Dynamical Symmetries of Schroedinger Equations and Geometrical Symmetries of Classical Total Energy Surfaces

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A correspondence between dynamical groups of Schroedinger equations and dynamical groups of Hamilton's equations enables one to intrepret both quantal and classical dynamical symmetries as Lie symmetries of total energy surfaces in a phase space. Suitable choices of Cartesian coordinates in the phase space may often be used to express these energy surfaces, whose symmetries are seldom obvious, as group-invariant manifolds with evident geometric symmetries. These invariant manifolds retain their form when a Hamiltonian is subjected to a wide variety of perturbations and may sometimes be constructed without knowing the transformation between their Cartesian coordinates and laboratory coordinates.

1. Introduction

This paper develops a geometric interpretation of groups whose transformations convert solutions of Schroedinger equations into solutions and depend on the independent variables in the equations.[1] The classical analogues of these transformations can be shown to convert solutions of Hamilton's equations into solutions. We shall refer to groups of such transformations as dynamical groups. The transformations of a dynamical group of Hamilton's equations are also invariance transformations of total energy surfaces. Solutions of the equations of motion are represented by trajectories on these surfaces, and operations of a dynamical group interconvert these trajectories. The energy surfaces, or Hamiltonian manifolds, are commonly defined by the expression $H(q,p) - E = 0$, but it is the geometric object and its symmetries, rather than its analytical expression, which will be of central interest. Here and throughout the discussion, $q = (q_1, q_2, ...)$ denotes position variables and $p = (p_1, p_2, ...)$ denotes their conjugate momentum variables; E denotes the energy, and t will be used to denote time. As dynamical groups carry solution trajectories into solution trajectories, they are at least subgroups of the invariance group of energy surfaces.

Most of the operations of dynamical groups are operations of Lie groups. As explained below, the major symmetries of total energy surfaces—their Lie symmetries—are often much larger than one might expect. This property is inherited by the dynamical groups of Schroedinger equations, which commonly express symmetries of Hamiltonian manifolds that are far from obvious.

The recent monograph by Iachello and Levine[2] and the many references it contains amply demonstrate the utility of dynamical groups and their Lie algebras in the analysis and prediction of rovibrational spectra; a host of recently uncovered relationships and simplifications are brought to the fore. The recognition that electronic motion in hydrogen-like atoms possesses the dynamical symmetry of a hypersphere dates back to the 1935 work of Fock and Bargmann.[3] Dynamical symmetries of electronic motions are apparently responsible for the general form of the periodic chart.[4a] They are responsible for surprising relationships in the energy spectra of one-electron diatomics[4b] and in the spectra of the doubly excited states of helum-like atoms.[4c−f] Quantum chemistry computer programs that exploit dynamical symmetries are currently undergoing rapid development.[5]

Two particularly useful types of dynamical group may be distinguished. Quantum mechanical degeneracy groups are dynamical groups that convert solutions of Schroedinger's time-independent equation into solutions of the same energy. Energy eigenstates may be labeled by their transformation properties under the action of these groups, and it is the symmetries defined by these dynamical groups that are relevant to the noncrossing rule.[6] Slightly breaking these symmetries can yield nearly degenerate states and lead to avoided crossings. The symmetries need not be symmetries in position space: many chemicaly significant examples are provided by the breaking of Hartree−Fock degeneracies and the breaking of degeneracies that occur in naive LCAO MO and other one-electron appproximations—degeneracies that are not due to ordinary molecular symmetry.

Quantum mechanical spectrum-generating groups have generators that convert eigenstates of one energy into eigenstates of another energy.[7] Their time-dependent versions generate dynamical groups that convert solutions of Schroedinger's time-dependent equation into solutions.[8]

It turns out that degeneracy groups are associated with Lie symmetries in classical PQ space, the phase space of positions, and momenta. They need not be Lie symmetries in momentum space or position space separately: the group operations may interconvert positions and momenta. Degeneracy groups may be different for different ranges of E values. Spectrum-generating groups and other invariance groups of time-dependent Schroedinger equations are associated with Lie symmetries in classical PQET phase space. (Because t is canonically conjugate to $-E$, it can become necessary to enlarge PQE space to include t if one wishes to transform E.)

Symmetries as commonly understood in chemistry, solid-state physics, and the sciences in general are special cases of Lie symmetries. Lie's more general concept arose from a consideration of invariance transformations of equations. If an equation is left unchanged by a transformation of its variables and by the inverse of this transformation, then it possesses an invariance group defined by these transformations and the identity transformation. The operations of the group convert

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solutions of the equation into solutions of the equation. This property may itself be used to define invariance transformations of equations. Because groups define symmetries, equations have associated symmetries if they possess more than one solution. For this reason, almost all differential equations have associated symmetries.[9]

Sophus Lie's extensive development of the concept of symmetry appropriate to studies of differential equations is one of the glories of 19th century mathematics.[10] Pondering its implications, Felix Klein realized that Lie's discoveries provided a new view of geometry.[11] The view is more general than that of Riemann for it enables one to define geometries that have no metric. This has a most profound physical consequence: Lie groups can unambiguously define the symmetry of objects whose measurements cannot even be agreed upon in principle!

