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Isoelectronic Molecules

First- and Second-Order Properties and the Continuous Group $\boldsymbol{L}(\boldsymbol{l})$

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The simple variation of the physical properties of isoelectronic molecules with nuclear charge and internuclear distance is shown to be the result of a symmetry property of their Hamiltonians and operators under the continuous group $\boldsymbol{L}(\boldsymbol{l})$.

Es wird gezeigt, daß bei isoelektronischen Molekülen die Änderung der physikalischen Eigenschaften in Abhängigkeit von Kernladung und internuklearem Abstand aus einer Symmetrieeigenschaft ihrer Hamiltonoperatoren und Operatoren der kontinuierlichen Gruppe $\boldsymbol{L}(\boldsymbol{l})$ resultieren.

1. Introduction

In a series of papers [1–3] we have shown that the NMR shielding constants of a sequence of isoelectronic atoms or molecules are rigorously interrelated in a simple way. This result is valid even in the presence of electron-electron repulsion [3]. Although we have used the NMR shielding constant as an example, the same could be said for many other properties.

More precisely, and by way of summary of the previous work, the first- and second-order properties defined as

$$\begin{aligned} \mathscr{P}_n^{(1)} &= \langle \Phi_n | \boldsymbol{A} | \Phi_n \rangle , \\ \mathscr{P}_n^{(2)} &= \sum_{m \neq n} \langle \Phi_n | \boldsymbol{A} | \Phi_m \rangle \langle \Phi_m | \boldsymbol{B} | \Phi_n \rangle / (E_n - E_m) , \end{aligned} \tag{1}$$

in the case of homonuclear diatomic molecules have been shown to be given by

$$\begin{aligned} \mathscr{P}_n^{(1)} &= Z^{(\alpha' - \alpha)} g^{(1)}(ZR, z/Z) , \\ \mathscr{P}_n^{(2)} &= Z^{(\alpha' - \alpha + \beta' - \beta - 2)} g^{(2)}(ZR, z/Z) , \end{aligned} \tag{2}$$

respectively. In the equations above Φ_n is an eigenfunction of the electronic Schrödinger equation

$$\boldsymbol{H}_e \Phi_n = (T_e + V) \Phi_n = E_n \Phi_n , \tag{3}$$

Where T_e is the total electronic kinetic energy and V is the total potential energy

$$V = - \sum_{k=1}^{N} \left\{ \frac{Z}{|\boldsymbol{r}_k - \boldsymbol{R}/2|} + \frac{Z}{|\boldsymbol{r}_k + \boldsymbol{R}/2|} \right\} + \sum_{k > j}^{N} \frac{z}{|\boldsymbol{r}_k - \boldsymbol{r}_j|} . \tag{4}$$

$\boldsymbol{A}$ and $\boldsymbol{B}$ are, respectively, appropriate homogeneous operators [2] of degree α and β in the position variables $\boldsymbol{r}$ and $\boldsymbol{R}$ and of degree α' and β' in the nuclear charges.

The functions $g^{(1)}$ and $g^{(2)}$ can in principle be determined from the boundary conditions [1]. Eqs. (2) make it clear that if we determine a property for one member of an isoelectronic sequence that all of them are determined; electron correlation having been taken care of in that one member-once and for all. Further, the equation is useful as a check on numerical calculations and gives assurance that one can interpolate between numerical results.

In obtaining Eqs. (2) the virial theorem [4] as well as the homogeniety of $\boldsymbol{A}$ and $\boldsymbol{B}$ were used. However, the results seemed to be of such a general and rigorous nature that it was felt that perhaps there was a more fundamental reason for their validity. This is indeed the case as we shall show below. We have found that Eqs. (2) arise as a result of the symmetry properties of the physical properties under the linear group $\boldsymbol{L}(\boldsymbol{l})$ [5]. Indeed, one might say that isoelectronic atoms and molecules behave similarly because of the symmetry of their Hamiltonians and physical properties under $\boldsymbol{L}(\boldsymbol{l})$. In view of the impact which the theory of symmetry is having in all branches of science we feel that it is worthwhile pointing out its underlying presence in the theory of isoelectronic species.

