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# Isoelectronic Molecules

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We have used the molecular virial theorem together with the fact that the potential energy for a series of isoelectronic molecules is a homogeneous function of the nuclear charges to show that the electronic energies of isoelectronic molecules, *e.g.* $H_2^+$, $He_2^{+3}$, $Li_2^{+5}$, ... are related in a simple way. That is, if the electronic energy for $H_2^+$ is a known function of $R$, *i.e.*, $g(R)$, then the energies for the other members of the sequence are $Z^2 g(ZR)$ where $Z$ is the nuclear charge. The method is extended to heteronuclear as well as multi-electronic molecules.

Unter Berücksichtigung des molekularen Virialsatzes und der Tatsache, daß die potentielle Energie für eine Reihe von iso-elektronischen Molekülen eine homogene Funktion der Kernladungen ist, läßt sich ein einfacher Zusammenhang zwischen den Elektronenenergien iso-elektronischer Moleküle wie z. B. $H_2^+$, $He_2^{+3}$, $Li_2^{+5}$, ... zeigen. Ist die Elektronenenergie für $H_2^+$ z. B. eine bekannte Funktion $g(R)$, dann betragen die Energien der übrigen Mitglieder einer solchen iso-elektronischen Folge $Z^2 \cdot g(ZR)$, wobei $Z$ die Kernladungszahl ist. Die Methode wird sowohl auf heteronukleare als auch auf Mehrelektronenmoleküle ausgedehnt.

En utilisant le théorème virial moléculaire et le fait que l'énergie potentielle pour une série isoélectronique des molécules est une fonction homogène de charge nucléaire on montre une relation simple entre les énergies électroniques des molécules $H_2^+$, $He_2^{+3}$, $Li_2^{+5}$, .... Quand l'énergie électronique pour $H_2^+$ est une fonction connue $g(R)$ les énergies des membres de la série se donnent à $Z^2 g(ZR)$ ou $Z$ est la charge nucléaire. La méthode est étendue aux molécules hétéronucléaires et aux molécules multiélectroniques.

Recently there has been renewed interest in the molecular virial theorem [1] as a point of departure for studies on electronic energy curves and force constants. In this communication we wish to show that the virial theorem can be developed a step further for isoelectronic molecules.

Because the potential energy of a molecule is a homogeneous function of its position variables, of nuclear charges, etc. it is possible to show that the electronic energies of a series isoelectronic molecules are related in a simple way.

We begin by recalling a rigorous result of molecular quantum mechanics the virtual theorem [2]

$$\sum_\alpha Q_\alpha \cdot \nabla_\alpha E(Q) + 2E(Q) - \bar{V} = 0 . \tag{1}$$

In this equation $(Q)$ represents the set of nuclear coordinates and $E$ is the electronic energy minus nuclear repulsion. The integral $\bar{V}$ is the potential energy of the molecule averaged with the electronic wave function $\varphi$. We have

$$\mathcal{H}_e \, \varphi(Q, q) = (T_e + V)\, \varphi(Q, q) = E(Q)\, \varphi(Q, q) . \tag{2}$$

Consider first the case of a one-electron heteronuclear diatomic molecule. The potential energy appearing in $\bar{V}$

$$\bar{V} = \langle \varphi | - \frac{Z}{|r - R/2|} - \frac{Z'}{|r + R/2|} | \varphi \rangle , \tag{3}$$

is a homogeneous function of degree $(+1)$ in the nuclear charges $Z, Z'$ therefore Eq. (3) can be rewritten as

$$\bar{V} = \langle\varphi|\, Z\frac{\partial V}{\partial Z} + Z'\frac{\partial V}{\partial Z'}\,|\varphi\rangle\,, \tag{4}$$

where we have used Euler's theorem for homogeneous functions. The integrals in Eq. (4) can now be related to derivatives of the electronic energy with respect to the nuclear charges by the Hellmann-Feynman [3] theorem, *i.e.*

$$\langle\varphi|\,\frac{\partial \mathscr{H}_e}{\partial\lambda}\,|\varphi\rangle = \frac{\partial E}{\partial\lambda}\,, \tag{5}$$

where $\lambda$ is a parameter contained in $\mathscr{H}_e$. Combining Eqs. (1), (4) and (5) we obtain

$$-R\frac{\partial E}{\partial R} + Z\frac{\partial E}{\partial Z} + Z'\frac{\partial E}{\partial Z'} = 2E\,. \tag{6}$$

This equation is an example of a first-order partial differential equation the theory of which is well developed [4, 5]. It is easily verified that the general solution of Eq. (6) may be written as

$$E = ZZ'\,f(ZR, Z'R)\,, \tag{7}$$

where $f$ is any arbitrary function of the variables $ZR$ and $Z'R$. It is clear that $E$ is far from being determined by the differential equation alone. Only the application of boundary conditions will pick out a unique function from the infinity of solutions generated by Eq. (7). At this point, however, we note that the general solution alone will suffice to demonstrate that the energies of $H_2^+$, $HHe^{+2}$, $HLi^{+3}$, $He_2^{+3}$, etc. are all special cases of Eq. (7).