These properties of Lie groups are essential to the discussion that follows. The discussion begins by clarifing the correspondence between the Lie algebras of groups of transformations that convert solutions of Schroedinger equations into solutions and the Lie algebras of groups of canonical transformations that convert solutions of Hamilton's equations into solutions. This Lie algebraic correspondence sets up a correspondence between the dynamical groups of corresponding quantal and classical systems. This establishes the relationship between dynamical symmetries of Schroedinger equations and Lie symmetries of classical total energy surfaces. Interpreting the Lie symmetries of these surfaces as geometric symmetries provides a geometric interpretation of dynamical symmetries of Schroedinger equations.

Because transformations in a phase space need not leave invariant any imposed measure of distance in the space, the Lie symmetry of a total energy surface may be larger than its evident symmetry in any natural set of laboratory coordinates. The ability of Lie theory to define symmmetries *sans* measure thus proves of central importance. However, it provides no unique connection between symmetries in phase space and metrical symmetries: one has some freedom in choosing this connection. The choice we adopt makes it possible to assign Hamiltonian manifolds a symmetry in a metrical sense that they possess in the more general sense due to Lie.[12] This is illustrated in Figure 1. Figure 1a depicts the Hamiltonian manifold for a one-dimensional Morse oscillator, defined by $H - E = 0$, with Hamiltonian

$$H = p^2/2m - D(\exp(-2aX) - 2\exp(-aX)),\ X = x - x_0 \tag{1}$$

In Figure 1a, x, p, and E are considered as Cartesian coordinates in a Euclidean space. A point with coordinates p,q,E on the surface represents a state of the classical oscillator at some moment t, and this point moves along a trajectory of constant energy as time evolves. The constant energy contours in the figure are consequently evolution trajectories. A "transition state" is the lowest energy state that dissociates. It has a trajectory leading off to arbitrarly large q. The projection of a trajectory in phase space onto a q or p axis defines a solution of Hamilton's equations for that q or p. As time goes on, each q_j becomes a function $f_j(t)$ and each p_j becomes a function $g_j(t)$.

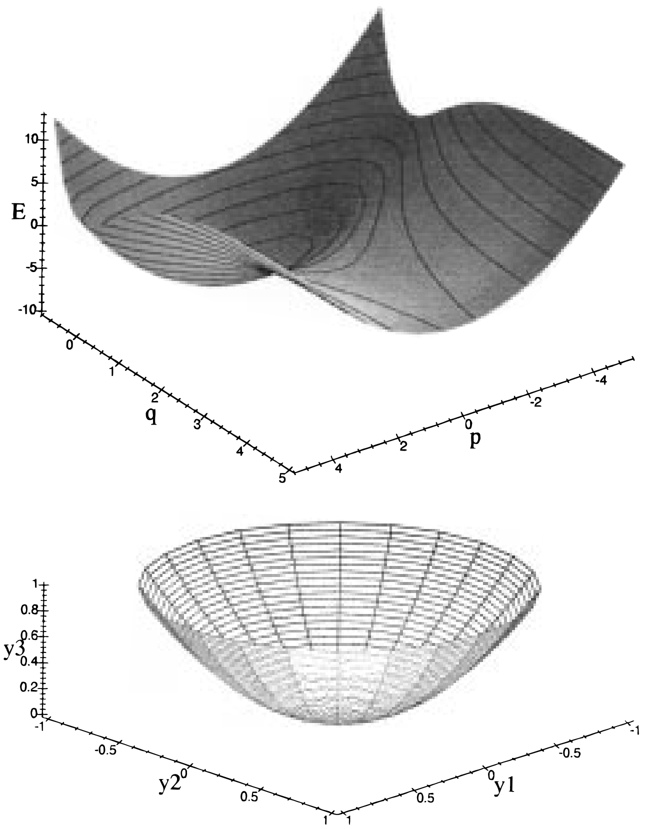

Figure 1. (a) Total energy surface and evolution trajectories of a Morse oscillator in PQE space. (b) Morse manifold transformed to display its SO(2,1) symmetry.

The time-dependent Schroedinger equation of a Morse oscillator is known to be left invariant by transformations of the isomorphic local Lie groups Sp(2,R), SU(1,1), and SO(2,1).[13] Despite the uncertainty principle, these groups are also local invariance groups of the total energy surface of a Morse oscillator and local invariance groups of it's Hamiltonian equations of motion in PQET phase space. Smooth invertible canonical transformations of PQET phase space cannot change these groups but can yield a different set of coordinates in which the Hamiltonian manifold is the hyperboloid of revolution indicated in the quite different Cartesian coordinate system of Figure 1b. (Trajectories on this manifold will be considered in section 5.) The SO(2,1) symmetry of this manifold gives rise to the SO(2,1) invariance of Hamilton's equations of motion for the Morse oscillator in PQET space and is responsible for the corresponding symmetry of Schroedinger's equation.