2. Theory

A. The Group SL(2)

For simplicity we will consider only one-electron, homonuclear diatomic molecules. More complicated cases can be treated using the same methods.

The set of operators $\boldsymbol{S}(a)$ which transform the internuclear distance R and the nuclear charge Z according to

$$\begin{aligned} \boldsymbol{S}(a)R &= aR, \\ & \qquad 0<a<\infty \\ \boldsymbol{S}(a)Z &= a^{-1}Z, \end{aligned} \tag{5}$$

is an example of a one-parameter (a) continuous Lie Group. In fact, it is the special linear group $\boldsymbol{SL}(2)$ [5]. This is a simple, non-compact, Abelian group. The group elements corresponding to the identity and inverse are $\boldsymbol{S}(1)$ and $\boldsymbol{S}(a^{-1})$ respectively. We note also that the quantity ZR is invariant under the group.

A representation of the infinitesimal transformation (away from the identity) can be obtained as follows. We have for small δa

$$\begin{aligned} \boldsymbol{S}(1+\delta a)R &= (1+\delta a)R, \\ \boldsymbol{S}(1+\delta a)Z &= (1+\delta a)^{-1}Z = (1-\delta a)Z, \end{aligned} \tag{6}$$

which can be written as

$$\begin{aligned} \boldsymbol{S}(1+\delta a)R &= \left(1+\delta a\left[R\frac{\partial}{\partial R} - Z\frac{\partial}{\partial Z}\right]\right)R, \\ \boldsymbol{S}(1+\delta a)Z &= \left(1+\delta a\left[R\frac{\partial}{\partial R} - Z\frac{\partial}{\partial Z}\right]\right)Z. \end{aligned} \tag{7}$$

The operator in square brackets is called the generator of the infinitesimal transformation and will be denoted by $\mathscr{T}$.

In addition to the operators $\boldsymbol{S}(a)$ we introduce a group of operators $\boldsymbol{O}_s$ which is isomorphic to $\boldsymbol{S}$. These act on functions and in keeping with the usual conventions [6] we have

$$\begin{aligned} \boldsymbol{O}_s f(R,Z) &= f(\boldsymbol{S}^{-1}R, \boldsymbol{S}^{-1}Z), \\ \boldsymbol{O}_s(f\,g) &= (\boldsymbol{O}_s f)(\boldsymbol{O}_s g). \end{aligned} \tag{8}$$

It is not difficult to show that the generator of the infinitesimal transformation determines the form of the operators $\boldsymbol{O}_s$ and in fact it is [5]

$$\boldsymbol{O}_s f(R,Z) = \exp(-[\ln a]\mathscr{T}) f(R,Z). \tag{9}$$

B. The Physical Properties

We begin by considering the effect of $\boldsymbol{O}_s$ on the electronic energy of a one-electron, homonuclear diatomic molecule. Or, more conveniently we consider the effect of $\boldsymbol{O}_s$ on E_n/Z^2. We have

$$\boldsymbol{O}_s(E_n/Z^2) = \int (\boldsymbol{O}_s \Phi_n)(\boldsymbol{O}_s H_e/Z^2)(\boldsymbol{O}_s \Phi_n)\, d\boldsymbol{r}. \tag{10}$$

Since the electronic wave function has the general form [7] $\Phi_n = Z^{3/2}\,\Psi(ZR, Z\boldsymbol{r})$ it is clear that

$$\boldsymbol{O}_s \Phi_n(Z,R,\boldsymbol{r}) = a^{3/2}\,\Phi_n(Z,R,a\boldsymbol{r}), \tag{11}$$

further, the result for the Hamiltonian is just

$$\boldsymbol{O}_s[\boldsymbol{H}_e(\boldsymbol{r})/Z^2] = [\boldsymbol{H}_e(a\boldsymbol{r})/Z^2]. \tag{12}$$

