# Maximal symmetry group of the time-dependent Schrödinger equation: Atoms and molecules

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Lie's method of extended-group theory has been used to obtain explicit forms of the generators and the structure constants of the maximal symmetry group of point transformations for the nonrelativistic Schrödinger equation. For atoms and molecules this symmetry group is an infinite-parameter Lie group with an infinite-parameter invariant subgroup. The corresponding factor group is a 14-parameter Lie group containing a proper subgroup locally isomorphic to SO(4), the orthogonal group in four dimensions.

## I. INTRODUCTION

Fock[1] showed that the orthogonal group in four dimensions, O(4), is the dynamical symmetry group of the hydrogen atom and this symmetry explained the "accidental" degeneracy[2] of hydrogen spectra. Bargmann[3] pointed out that this larger group appears since the Runge-Lenz vector, in addition to the angular momentum, is required for a complete description of the classical orbits in the Coulomb problem. The symmetry group involved in these studies of the linear integrals of the system is the group of contact transformations.[4,5]

There is a parallel line of study investigating the symmetry group of point transformations for physical systems. Wulfman and Wybourne[6] showed that the symmetry group of point transformations for the classical one-dimensional harmonic oscillator is the eight-parameter noncompact Cartan group $A_2$. Leach solved[7] a similar problem for the classical $N$-dimensional harmonic oscillator. Winternitz and his co-workers[8,9] investigated both linear and nonlinear Schrödinger equations. Vinet[10] considered linear hyperbolic equations in two dimensions; Kalnins, Miller, and Boyer[11,12] investigated the time-dependent Schrödinger equation for free particles.

We have restricted our investigation to the classic problem of nuclei and electrons interacting through a Coulomb potential. For many-electron atoms the usual practice is to start with the wave functions of single-electron ions and to construct linear combinations of Slater determinants. Our object is to find out the maximal symmetry group of point transformations for the many-electron atom so that this symmetry can be incorporated in the construction of the many-electron wave function. The role of O(4) for a many-electron atom has previously been investigated by many authors.[13–18] In molecular quantum chemistry, the basis is the molecular-ion system. As the wave functions of many-electron atoms are built from those of single-electron ions, so the wave functions of a molecule are built from those of the corresponding molecular ion in the Hund-Mulliken scheme.[19] Wulfman[20,21] considered O(5), the orthogonal group in five dimensions, as the dynamical noninvariance group for a one-electron system containing any number of fixed nuclei. Our investigation shows that for both atoms and molecules the maximal symmetry group of point transformations is an infinite-parameter Lie group $G$ with an infinite-parameter invariant subgroup $G_\infty$, so that the factor group $\bar{G} \approx G/G_\infty$ is a 14-parameter Lie group containing a proper subgroup locally isomorphic to SO(4). This is a generator-rich group structure for the system. Even if we neglect $G_\infty$ which corresponds to a change in the wave function only without any change in the time and space coordinates, the factor group $\bar{G}$ is larger than the Schrödinger kinematic group consisting of the Galilean and gauge transformations.

In Sec. II we have used Lie's method of extended-group theory[22–25] to obtain the partial differential equations satisfied by the vectors of the generators[26] of the maximal symmetry group of point transformations of the time-dependent Schrödinger equation. In Sec. III we have solved these sets of equations for the system of nuclei and electrons in their mutual Coulomb field and obtained explicit expressions for the generators of the maximal symmetry group of point transformations and the corresponding structure constants.

It is again pointed out that the symmetry group investigated here is the group of point transformations in the space of wave-function and space-time coordinates and not that of contact transformations.