It is important to note that the original Hamiltonian manifold of Figure 1a also possesses SO(2,1) Lie symmetry in phase space! In the ordinary (Euclidean) sense of the term "symmetry", the symmetry of the manifold has clearly been altered by the change of canonical coordinates. On the other hand, its *Lie* symmetry has remained unchanged. Dynamical symmetries are always Lie symmetries if they are described by continuous groups. They may also be ordinary Euclidean-geometric symmetries.

The difference between Euclidean symmetry and Lie symmetry as it applies to objects in phase space is worth examining in a little more detail. Consider, for example, the spheres defined in Cartesian coordinates by $x^2 + y^2 + z^2 = r^2$. They are left invariant by the rotation operator $\exp(aR_x)\exp(bR_y)\exp(cR_z)$ with group parameters a, b, c and generators

$$R_x = (y\,\partial/\partial z - z\,\partial/\partial y),\ R_y = (z\,\partial/\partial x - x\,\partial/\partial z),\ R_z = (x\,\partial/\partial y - y\,\partial/\partial x) \tag{2}$$

The ranges allowed with the parameters are such as to ensure that any point on each such sphere can be carried into any other point on the sphere. The commutation relations of the generators are

$$[R_x,R_y] = -R_z,\ [R_y,R_z] = -R_x,\ [R_z,R_x] = -R_y \qquad (3)$$

The commutation relations establish the local Lie group to be either SU(2) or SO(3)—the two groups are locally isomorphic. Now the transformation $x \rightarrow x/a$, $y \rightarrow y/b$, $z \rightarrow z/c$ converts the spheres into ellipsoids. However, it does not alter the commutation relations. Furthermore, allowing the group parameters to vary over identical ranges ensures that every point on an ellipsoid or sphere can be carried into any other point, so the global Lie symmetry group of both is SO(3) rather than SU(2). (In subsequent sections, all Lie groups will be considered to be local Lie groups: it would take us too far afield to determine their global character.)

Suppose now that x is a position coordinate and y the momentum coordinate conjugate to x, so that the Poisson bracket of x,y defined by $\{x,y\} = \partial x/\partial q\ \partial y/\partial p - \partial y/\partial p\ \partial x/\partial q$ has the value 1. If z were E and r a constant, the space would be a PQE space. The transformation $x \rightarrow x/a$, $y \rightarrow ay$ would then be a canonical transformation because the Poisson bracket $\{(x/a), (ay)\} = 1$. The transformation reduces the Euclidean symmetry of the sphere but leaves its Lie symmetry unchanged. As the units in which momentum is measured are quite independent of those used for position, any investigator would be free to use a different system of units in which the Euclidean symmetry of the sphere was restored. A scaling invariance in mechanics is, therefore, not too surprising.

In this example the scale changes have been the same throughout the space. However, canonical transformations allow scale changes which vary (smoothly) from point to point. In such circumstances, both the passive and active pictures of the transformation mislead. A "hyperactive" picture which moves from one Euclidean space to another is less confusing. Thus, in Figure 1, one must not suppose that the Cartesian coordinate system in Figure 1a and the Cartesian coordinate system in Figure 1b belong in the same three-dimensional Euclidean space. The connection is more akin to that between local Cartesian coordinates in a plane tangent to the surface of the earth at one point and local Cartesian coordinates in a plane tangent to the surface of the earth at some other point, perhaps using different units. To gain a consistent geometric picture of both two-dimensional coordinate systems, one may envision a higher dimensional Euclidean space, in this geographical example a space of three dimensions, in which both systems coexist.

2. Correspondence between Schroedinger Operators and Lie Operators in Phase Space

Dirac's correspondence principle[14] associates a unique classical function $G(q,p)$ with each Schroedinger operator $G(q,p_{\mathrm{op}})$. Because the q_j's and $p_{j\mathrm{op}}$'s do not commute, different Schroedinger operators may, however, correspond to the same classical function $G(q,p)$. Observing that commutators possess key algebraic properties possessed by Poisson brackets, Dirac established the correspondence $\{q_j,p_j\} = 1 \leftrightarrow [q_j,p_{j\mathrm{op}}] = i\hbar$ for Cartesian coordinates q and their conjugate variables p. He showed that such non-Cartesian q's as radial coordinates and their conjugate p's obey all the canonical commutation relations obeyed by their Cartesian analogues, viz

$$[q_m,p_{n\mathrm{op}}] = i\hbar\ \delta_{mn},\ [q_m,q_n] = 0,\ [p_{m\mathrm{op}},p_{n\mathrm{op}}] = 0 \qquad (4a)$$