At first glance one might think that given Eq. (7) together with suitable boundary conditions it would be possible to obtain the electronic energy without solving the molecular Schrödinger equation. We shall see that this is not entirely true however.

The nature of the boundary conditions which are needed to make $E$ unique (the Cauchy problem) is complicated. Therefore, we will treat the homonuclear case first. Here the electronic energy expression has the form

$$E = Z^2\,g(ZR)\,, \tag{8}$$

where $g$ is arbitrary. It can be shown [4] that a unique solution is obtained if $E$ is specified along some curve in the $R, Z$-plane. However, not just any curve will do. Consider for example the case in which we specify the energy to be $-2Z^2/n^2$ (the united atom energy) along the curve $R = 0$. This choice of boundary conditions determines $E$ only to the extent that $g(0) = -2/n^2$. There are still an infinite number of solutions possible. Alternately if we set $E = 0$ along $Z = 0$ we see that $E$ isn't determined at all. Both of these cases are contained in the statement that the solution cannot be made unique by specifying $E$ along the *characteristic base curve* [4] $ZR = C$ where $C$ is any constant. If now we consider the case in which $E$ is prescribed along a curve which cuts across the characteristic base curves, say $Z = 1$, then a unique solution will result. That is to say if $E = U(R)$ ($U$ is a known function) along $Z=1$, then the solution to the problem is exactly

$$E=Z^2\,U(ZR)\,. \tag{9}$$

From this we conclude that if the Schrödinger equation can be solved for one homonuclear molecule the electronic energy for any isoelectronic one can be obtained from Eq. (9).

Returning to the heteronuclear molecule we see that it can be treated similarly. In particular, if one has obtained a solution of the Schrödinger equation for the case where $Z=1$ with $Z'$ and $R$ arbitrary that is $E=Z'\,U(R, Z'R)$ the energy for the general situation is simply

$$E=ZZ'\,U(ZR, Z'R)\,. \tag{10}$$

In order to demonstrate the method for multi-electron systems consider a homonuclear two-electron diatomic molecule. The potential energy for the molecule contains the nuclear charge $Z$ and we will introduce the artificial effective charge $z$ so that

$$\bar{V}=\left\langle \varphi \right| \sum_{i=1}^{2} \left\{ -\frac{Z}{|r_i-R/2|}-\frac{Z}{|r_i+R/2|} \right\} + \frac{z}{r_{12}} \left| \varphi \right\rangle . \tag{11}$$

Because of the formal similarity of Eqs. (11) and (3) the electronic energy Eqs. (6) and (7) have the same form; however, the general expression for the energy can be written

$$E=Z^2 f(ZR, zR) \tag{12}$$

where $f$ is arbitrary. Note that if $z$ is set equal to unity we are describing the isoelectronic sequence $H_2$, $He_2^{+2}$ etc. As before, if one could solve the Schrödinger equation for the case $Z=1$ with $z$ and $R$ arbitrary, all of the heteronuclear energy curves would become available. Although this procedure may be difficult to achieve [6] in practice the relationship among the various energies none the less exists.

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## References

1. Parr, R. G., and R. F. Borkman: J. chem. Physics **46**, 3683 (1967); **48**, 1116 (1968); **48**, 1426 (1968). Also Knöll, L.: Theoret. chim. Acta (Berl.) **10**, 357 (1968).
2. Laurenzi, B. J., and D. D. Fitts: J. chem. Physics **43**, 317 (1965).
3. Feynman, R. P.: Physic. Rev. **56**, 340 (1939).
4. Courant, R., and D. Hilbert: Methods of mathematical physics, Vol. II. Chap. 2. New York: Interscience Publishers 1962
5. Hildebrand, F. B.: Advanced calculus for applications, Chap. 8. Englewood Cliffs, New Jersey: Prentice-Hall, Inc. 1948.
6. Ellison, F. O., and A. A. Wu: J. chem. Physics **47**, 4415 (1967).

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