## II. LIE'S METHOD OF EXTENDED-GROUP THEORY

In this section we describe Lie's method of extended-group theory and develop it in a form suitable for the time-dependent Schrödinger equation. We consider a set of partial differential equations

$$\Delta^\alpha(q,\Psi;r)=0 \ , \quad \alpha=1,\ldots,p \ , \tag{1}$$

in $s$ dependent variables $\Psi^k, k=1,\ldots,s$, and $n$ independent variables $q^i, i=1,\ldots,n$. Here $r$ denotes the highest order of partial derivatives of $\Psi^k$'s. We first construct a space of all variables and derivatives $q^i$, $\Psi^k$, and $\Psi^k_J$, where

$$\Psi^k_J=\partial^{|J|}\Psi^k \Big/ \prod_{i=1}^{n}(\partial q^i)^{j_i} \ ,$$

with (2)

$$J\equiv(j_1,\ldots,j_n) \ , \quad |J|=\sum_i j_i \ .$$

Here $j_i$'s are non-negative integers. If

 

$$X=\sum_i \xi^i(q,\Psi)\partial/\partial q^i+\sum_k \phi_k(q,\Psi)\partial/\partial\Psi^k \tag{3}$$

is the generator in the product space $(q,\Psi)$, then the $r$th extension of $X$ is given by

$$X^{(r)}=X+\sum_k \sum_{(1\le|J|\le r)} \phi_k^J(q,\Psi,\Psi_J)\partial/\partial\Psi_J^k \ . \tag{4}$$

Here

$$\phi_k^J=D^J\left[\phi_k-\sum_i \Psi_i^k\xi^i\right]+\sum_i \Psi_{(J,i)}^k\xi^i \ , \tag{5}$$

$$\Psi_i^k=\partial\Psi^k/\partial q^i \ , \quad (J,i)\equiv(j_1,\ldots,j_{i-1},j_i+1,j_{i+1},\ldots,j_n) \ , \tag{6}$$

$$D^J=\prod_{i=1}^n D_i^{j_i} \ , \quad D_i=\partial/\partial q^i+\sum_k \sum_{(0\le|J|\le r)} \Psi_{(J,i)}^k\partial/\partial\Psi_J^k \ . \tag{7}$$

The system of partial differential equations (1) has the maximal symmetry group $G$ with the generators $X$, if

$$X^{(r)}\Delta^\alpha(q,\Psi;r)=0 \ , \quad \alpha=1,\ldots,p \ . \tag{8}$$

In Eqs. (3)–(8) $q^i$, $\Psi^k$, and $\Psi_J^k$'s are to be considered as independent variables. On the left-hand side of Eq. (8) we use Eq. (1) and separately equate to zero the coefficients of the different powers and their products of the partial derivatives of $\Psi^k$, thus obtaining a set of partial differential equations for $\xi$'s and $\phi$'s. Their solutions give us the most general form of $X$ and hence the maximal symmetry group $G$.

We now apply this method to the time-dependent Schrödinger equation

$$\Delta\equiv i\Psi_t+\sum_s a_s\sum_\sigma \Psi_{s\sigma,s\sigma}-v\Psi=0 \ . \tag{9}$$

Here the independent variables are time $t$ and space variables $q^{s\sigma}$,$\sigma$ and other Greek variables in general denoting the three Cartesian components, and $s$ denoting either the particles or other identification of the space coordinates. Lower suffixes to $\xi$, $\phi$, and $\Psi$ will denote the corresponding partial derivatives. Here $a_s$ and $v$ are functions of $q$'s only. Taking $X$ of the form

$$X=\xi^t(q,t,\Psi)\partial/\partial t+\sum_{s,\sigma}\xi^{s\sigma}(q,t,\Psi)\partial/\partial q^{s\sigma}+\phi(q,t,\Psi)\partial/\partial\Psi \ , \tag{10}$$

we get

$$\begin{aligned}X^{(2)}=X&+\phi^t\partial/\partial\Psi_t+\sum_{s,\sigma}\phi^{s\sigma}\partial/\partial\Psi_{s\sigma}+\phi^{tt}\partial/\partial\Psi_{tt}\\&+\sum_{s,\sigma}\phi^{t,s\sigma}\partial/\partial\Psi_{t,s\sigma}+\sum_{s,\sigma}\phi^{s\sigma,s\sigma}\partial/\partial\Psi_{s\sigma,s\sigma}\\&+\tfrac{1}{2}\sum_{(s\sigma\neq n\nu)}\phi^{s\sigma,n\nu}\partial/\partial\Psi_{s\sigma,n\nu} \ ,\end{aligned}$$