Dirac clearly viewed these results as special cases of a more general one-way correspondence

$$[G_a(q,p_{\mathrm{op}}),G_b(q,p_{\mathrm{op}})] = i\hbar\ G_c(q,p_{\mathrm{op}}) \rightarrow \{G_a(q,p),G_b(q,p)\} = G_c(q,p) \qquad (4b)$$

and he argued that eq 4a can imply eq 4b if the G's can be expressed as power series in their variables. In establishing that eq 4b is consistent with eq 4a, one does not make any use of the identity $AB = [A,B] + BA$ which is true for commutators but not Poisson brackets. The correspondence (eq 4b) also holds for G's that are polynomial functions of one member of a pair of conjugate variables and analytic functions of the other. Henceforth, we shall use the notation $Q_j(q,p_{\mathrm{op}})$ to denote members of a set of operators for which Dirac's correspondence principle (eq 4b) is consistent with eq 4a.

In the currently known cases, the generators of dynamical groups of Schroedinger equations may be expressed as polynomials in the momentum operators and may be denoted $Q(q,p_{\mathrm{op}})$. Solutions Ψ of Schroedinger equations are converted into solutions by the operators of this form and by the group operators $\exp(iaQ(q,p_{\mathrm{op}})/\hbar)$. When dealing with time-independent Schroedinger equations, the energy E and the time t may be considered parameters in the functions Q. When working with time-dependent Schroedinger equations, t is a dynamical coordinate q and $-E$ becomes its conjugate momentum operator $-i\hbar\ \partial/\partial t$.

Now one may associate with any classical function $G(q,p)$ the Lie operator[15]

$$\{\mathrm{G}\ \bullet\} = \sum_{i=0} (\partial G(q,p)/\partial q_i\ \partial/\partial p_i - \partial\ G(q,p)/\partial p_i\ \partial/\partial p_i) \qquad (5)$$

Here $\{\mathrm{G}\ \bullet\}$ is a "Poisson bracket waiting to happen", i.e, $\{\mathrm{G}\ \bullet\}f(q,p) = \{G, f\}$. For the functions Q, the chain of relationships $Q(q,p_{\mathrm{op}}) \rightarrow Q(q,p) \rightarrow \{Q\ \bullet\}$ sets up a correspondence between Schroedinger operators and operators acting in classical phase space. Here it will be used to relate generators of groups that act on Schroedinger equations and their solutions to generators of groups that act in phase space. The angular momentum operator $Q_{\mathrm{op}} = -i\hbar(q_1\ \partial/\partial q_2 - q_2\ \partial/\partial q_1)$ provides an example. Dirac's correspondence principle associates it with the classical function $q_1p_2 - q_2p_1$. The corresponding classical mechanical operator $\{Q\ \bullet\}$ is

$$\{(q_1p_2 - q_2p_1)\ \bullet\} = (q_2\ \partial/\partial q_1 - q_1\ \partial/\partial q_2) + (p_2\ \partial/\partial p_1 - p_1\ \partial/\partial p_2) \qquad (6a)$$

It is the generator of coordinated rotations of the position and momentum vectors of an object, rotations in which $(q_1,q_2) \rightarrow (q_1',q_2')$ and $(p_1,p_2) \rightarrow (p_1',p_2')$. Another example is provided by the two-dimensional oscillator Hamiltonian, $(p_1^2 + q_1^2 + p_2^2 + q_2^2)/2$. For it,

$$\{Q^{\bullet}\} = (q_1\ \partial/\partial p_1 - p_1\ \partial/\partial q_1) + (q_2\ \partial/\partial p_2 - p_2\ \partial/\partial q_2) \qquad (6b)$$

This generates rotations that can carry the position vector (q_1,q_2) into the momentum vector (p_1,p_2), and vice versa.

The correspondence $Q(q,p) \rightarrow \{Q(q,p)\ \bullet\}$ associates a unique $\{Q(q,p)\ \bullet\}$ with each $Q(q,p)$. However, the inverse of this correspondence is not unique because, for any constant, c, $\{c\ \bullet\} = 0$. Therefore, $\{(Q(q,p) + c)\ \bullet\} = \{Q(q,p)\ \bullet\}$. As a consequence, although the chain of correspondences $Q(q,p_{\rm op}) \rightarrow Q(q,p) \rightarrow \{{\rm Q}\ \bullet\}$ associates a unique $\{{\rm Q}\ \bullet\}$ with each $Q(q,p_{\rm op})$, neither of the inverse correspondences is unique. It will be seen below that the ambiguity in going from $\{{\rm Q}\ \bullet\}$ to $Q(q,p)$ is solely responsible for any lack of local isomorphism between the dynamical groups of Hamilton's equations with generators $\{{\rm Q}\ \bullet\}$ and the dynamical groups of the corresponding Schroedinger equations with generators $Q(q,p_{\rm op})$.