As a consequence of these two equations Eq. (10) becomes

$$\boldsymbol{O}_s(E_n/Z^2) = (E_n/Z^2). \tag{13}$$

The quantity (E_n/Z^2) is invariant under the group $\boldsymbol{SL}(2)$. This alone establishes the fact that (E_n/Z^2) is a function of only the invariant quantity ZR. More formally one has

$$\exp(-[\ln a]\mathscr{T})(E_n/Z^2) = (E_n/Z^2). \tag{14}$$

However, in order for this equation to be valid for all values of a we must have

$$\mathscr{T}(E_n/Z^2) = 0, \tag{15}$$

which leads to

$$\left(R\frac{\partial}{\partial R} - Z\frac{\partial}{\partial Z}\right) E_n = -2E_n. \tag{16}$$

This partial differential equation for the electronic energy had been obtained in a previous paper [1]. There it was found that the general solution is

$$E_n(Z,R) = Z^2 E_n(ZR), \tag{17}$$

where $E_n(R)$ is the energy for the molecule H_2^+.

Next, we consider the first- and second-order properties whose operators are homogeneous functions of degree α in $\boldsymbol{r}$ and R and α' in Z, i.e.

$$\begin{aligned} A(a\boldsymbol{r}, aR, Z) &= a^{\alpha} A(\boldsymbol{r}, R, Z)\,, \\ \text{and}\quad A(\boldsymbol{r}, R, aZ) &= a^{\alpha'} A(\boldsymbol{r}, R, Z)\,. \end{aligned} \tag{18}$$

Using these equations we find that

$$\boldsymbol{O}_s \boldsymbol{A}(\boldsymbol{r}, R, Z) = a^{(\alpha-\alpha')} \boldsymbol{A}(a\boldsymbol{r}, R, Z) \tag{19}$$

and so we are led to the result

$$\boldsymbol{O}_s(\mathscr{P}_n^{(1)}/Z^{\alpha-\alpha'}) = (\mathscr{P}_n^{(1)}/Z^{\alpha-\alpha'})\,, \tag{20}$$

as before. The second-order properties go through in the same way.

In order to include the effect of electron-electron repulsion it is only necessary to consider the group $\boldsymbol{L}(3)$ which is isomorphic to [8] $\boldsymbol{SL}$ (2), i.e.

$$\begin{aligned} \boldsymbol{T}(a)R &= aR\,, \\ \boldsymbol{T}(a)Z &= a^{-1}Z\,, \\ \boldsymbol{T}(a)z &= a^{-1}z\,. \end{aligned} \tag{21}$$

Here the generator ($\mathscr{L}$) is

$$\mathscr{L} = R\frac{\partial}{\partial R} - Z\frac{\partial}{\partial Z} - z\frac{\partial}{\partial z}\,. \tag{22}$$

With the help of functional operators $\boldsymbol{O}_T$, together with the same reasoning which was used above we obtain Eqs. (2).

Having established a connection between Group Theory and the theory of isoelectronic systems it is hoped that this powerful and enormous field of mathematics will shed further light on the regularities observed in these systems as well as uncovering new ones.

References

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5. Hamermesh, M.: Group Theory, Chapter 8. Mass: Addison-Wesley, 1962.
6. Ref. 5, p. 81.
7. In Ref. 3 we show that $(\mathscr{T} + \boldsymbol{r} \cdot \boldsymbol{\nabla})\,\Phi = (3/2)\Phi$. The general solution of this equation is $\Phi = Z^{3/2}$ $\Psi(ZR, Z\boldsymbol{r})$ where Ψ is arbitrary.
8. Note that there are two invariants in this case, ZR and z/Z.

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