and

$$\begin{aligned}X^{(2)}\Delta\equiv i\phi^t&+\sum_{s,\sigma}a_s\phi^{s\sigma,s\sigma}-\sum_{s,\sigma}\xi^{s\sigma}\Psi\partial v/\partial q^{s\sigma}-v\phi\\&+\sum_{s,\sigma}\xi^t\Psi_{s\sigma,s\sigma}\partial a_s/\partial t+\sum_{s,\sigma}\xi^{s\sigma}\sum_{n,\nu}\Psi_{n\nu,n\nu}\partial a_n/\partial q^{s\sigma}=0 \ .\end{aligned} \tag{11}$$

Equating the coefficients of different partial derivatives and their products and powers separately to zero we get the following set of partial differential equations for $\xi$'s and $\phi$:

$$\xi_\Psi^t=\xi_{s\sigma}^t=\xi_\Psi^{s\sigma}=\phi_{\Psi\Psi}=0 \quad (\text{for all } s\sigma) \ , \tag{12a}$$

$$a_s\xi_{s\sigma}^{n\nu}+a_n\xi_{n\nu}^{s\sigma}=0 \quad [\text{for } all \ (s\sigma)\neq(n\nu)] \ , \tag{12b}$$

$$a_s(\xi_t^t-2\xi_{s\sigma}^{s\sigma})+\sum_{n,\nu}\xi^{n\nu}\partial a_s/\partial q^{n\nu}+\xi^t\partial a_s/\partial t=0 \ , \tag{12c}$$

$$-i\xi_t^{s\sigma}+2a_s\phi_{s\sigma,\Psi}-\sum_{n,\nu}a_n\xi_{n\nu,n\nu}^{s\sigma}=0 \quad (\text{for all } s\sigma) \ , \tag{12d}$$

$$i\phi_t-v\phi-v\Psi(\xi_t^t-\phi_\Psi)-\Psi\sum_{s,\sigma}\xi^{s\sigma}\partial v/\partial q^{s\sigma}+\sum_{s,\sigma}a_s\phi_{s\sigma,s\sigma}=0 \ . \tag{12e}$$

In obtaining these equations we have replaced all $\Psi_t$ and its derivatives in $X^{(2)}\Delta$ by the corresponding space derivatives of $\Psi$ and $\Psi$ itself according to Eq. (9). Thus only $\Psi$ and its space derivatives occur in Eq. (11) and these are taken to be independent variables.

Equation (12a) immediately gives us

$$\begin{aligned}&\xi^t\equiv\xi^t(t) \ , \quad \xi^{s\sigma}\equiv\xi^{s\sigma}(q,t) \ ,\\&\phi=C^0(q,t)+\Psi C^1(q,t) \ .\end{aligned} \tag{13}$$

In the case that we shall consider, all $a_s$'s are constants and we now obtain the general form of $\xi$'s and $\phi$ for this special case. From Eq. (12c) we get

$$\xi_{s\sigma}^{s\sigma}=\xi_t^t/2=b(t) \ . \tag{14}$$

From Eqs. (12a), (12b), and (14) it can be shown that $\xi_{s\sigma,n\nu}^{l\lambda}=0$ for all $l\lambda$, $s\sigma$, and $n\nu$. Thus

$$\xi^{s\sigma}=b_0^{s\sigma}(t)+\sum_\nu b_{s\nu}^{s\sigma}(t)q^{s\nu}+a_s\sum_{(n\neq s)}\sum_\nu b_{n\nu}^{s\sigma}(t)q^{n\nu} \ . \tag{15}$$

Equations (12a) and (12b) now give

$$b_{s\sigma}^{s\sigma}(t)=b(t) \ , \ b_{s\nu}^{s\sigma}(t)+b_{s\sigma}^{s\nu}(t)=0 \ , \text{ for } \sigma\neq\nu \ ,$$

hence,

$$b_{s\nu}^{s\sigma}(t)=\sum_\lambda e_{\sigma\nu\lambda}b_1^{s\lambda}(t) \ ,$$

and

$$b_{n\nu}^{s\sigma}(t)+b_{s\sigma}^{n\nu}(t)=0 \quad \text{for all } s\neq n \ . \tag{16}$$