The quantum mechanical group operator $\exp(iaQ(q,p_{\rm op})/\hbar)$ gives rise to a unique classical mechanical group operator $\exp(a\{Q(q,p)\ \bullet\})$. The later is the operator of a one-parameter Lie group of canonical transformations.[15] As such, it carries points in the phase space PQ, or PQET, into points in this space. When $W = H - {\rm E}$, the quantum mechanical evolution operator is $\exp(-itH_{\rm op}/\hbar)$ and the classical evolution operator is $\exp(-t\{H\ \bullet\})$. (The evolution operator of the oscillator of eq 6b is, for example, a rotation operator in phase space.) When W is $f(q)(H - E)$, H is replaced by W and t by τ, where $dt/d\tau = f$.[16]

3. Relation between Quantal and Classical One-Parameter Local Dynamical Groups

It can be shown that the following relations exist whenever the actions of the operators are well-defined[17]:

(i) If $\exp(iaQ(q,p_{\rm op})/\hbar)$ converts solutions $\Psi(q,t)$ of the Schroedinger equation

$$H(q,p_{\rm op})\Psi(q,t) = i\hbar\ \partial\Psi(q,t)/\partial t \qquad (7)$$

into solutions, then $\exp(a\{Q(q,p)\ \bullet\})$ converts evolution trajectories on the corrersponding Hamiltonian manifold into evolution trajectories and it leaves the manifold invariant.

(ii) If $\exp(iaQ(q,p_{\rm op})/\hbar)$ converts eigenstates of the corresponding time-independent Schroedinger equation into eigenstates of the same energy E, then $\exp(a\{Q\ \bullet\})$ converts solutions of Hamilton's equations into solutions with the same energy and leaves the Hamiltonian manifold invariant.

When $H(q,p)$ has singularities, the foregoing statements need modification. If possible, one defines the Hamiltonian manifold by an equation $W = 0$, where $W = f(q)(H - E)$ and the function f is so chosen as to make W and its required derivatives well-defined. To set up the correspondence above, one must multiply Schroedinger's equations by the same function f. In the case of a hydrogen atom, multiplying through by r removes the singularity in the Schroedinger equation

$$({p_{\rm op}}^2/2m - 1/r - E)\Psi = 0 \qquad (9a)$$

yielding[18]

$$r({p_{\rm op}}^2/2m - E) - 1)\Psi = 0 \qquad (9b)$$

4. Relation between Quantal and Classical Many-Parameter Dynamical Groups

If a set of quantum mechanical operators $Q_i(q,p_{\rm op})$ comprise a commutator Lie algebra defined by

$$[Q_i(q,p_{\rm op}),Q_j(q,p_{\rm op})] = {d_{ij}}^k Q_k(q,p_{\rm op}) \qquad (10)$$

then for operators of the form Q, Dirac's correspondence principle ensures that there is an isomorphic Poisson bracket Lie algebra

$$\{Q_i(q,p),Q_j(q,p)\} = {c_{ij}}^k Q_k(q,p) \qquad (11)$$

with ${d_{ij}}^k = i\hbar {c_{ij}}^k$. Jacobi's relation for Poisson brackets can be used to show that this implies

$$[\{Q_i(q,p)\ \bullet\},\ \{Q_j(q,p)\}\ \bullet] = \{{c_{ij}}^k Q_k(q,p)\ \bullet\} \qquad (12)$$

Here an ambiguity can result for a zero may appear on the right-hand side of the equation if a ${c_{ij}}^k$ vanishes or if a $\{Q_k(q,p)\ \bullet\}$ vanishes. Henceforth, we will use the symbol Γ to denote $\{Q\ \bullet\}$ that do not vanish identically.

If the Lie algebra (eq 11) has no basis in which some element Q is a constant, then none of the $\{Q\ \bullet\}$ can vanish. Then every $\{Q(q,p)\ \bullet\}$ is a Γ and is an element of a Lie algebra defined by

$$[\Gamma_i,\Gamma_j] = {c_{ij}}^k \Gamma_k \qquad (13)$$

The Lie algebra of eq 13 is consequently isomorphic to that of eq 11.

If there is a basis for the quantum mechanical Lie algebra such that a constant generator exists, call it Q_0. Remove it from the algebra and in eq 12 set the ${c_{ij}}^0$ to zero. (The ${c_{0j}}^k$ and ${c_{i0}}^k$ already vanish.) The resulting Lie algebra involves only Γ's and has a dimension of one less than the quantal Lie algebra. As $Q_0 = c$, if c is a real number, the group operator, $\exp(ac)$, simply multiplies any function by a factor and the operator $\exp(iac/\hbar)$ multiplies any function by a phase factor. The corresponding classical operator $\exp(a\{c\ \bullet\}) = \exp(0)$ and multiplies any operand by unity.

