac{\partial}{\partial t} - p^2 \quad (A6)$$

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and the non-relativistic limit of the conformal group is the Schrödinger group. In particular the Schrödinger operator is invariant under the operators of the dilatation and special conformal transformation. Those transformations have the geometrical meaning of a change of scale and of a change of scale from point to point, e.g. dilatation is the change of scale for time and space coordinates

$$t' = \kappa t \quad (A7)$$

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$$x' = \kappa x \quad (A8)$$

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The wave equation for the mass-less particle

$$\left( \frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2} \right) \Phi = 0 \quad (A9)$$

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is invariant under the dilatation (A7), (A8).

For a massive particle, dilatation and special conformal transformation symmetries require, however, a transformation of the mass e.g. for the dilatation symmetry in (A6)

$$m' = \kappa m \quad (A10)$$

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The last equation is, of course, not a symmetry in the usual sense as it connects a particle of mass  $m$  with another particle of mass  $m'$ .

The way out of this difficulty was proposed by Barut [8]. If we keep the mass unchanged but change the metric properties of the time and space coordinates

$$t' = \kappa^2 t \quad (A11)$$

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$$x' = \kappa x \quad (A12)$$

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Then  $S$  in (A6) is invariant under the dilatation (A11), (A12).

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In the present paper we focused our attention on (112) which can be considered as the simplest (or fundamental) molecular invariant of the Gallilei transformation, because the total energy in (112) is the same as in (114).

The Schrödinger equations for a quantum oscillator or an electronic pair are now changed compared with that in (112). The quantum oscillator is now, by (21), a linear combination of the  $\tau_i$  operators and  $\tau_2$  and  $\tau_1$  are the quantum –mechanical forms [8],[9] of the non-relativistic limits of the dilatation and special conformal transformations.

The final forms of the Schrödinger equations for a quantum oscillator and an electronic pair in (114) keep the corresponding mass unchanged, but the metric properties for the time and space coordinates are changed to those of the hyperbolic geometry.

#### References

1. M.Born and R.Oppenheimer, Ann.Phys.(Leipzig), 457 (1927), 84
2. M.Born, Gött. Nachr.Math.Phys.Kl.1, (1951); M.Born and Kun Huang, Dymaical Theory of Cristal Lattices (appendix 8), Oxford at the Clarendon Press 19
3. A.Witkowski, Chem.Phys, 328 (2006), 17
4. A.Witkowski, Phys.Rev. A41 (1990) 3511
5. H.C.Longuett-Higgins, Adv.Spectrosc. 2, (1961)429
6. I.B.Bersuker and W.Z.Polinger, Vibronic Interactions in Molecules and Crystals, Nauka, Moscow 1983
7. A.Witkowski and W.Moffitt, J.Chem.Phys. 33, (1960)872
8. A.O.Barut, Helv.Phys.Acta 46, (1973) 496
9. A.O.Barut and R.R'czka, Theory of Group Representations and Applications, Polish Scientific Publishers, Warsaw 1980 (in English)
10. A.O.Barut and L.Giraedello, Commun. Math. Phys., 21, 41(1971)
11. The Hydrogen Bond – Recent Development in Theory and Experiments, P.Schuster, G.Zundel and C.Sandorfy eds., North Holland, 1976
12. Theoretical Treatments of Hydrogen Bonding D.Hadzi (ed), Wiley, 1997
13. O.Henri-Rousseau and P.Blaise, Adv.Chem.Phys. 103, (1998)
14. Y.Marechal, Hydrogen Bond and the Water Molecule, Elsevier 2007

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15. M.Avalos, R.Babiano, P.Cintas, J.L.Jimenez, J.C.Polacios and L.D.Barron, Chem.Rev. 98 (1998), 2391
16. Barron L.D., Mol. Phys. 43, (1981), 1395
17. Barron L.D., Molecular Light Scattering and Optical Activity, Cambridge University Press, Cambridge 1982
18. Barron L.D., Chem.Phys.Lett. 123 (1986) 423
19. H.J. Monkhorst, Phys.Rev.A 36,1544 (1987),1544
20. A.Fröman, J.Chem.Phys., 36 (1962) 1490
21. H.Essen, Int.J.Quantum Chem., 12, (1987) 721
22. A.Fröman and J.L.Kinsey, Phys.Rev., 123, (1961) 2077
23. M.D.Girardeau, Phys.Rev., A28, (1983) 3635

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