Here, $e_{\sigma\nu\lambda}$ are the permutation symbols. We can now write

$$\begin{aligned}\xi^{s\sigma}=b_0^{s\sigma}(t)&+b(t)q^{s\sigma}+\sum_{\nu,\lambda}e_{\sigma\nu\lambda}b_1^{s\lambda}(t)q^{s\nu}\\&+a_s\sum_{(n<s)}\sum_\nu b_{n\nu}^{s\sigma}(t)q^{n\nu}-a_s\sum_{(n>s)}\sum_\nu b_{s\sigma}^{n\nu}(t)q^{n\nu} \ .\end{aligned} \tag{17}$$

From Eqs. (12d), (13), and (17) we now get

$$\begin{aligned}-2ia_s\frac{\partial C^1}{\partial q^{s\sigma}}=\xi_t^{s\sigma}=[b_0^{s\sigma}(t)]'&+b'(t)q^{s\sigma}+\sum_{\nu,\lambda}e_{\sigma\nu\lambda}[b_1^{s\lambda}(t)]'q^{s\nu}\\&+a_s\sum_{(n<s)}\sum_\nu[b_{n\nu}^{s\sigma}(t)]'q^{n\nu}\\&-a_s\sum_{(n>s)}\sum_\nu[b_{s\sigma}^{n\nu}(t)]'q^{n\nu} \ .\end{aligned} \tag{18}$$

Here the prime indicates differentiation with respect to $t$. It thus follows that

$$-2ia_s C^1(q,t)=[b_0^{s\sigma}(t)]'q^{s\sigma}+b'(t)(q^{s\sigma})^2/2+\sum_{\nu,\lambda}e_{\sigma\nu\lambda}[b_1^{s\lambda}(t)]'q^{s\sigma}q^{s\nu}$$
$$+a_s\sum_{(n<s)}\sum_{\nu}[b_{n\nu}^{s\sigma}(t)]'q^{s\sigma}q^{n\nu}-a_s\sum_{(n>s)}\sum_{\nu}[b_{s\sigma}^{n\nu}(t)]'q^{s\sigma}q^{n\nu}+f^{s\sigma}(q\neq q^{s\sigma},t)\ . \tag{19}$$

Differentiating Eq. (19) with respect to $q^{s\alpha}$ $(\alpha\neq\sigma)$ and comparing it with Eq. (18), with $\sigma$ being replaced by $\alpha$ (the coefficient of $q^{k\lambda}$), we get $b'(t)=[b_1^{s\sigma}(t)]'=0$, i.e., $b(t)=b$, a constant, and $b_1^{s\sigma}(t)=b_1^{s\sigma}$, a constant. A similar procedure will give us $b_{n\nu}^{s\sigma}(t)=b_{n\nu}^{s\sigma}$, a constant for all $s>n$, and

$$C^1(q,t)=c_1(t)+\sum_{s,\sigma}(i/2a_s)[b_0^{s\sigma}(t)]'q^{s\sigma}\ .$$

From Eq. (14) we obtain $\xi^t=b_0+2bt$.

We now turn to the term independent of $\Psi$ in Eq. (12): $iC_t^0+\sum_{s,\sigma}a_sC^0_{s\sigma,s\sigma}-vC^0=0$. Since we are searching for a Lie group structure whose velocity vectors are analytic functions of $q$'s and $t$, we expand $C^0(q,t)$ in powers of $q$'s and $t$,

$$C^0(q,t)=\sum_{n_t}\sum_{\{n_{s\sigma}\}}[n!/n_t!\prod_{s,\sigma}(n_{s\sigma})!]K(\{n_{s\sigma}\},n_t)(t)^{n_t}$$
$$\times\prod_{s,\sigma}(q^{s\sigma})^{n_{s\sigma}} \tag{20}$$

with $n=n_t+\sum_{s\sigma}n_{s\sigma}$. The $K$'s are not, however, all independent.