The foregoing connections between the quantal and classical Lie algebras have the following consequences:

(i) Local invariance groups of Schroedinger's equations generated by operators $Q_j(q,p_{\rm op})$ have as their classical analogues local invariance groups of Hamilton's equations of motion that are also local invariance groups of Hamiltonian manifolds.

(ii) The groups are isomorphic if the quantum mechanical Lie algebra has no basis in which some generator is a constant and are simply related if there is such a basis.

Harmonic oscillator systems exemplify these conclusions. The well-known single-jump Lie algebra of the harmonic oscillator has three operators that interconvert solutions of Schroedinger's time-dependent equation and are generators of a three-parameter group of invariance transformations of the equation. For unit mass and unit force constant, the generators Q may be chosen to be 1 and

$$b_t = \exp(it)(p_{\rm op} + iq)/2^{1/2},\ {b_t}^+ = \exp(-it)(p_{\rm op} - iq)/2^{1/2} \qquad (14a)$$

The corresponding nonzero $\{Q\ \bullet\}$ are

$$\beta_t = \exp(it)\ (i\ \partial/\partial p - \partial/\partial q + (q - ip)\partial/\partial E)/2^{1/2} \qquad (14b)$$

$${\beta_t}^+ = \exp(-it)(-i\ \partial/\partial p - \partial/\partial q + (q + ip)\partial/\partial E)/2^{1/2}$$

The quantal and classical groups are not isomorphic. In contrast, the quantum mechanical double-jump invariance algebra with generators $(b_t)^2$, $({b_t}^+)^2$, ${b_t}^+ b_t + b_t {b_t}^+$ is isomorphic to the corresponding classical invariance algebra.

For Kepler and hydrogen-atom systems at fixed E, the equations of motion have six time-independent generators which obey isomorphic commutation relations. For bound states, the quantal and classical degeneracy groups are locally isomorphic SO(4) groups. Both have operations which interconvert kinetic and potential energies. The SO(4,2) spectrum-generating group of the quantum mechanical system[19] also has an isomorphic classical analog.[20] Operations of the latter can convert any bound trajectory, that is one with $E < 0$, into any other one with $E < 0$. They can convert any trajectory with $E = 0$ into any other one with $E = 0$ and convert any dissociating state with $E > 0$ into any other such state.

The generators of dynamical groups may be determined systematically by using Lie's methods for finding the invariance generators of differential equations.[9c,d,8b,c] The commutation relations of the resulting $Q_j(q,p_{\mathrm{op}})$ or $\{Q_j(q,p)\ \bullet\}$ then determine local Lie symmetries of the equations of motion, and the $\{\mathrm{Q}\ \bullet\}$ define local symmetries of energy surfaces under canonical transformations.

5. Geometric Expression of Dynamical Symmetry

As noted in the Introduction, dynamical symmetries are usually well hidden and removed from the ken of geometric intuition because, in commonly used coordinate systems, the transformation groups that leave energy surfaces invariant stretch and compress position and momentum coordinates by amounts that vary from point to point. However, Figure 1 (parts a and b) illustrate the fact that it may be possible to find smooth invertible canonical transformations to new sets of coordinates that do not suffer from this confusing feature. In Figure 1b, a coordinate system has been chosen so that in it the energy surface becomes a hyperboloid of revolution defined by

$$y_1^2 + y_2^2 - y_3^2 = -|\mathrm{const}| \qquad (15)$$

Smooth invertible transformations cannot alter topologies. Choosing the right-hand side of eq 15 to be negative ensures that the surface it defines and the original energy surface have the same topology. The three generators of the SO(2,1) group that leaves this surface invariant are

$$J_3 = (y_1\ \partial/\partial y_2 - y_2\ \partial/\partial y_1),\ J_2 = (y_3\ \partial/\partial y_1 + y_1\ \partial/\partial y_3) \qquad (16)$$

$$J_1 = (y_2\ \partial/\partial y_3 + y_3\ \partial/\partial y)$$

Figure 1b possesses rotational symmetry in the usual sense of the term. In particular, the operations carried out by exp(aJ_3) move points around the axis of the hyperbola and preserve the Cartesian distance between points with coordinates (y_1, y_2, y_3) and (y_1', y_2', y_3'). In contrast, this distance, defined by the cartesian metric

$$\mathrm{d}s^2 = \mathrm{d}y_3^{\,2} + \mathrm{d}y_2^{\,2} + \mathrm{d}y_1^{\,2} \qquad (17)$$

is not left invariant by operations of the subgroups generated by J_1 and J_2.