The final form of the vectors of the generators are thus

$$\xi^{s\sigma}=b_0^{s\sigma}(t)+bq^{s\sigma}+\sum_{\nu,\lambda}e_{\sigma\nu\lambda}b_1^{s\lambda}q^{s\nu}$$
$$+a_s\sum_{(n<s)}\sum_{\nu}b_{n\nu}^{s\sigma}q^{n\nu}-a_s\sum_{(n>s)}\sum_{\nu}b_{s\sigma}^{n\nu}q^{n\nu}\ ,$$
$$\xi^t=b_0+2bt\ , \tag{21a}$$
$$\phi=C^0(q,t)+\Psi C^1(q,t)\ ,$$

with

$$C^1(q,t)=c_1(t)+\sum_{s,\sigma}(i/2a_s)[b_0^{s\sigma}(t)]'q^{s\sigma}\ ,$$
$$i\partial C^1(q,t)/\partial t-2bv-\sum_{s,\sigma}\xi^{s\sigma}\partial v/\partial q^{s\sigma}=0\ ,$$

$$\sum_{n_t}\sum_{\{n_{s\sigma}\}}\left[(n+1)!/n_t!\prod_{s,\sigma}(n_{s\sigma})!\right](t)^{n_t}\prod_{s,\sigma}(q^{s\sigma})^{n_{s\sigma}}\left[iK(\{n_{s\sigma}\},n_t+1)+(n+2)\sum_{l,\lambda}a_lK(n_{l\lambda}+2,\{n_{s\sigma}\}',n_t)\right]$$
$$-v\sum_{n_t}\sum_{\{n_{s\sigma}\}}\left[n!/n_t!\prod_{s,\sigma}n_{s\sigma}!\right](t)^{n_t}\prod_{s,\sigma}(q^{s\sigma})^{n_{s\sigma}}K(\{n_{s\sigma}\},n_t)=0\ , \tag{21b}$$

where $n=n_t+\sum_{s,\sigma}n_{s\sigma}$. The prime within the parentheses in the $K$ in the last equation means that the suffix $l\lambda$ is shown separately and not in the set within the curly brackets. The last two equations have been derived from Eq. (12e) by equating the terms linear in $\Psi$ and independent of $\Psi$ to zero. Equating to zero the coefficients of different powers of $q^{s\sigma}$ and $t$ in the last equation, we get relations between the $K$'s. In Sec. III we apply this procedure to the particular form of $v$ under consideration.

## III. ATOMS AND MOLECULES

We consider a Coulombic system of $N_e$ electrons of mass $m$ and charge $e$ with the $k_e$th electron $(k_e=1,\ldots,N_e)$ at the position $\mathbf{q}^{k_e}$ and $T$ types of nuclei with the $k_n$th nucleus $(k_n=1,\ldots,N_n)$ of mass $M_n$ and atomic number $Z_n$ of the $n$th type $(n=1,\ldots,T)$ at the position $\mathbf{q}^{nk_n}$. With this notation the time-dependent Schrödinger equation (9) has the parameters

$$a_e=\hbar/2m\ ,\quad a_n=\hbar/2M_n\ ,$$
$$v=\sum_{n,k_n,s,k_s}{}'\ Z_nZ_se^2/2\hbar\,|\mathbf{q}^{nk_n}-\mathbf{q}^{sk_s}|$$
$$-\sum_{n,k_n,k_e}Z_ne^2/\hbar\,|\mathbf{q}^{nk_n}-\mathbf{q}^{k_e}|\tag{22}$$
$$+\sum_{k_e,k_e'}{}'\,e^2/2\hbar\,|\mathbf{q}^{k_e}-\mathbf{q}^{k_e'}|\ .$$

Equation (21a) becomes in this case

$$\xi^{sk_s\sigma}=b_0^{sk_s\sigma}(t)+bq^{sk_s\sigma}+\sum_{\nu,\lambda}e_{\sigma\nu\lambda}b_1^{sk_s\lambda}q^{sk_s\nu}+a_s\sum_{(n<s)}\sum_{k_n}\sum_{\nu}b_{nk_n\nu}^{sk_s\sigma}q^{nk_n\nu}+a_s\sum_{(k_n<k_s)}\sum_{\nu}b_{sk_n\nu}^{sk_s\sigma}q^{sk_n\nu}$$
$$-a_s\sum_{(k_n>k_s)}\sum_{\nu}b_{sk_s\sigma}^{sk_n\nu}q^{sk_n\nu}-a_s\sum_{(n>s)}\sum_{k_n}\sum_{\nu}b_{sk_s\sigma}^{nk_n\nu}q^{nk_n\nu}-a_s\sum_{k_e}\sum_{\nu}b_{sk_s\sigma}^{k_e\nu}q^{k_e\nu}\ ,$$
$$\xi^{k_e\sigma}=b_0^{k_e\sigma}(t)+bq^{k_e\sigma}+\sum_{\nu,\lambda}e_{\sigma\nu\lambda}b_1^{k_e\lambda}q^{k_e\nu}+a_e\sum_{n,k_n}\sum_{\nu}b_{nk_n\nu}^{k_e\sigma}q^{nk_n\nu}+a_e\sum_{(k_e'<k_e)}\sum_{\nu}b_{k_e'\nu}^{k_e\sigma}q^{k_e'\nu}-a_e\sum_{(k_e'>k_e)}\sum_{\nu}b_{k_e\sigma}^{k_e'\nu}q^{k_e'\nu}\ ,$$
$$\xi^t=b_0+2bt\ ,\quad \phi=C^0(q,t)+\Psi C^1(q,t)\ ,$$

with

$$C^1(q,t)=c_1(t)+i\sum_{n,k_n}\sum_{\nu}[b_0^{nk_n\nu}(t)]'q^{nk_n\nu}/2a_n$$

$$+i\sum_{k_e}\sum_{\nu}[b_0^{k_e\nu}(t)]'q^{k_e\nu}/2a_e\ ,$$

$$i\partial C^1(q,t)/\partial t-\sum_{s,k_s,\sigma}\xi^{sk_s\sigma}\partial v/\partial q^{sk_s\sigma}$$

$$-\sum_{k_e\sigma}\xi^{k_e\sigma}\partial v/\partial q^{k_e\sigma}+2bv=0\ , \quad (23)$$

$$iC_t^0+\sum_{s,k_s,\sigma}a_sC^0_{sk_s\sigma,sk_s\sigma}+a_e\sum_{k_e,\sigma}C^0_{k_e\sigma,k_e\sigma}-vC^0=0\ .$$

Inserting Eq. (22) in Eq. (23) we get the following relations:

$$\begin{aligned}
&b=0\ ,\quad c_1'(t)=0\ ,\quad [b_0^{sk_s\sigma}(t)]''=[b_0^{k_e\sigma}(t)]''=0\ ,\\
&b_0^{sk_s\sigma}(t)-b_0^{nk_n\sigma}(t)=b_0^{sk_s\sigma}(t)-b_0^{k_e\sigma}(t)\\
&\qquad =b_0^{k_e\sigma}(t)-b_0^{k_e'\sigma}=0\ ,\\
&b^{k_e\nu}_{sk_s\sigma}+b^{k_e\sigma}_{sk_s\nu}=b^{k_e'\nu}_{sk_s\sigma}-b^{k_e\nu}_{sk_s\sigma}\\
&\qquad =a_sb^{k_e\nu}_{sk_s\sigma}-a_eb^{k_e\nu}_{k_e'\sigma}=0\ ,\ \text{for } k_e>k_e'\ ,\\
&a_sb^{sk_s\alpha}_{sk_n\beta}=a_eb^{k_e\alpha}_{sk_n\beta}\ ,\quad \text{for } k_n<k_s\ ,\\
&a_sb^{sk_s\alpha}_{nk_n\beta}=a_eb^{k_e\alpha}_{nk_n\beta}\ ,\quad \text{for } n<s\ ,\\
&\sum_\gamma e_{\alpha\beta\gamma}(b_1^{k_e\gamma}-b_1^{k_e'\gamma})=\sum_\gamma e_{\alpha\beta\gamma}(b_1^{sk_s\gamma}-b_1^{nk_n\gamma})\ ,\\
&\sum_\gamma e_{\alpha\beta\gamma}(b_1^{sk_s\gamma}-b_1^{k_e\gamma})+(a_s-a_e)b^{k_e\alpha}_{sk_s\beta}=0\ .
\end{aligned} \quad (24)$$