However, all operations of the group preserve "distance" if one relaxes ones definition of distance *a la* Riemann and defines it by a metric ds', with

$$\mathrm{d}s'^2 = \mathrm{d}y_3^{\,2} - \mathrm{d}y_2^{\,2} - \mathrm{d}y_1^{\,2} \qquad (18)$$

When a Riemannian metric is preserved by a dynamical group, confusions generated by group transformations which stretch and compress coordinates are much reduced and it becomes much easier to forsee the consequences of dynamical symmetry.

When, as in this case, a dynamical group is locally isomorphic to a metric-preserving group with a known realization on a space of the same dimension as the PQE space or PQET space of interest, one may sometimes, without knowing the required transformation of coordinates, use the isomorphism to express the symmetry group as a metric-preserving one. The method is available when operations of the classical dynamical group acting on a few initially chosen points on an energy surface sweep out the entire energy surface.[21] The operations of the locally isomorphic metric-preserving group can then sweep out a manifold which is left invariant by the metric-preserving expression of the dynamical group. Trajectories on the original energy surface are mapped into trajectories on this manifold that is more evidently invariant under the operations of the dynamical group.

Quantum mechanical analogues of the radial Kepler problem with zero angular momentum provide a further illustration of the process just sketched and also reveal some of the advantages of knowing W_{op} as a function of group generators. The Hamiltonian manifold is the two-dimensional surface defined in three-dimensional PQE space by the classical analogue of eq 9b on setting $L^2 = 0$, that is on replacing p^2 by p_{r}^2, where p_{r} is the radial momentum. Using atomic units the time-independent equation $W_{\mathrm{op}}\Psi = 0$ has[19]

$$W_{\mathrm{op}} = (^1/_2 - E)T_{3\mathrm{op}} + (^1/_2 + E)T_{1\mathrm{op}} - 1 \qquad (19\mathrm{a})$$

where

$$T_{1\mathrm{op}} = r(p_{r\mathrm{op}}^{\;2} - 1)/2,\ T_{3\mathrm{op}} = r(p_{r\mathrm{op}}^{\;2} + 1)/2;\ p_{r\mathrm{op}} = -i(\partial/\partial r + 1/r) \qquad (19\mathrm{b})$$

$\mathrm{T}_{3\mathrm{op}}$ has eigenvalues $n = 1,2..$, which label states of the discrete spectrum, while the eigenvalues of $\mathrm{T}_{1\mathrm{op}}$ are the values of the nonnegative continuous variable n which labels the states with a continuous spectrum. These noncommuting operators, together with $T_{2\mathrm{op}} = rp_{r\mathrm{op}}$, are generators of Sp(2,R), SO(2,1), and SU(1,1) groups whose classical analogues have generators $\{T_j(r,p)\ \bullet\}$. The $T_{j\mathrm{op}}$ have time-dependent versions, $T'_{j\mathrm{op}}$, which generate an SO(2,1) invariance of the corresponding time-dependent Schroedinger equation.[8b,c]

Neither the classical nor the quantal group operations leave distances in ordinary space unchanged. However, using the notation of the previous example, either the substitutions $\{T_3\ \bullet\} \rightarrow J_3$, $\{T_1\ \bullet\} \rightarrow J_1$, and $\{T_2\ \bullet\} \rightarrow J_2$ or the analogous substitutions with the time-dependent operators yields an isomorphic group which leaves a hyperboloid of revolution invariant. The local isomorphisms of the groups, in fact, define energy-dependent maps from PQE or PQET space to (y_1,y_2,y_3) space.[22]

For each E, the energy axis must be perpendicular to the plane of the trajectory, so the angle it makes with the axis of the hyperbola changes with E. This is illustrated in Figure 2 (parts b and c) which depict trajectories as intersections of planes of constant energy with the invariant hyperboloid. For E less than zero, the trajectories are closed curves. Bound-state trajectories of Morse oscillators give rise to analogous trajectories on the manifold of Figure 1b. (For both the Morse and the Kepler systems, we have chosen a map that represents ground states as circles.) Dissociating states of Morse and radial Kepler systems have open trajectories such as that suggested in Figure 2c.

The radial Kepler hyperboloid of Figure 2 is an invariant manifold for all quantum mechanical systems whose W_{op} is a function of the generators $T_{1\mathrm{op}}$, $T_{2\mathrm{op}}$, $T_{3\mathrm{op}}$ and variables which