The general solution of Eqs. (24) gives us

$$\begin{aligned}
&b=0\ ,\quad c_1(t)=c_1=\text{const}\ ,\\
&b_0^{sk_s\alpha}(t)=b_0^{k_e\alpha}(t)=b^{0\alpha}+c^{t\alpha}t\ ,\quad b_1^{k_e\alpha}=b_1^\alpha\ ,\\
&a_nb^{k_e\alpha}_{nk_n\beta}=a_eb^{k_e\alpha}_{k_e'\beta}=\sum_\gamma e_{\alpha\beta\gamma}b_0^\gamma\ ,\quad \text{for } k_e>k_e'\ ,\\
&b_1^{sk_s\alpha}=b_1^\alpha+(a_e/a_s-1)b_0^\alpha\ ,\\
&a_sb^{sk_s\alpha}_{sk_n\beta}=a_eb^{k_e\alpha}_{sk_n\beta}\\
&\qquad =(a_e/a_s)\sum_\gamma e_{\alpha\beta\gamma}b_0^\gamma\ ,\quad \text{for } k_n<k_s\ ,\\
&a_sb^{sk_s\alpha}_{nk_n\beta}=a_eb^{k_e\alpha}_{nk_n\beta}\\
&\qquad =(a_e/a_n)\sum_\gamma e_{\alpha\beta\gamma}b_0^\gamma\ ,\quad \text{for } n<s\ .
\end{aligned} \quad (25)$$

The generators of the symmetry group $G$ are generated from $b$'s, $c_1$, and $C^0$. It is seen that the generators $C^0\partial/\partial\Psi$ are to be determined from the last of Eq. (23) and no further restriction on $C^0$ exists other than this last equation. We note that $C^0$ satisfies the original Schrödinger equation. Thus $C^0$ has, in general, an infinite number of independent solutions giving an infinite-parameter Lie group $G_\infty$. These generators commute among themselves and thus $G_\infty$ is an Abelian subgroup of $G$. The relations (25) give us 14 generators for another subgroup $\overline{G}$, which is nonoverlapping with $G_\infty$:

$$X^{0\alpha}=-i\left[\sum_{n,k_n}\partial/\partial q^{nk_n\alpha}+\sum_{k_e}\partial/\partial q^{k_e\alpha}\right]\ ,$$

$$X^t=-i\partial/\partial t\ ,\quad X^\Psi=(M_0/\hbar)\Psi\partial/\partial\Psi\ ,$$

$$X^{t\alpha}=tX^{0\alpha}+R^\alpha X^\Psi\ ,\quad X_0^\alpha=\sum_{\beta\gamma}e_{\alpha\beta\gamma}R^\beta X^{0\gamma}\ ,$$

$$X_1^\alpha=-i\sum_{\beta,\gamma}e_{\alpha\beta\gamma}\left[\sum_{n,k_n}q^{nk_n\beta}\partial/\partial q^{nk_n\gamma}+\sum_{k_e}q^{k_e\beta}\partial/\partial q^{k_e\gamma}\right]\ ,$$

where $M_0$ is the total mass of the system,

$$M_0=mN_e+\sum_n M_nN_n$$

and $\mathbf{R}$ is the position of the center of mass of the system,

$$\mathbf{R}=\left[\sum_{n,k_n}M_n\mathbf{q}^{nk_n}+m\sum_{k_e}\mathbf{q}^{k_e}\right]\Big/M_0\ . \quad (26)$$