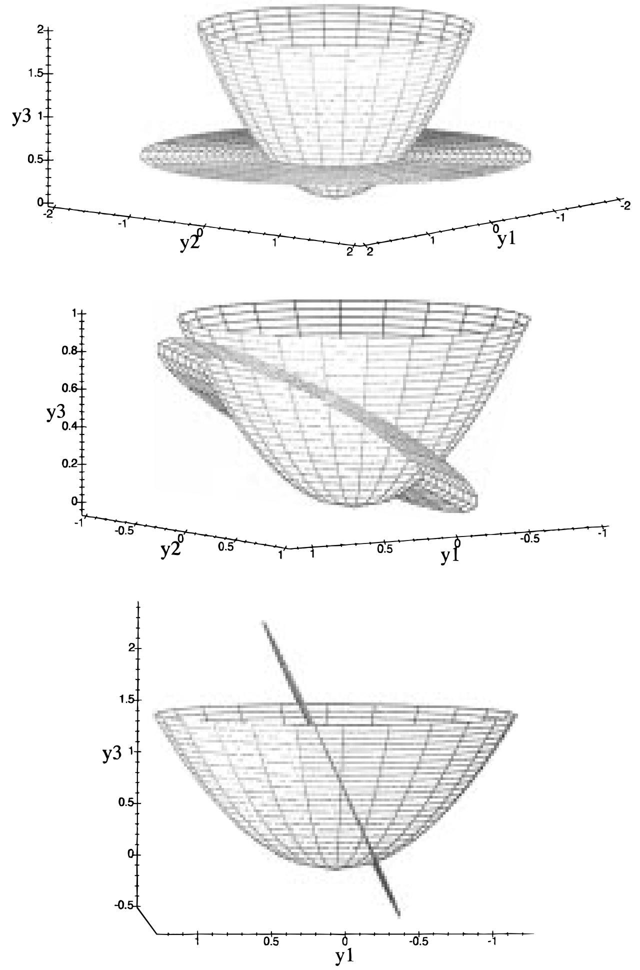

Figure 2. (a) Intersection of invariant manifold of radial Kepler system with surface of constant *E*, ground state. (b) Intersection of invariant manifold of radial Kepler system with surface of constant *E*, bound excited state. (c) Intersection of SO(2,1) invariant manifold with constant energy surface of a dissociating state.

commute with them. This illustrates two important features of invariant energy surfaces: They are very stable and they may be determined by investigating simpler systems than those of actual interest. They allow one to visualize a host of related systems as systems that simply evolve different sets of trajectories on the same invariant and highly symmetrical surface. In the corresponding Schroedinger equations, the dependence of energy eigenvalues upon quantum numbers may differ, as may the degeneracy groups.

Conclusion

Whenever Dirac's correspondence principle is valid, invariance groups of Schroedinger's equations that depend on position and time coordinates correspond to invariance groups of Hamilton's equations in the space of positions, momenta, energy, and time. Though the resulting quantal and classical dynamical groups need not be isomorphic, both are a consequence of Lie symmetries of total energy surfaces in classical PQE phase space. Trajectories defining the state of the classical system evolve on these surfaces, which bear analogy to the potential-energy surfaces of molecular quantum mechanics.

The total energy surface of a system generally possesses symmetries that are not possessed by its potential-energy surface because the symmetries express relations between positions and momenta of the particles in the system. These dynamical symmetries, and their physical and chemical consequences, may be well hidden because the symmetries are Lie symmetries defined in a phase space—a space in which distance is undefined.

Knowledge of dynamical symmetries can be used to establish maps from Hamiltonian energy surfaces to surfaces whose symmetries are more evident. Here we have considered the resulting group-invariant manifolds to be fixed objects whose relation to the physical world changes as the state of the system changes. These invariant manifolds are stable to a variety of alterations of the Hamiltonian itself.

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References and Notes

(1) The superposition principle implies that Schroedinger equations also admit unitary groups with operators that act directly upon Ψ but not *q*, *t*. The Lie generators are of the form $\Psi\ \partial/\partial\Psi$ and $\Psi'\ \partial/\partial\Psi$. The matrix representations of the corresponding groups, which are used to simplify many quantum chemistry computer programs, do not directly carry system-specific dynamical information if this is not imposed. Unitary representations of dynamical groups carry system-specific information analogous to that carried out by representations of the rotation group for systems with spherical symmetry.

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(18) The eigenstates of W are Sturmians, which are orthogonal under a scalar product in which the r^2 dr term of the Schroedinger scalar product is replaced by r dr. A similar change in the scalar product is necessary whenever W is not $H - E$.

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(21) A separate point is required for each class of group orbit—three points for SO(2,1). Here these are points on trajectories with $E < 0$, $E = 0$, $E > 0$, respectively. Because the original dynamical group and its metric-preserving expression need only be locally isomorphic, the parameter range required for the dynamical group to sweep through a trajectory on the original energy surface may be different than that required to sweep through the corresponding trajectory on the invariant manifold that possesses a metric.

(22) Standard methods of Lie (see ref 9a, pp 26−8) can be used to establish the transformation of variables once the realization of the dynamical group has been chosen. Different transformations are required for bound and unbound states. The transformations for the three-dimensional Kepler problem were first obtained by Gyorgi.[20] See also: Rogers, H. H. *J. Math. Phys*. **1971**, *43*, 1125.