The nonvanishing commutators are

$$\begin{aligned}
&[X^{0\alpha},X^{t\beta}]=-i\delta_{\alpha\beta}X^\Psi\ ,\quad [X^{0\alpha},X_1^\beta]=i\sum_\gamma e_{\alpha\beta\gamma}X^{0\gamma}\ ,\\
&[X^{0\alpha},X_0^\beta]=i\sum_\gamma e_{\alpha\beta\gamma}X^{0\gamma}\ ,\quad [X^t,X^{t\alpha}]=-iX^{0\alpha}\ ,\\
&[X^{t\alpha},X_1^\beta]=i\sum_\gamma e_{\alpha\beta\gamma}X^{t\gamma}\ ,\\
&[X^{t\alpha},X_0^\beta]=i\sum_\gamma e_{\alpha\beta\gamma}X^{t\gamma}\ ,\quad [X_1^\alpha,X_1^\beta]=i\sum_\gamma e_{\alpha\beta\gamma}X_1^\gamma\ ,\\
&[X_1^\alpha,X_0^\beta]=i\sum_\gamma e_{\alpha\beta\gamma}X_0^\gamma\ ,\quad [X_0^\alpha,X_0^\beta]=i\sum_\gamma e_{\alpha\beta\gamma}X_0^\gamma\ .
\end{aligned} \quad (27)$$

It is easily seen that $G_\infty$ is an invariant subgroup of $G$ so that $G/G_\infty\approx\overline{G}$.

Physically $X^{0\alpha}$ denotes space translation of the whole system, $X^t$ denotes time translation, $X^\Psi$ denotes $\Psi$ scaling, $X^{t\alpha}$ corresponds to Galilean transformations, $X_1^\alpha$ denotes rotation of the whole system, and $X_0^\alpha$ denotes rotation of the center of mass. In order to make the existence of the SO(4) group clear, we take the linear combinations $L^\alpha=X_1^\alpha$, $A^\alpha=2X_0^\alpha-X_1^\alpha$ and get the nonvanishing commutators

$$\begin{aligned}
&[X^{0\alpha},X^{t\beta}]=-i\delta_{\alpha\beta}X^\Psi\ ,\quad [X^{0\alpha},L^\beta]=i\sum_\gamma e_{\alpha\beta\gamma}X^{0\gamma}\ ,\\
&[X^{0\alpha},A^\beta]=i\sum_\gamma e_{\alpha\beta\gamma}X^{0\gamma}\ ,\\
&[X^t,X^{t\alpha}]=-iX^{0\alpha}\ ,\quad [X^{t\alpha},L^\beta]=i\sum_\gamma e_{\alpha\beta\gamma}X^{t\gamma}\ ,\\
&[X^{t\alpha},A^\beta]=i\sum_\gamma e_{\alpha\beta\gamma}X^{t\gamma}\ ,\\
&[L^\alpha,L^\beta]=i\sum_\gamma e_{\alpha\beta\gamma}L^\gamma\ ,\quad [L^\alpha,A^\beta]=i\sum_\gamma e_{\alpha\beta\gamma}A^\gamma\ ,\\
&[A^\alpha,A^\beta]=i\sum_\gamma e_{\alpha\beta\gamma}L^\gamma\ .
\end{aligned} \quad (28)$$

We see that $\bar{G}$ contains the proper subgroup $H=\{L^{\alpha},A^{\beta}\}$ which is locally isomorphic to SO(4). $\bar{G}$ has the invariant subgroup

$$N=\{X^{0\alpha},X^{t},X^{\Psi},X^{t\beta}\}$$

so that $\bar{G}/N\approx H$. Thus $\bar{G}$ is a semidirect product $\bar{G}=N \circledS H$. The center of $\bar{G}$ contains only $X^{\Psi}$. It is interesting to note that atoms as well as molecules, irrespective of the number and nature of the constituents, have the same maximal symmetry group of point transformations, provided the constituents interact among themselves with the inverse square law of forces.

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