Revisit the Hydrogen Molecular Ion

Abstract: In this paper we demonstrate how the concept of electron orbital compressing factor works in quantum calculation. By the quantum calculation of hydrogen molecular ion, the compressing factor method proposed in our previous work indeed reveal the true movement state of electron in atom/molecule. Based on the result we obtained in this work, the advantage/disadvantage among the different strategies in quantum calculation is discussed.

Keyword: hydrogen molecular ion; quantum calculation; the compressed electron orbital; variational method; “effective atomic number”;

1.Introduction

Since the quantum mechanics is setup, it already becomes essential tool in scientific research activity. The researchers utilize the quantum mechanics to elucidate the property of atoms/molecules, and to explore the electromagnetic property of materials (1-5). Based on the quantum mechanics, our understanding on materials reaches from the macro to micro level. However, during the application process of quantum mechanics, the researchers met a lot of difficulties, such as in most of cases, the calculation result deviates too much from the experimental data (6). Till now, to my knowledge, only for hydrogen atom, we can get the exact result which is consistent with the experimental data. In most of situation, the discrepancy between the calculation result and the experimental data becomes unacceptable.

For example, when we use the quantum mechanics to calculate the hydrogen molecular ion (7), the situation becomes if we keep the clear physical picture of the molecular orbital, the calculation result deviates too much from the experimental data, if we pursue the consistency between the calculation result and experimental data, we have to expand the orbital basis of the hydrogen molecular ion into the complete basis set (8), that means we have to give up pursuing the clear physical picture of orbital of the hydrogen molecular ion.

Traditional explanation about the expansion of the orbital of the hydrogen molecular ion into the complete basis set is described as the higher level orbital mixed into the lower level orbital, such as the electron 1s orbital of hydrogen atom mixed in some 2s, 2p,... orbital components, that means the electron 1s orbital of hydrogen atom can’t describe the electron orbital of the hydrogen molecular ion well.

The problem here is if the hydrogen molecular ion is broken into single hydrogen atom and proton, the electron orbital of the hydrogen molecular ion is recovered into the electron 1s orbital of hydrogen atom, the mixed components are disappeared. Therefore, some researchers suggest totally give up the electron 1s orbital of hydrogen atom in calculation, the typical one is the Hylleraas function which can get the calculation result almost the same as the experimental data (9). In this case, the big problem is still in that the clear physical picture of the orbital is totally or at least partly lost.

In order to overcome this difficulty, the researchers figure out different method, such as variational method (10-12), for instance, we take the atomic number of atom as variational parameter, then, the calculation result will be greatly improved. We call this parameter as “effective atomic number” and explain the difference between the “effective atomic number” and real atomic number as coming from the screening effect of the rest electrons. Some researchers go even furthermore, they use a series of Gaussian functions to mimic the orbital of electron in atom/molecule, the coefficients of each Gaussian function taken as variational parameters. The famous one is developed into the Gaussian program (13). For the variational method, the key problem is the cost of computer time, and even worse is in that if the calculation involves the electron transition between different orbital, usually, we can’t get reliable calculation result.

For multi-electron system, some researchers developed the density functional theory (14), that means we take the electron outside the nucleus as a electron distribution function, therefore, the calculation only involve three coordinate variable function. This theory opens an avenue to do quantum mechanics calculation for the macro system and the density functional method does reduce the computing time greatly indeed. However, the calculation result from the density functional method usually only can get coarse property of system but if we want to get the detail of the property of the system, it is still very difficult.

Some researchers think we should expand the basis into the complete basis set in calculation. In this way we do improve the calculation precision and the rationality to do so is due to the higher level orbital mixed in. With the computer technology developing, the computer becomes faster and faster, this method may meet our requirement in research work in the future.

Summary, all the cited methods above can’t avoid the tedious computer time and loss of the physical picture of electron orbital in atomic/molecular system. Some researchers continuously proposed different method or theory, such as perturbation theory (15), green functional theory (16) and energy band theory (17). These theories always more or less improve the calculation precision but at the cost of computer time and loss of the clear physical picture of the atomic/molecular orbital instead.

Here we try a way which is different from the traditional method. We will keep the clear physical picture of atomic/molecular orbital, improve the calculation precision and at the same time greatly reduce the computer time. In order to make our calculation simple, here, we take the hydrogen molecular ion as an example in this work to start our discussion.

2. Theory

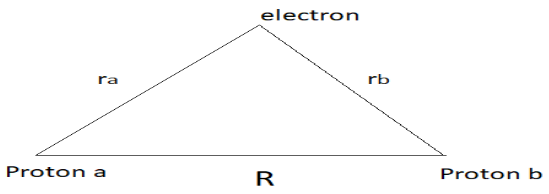

Fig. 1 The Illustration Of The Coordinates For The Hydrogen Molecular Ion.

In our previous work (18), we consider the variation of the electron orbital of hydrogen atom under different situation. Here we take the same idea, that is, add an compressing factor (α) onto the electron orbital of hydrogen atom and then optimize this compressing factor to get the optimized electron orbital of hydrogen molecular ion and its energy eigenvalue.

Based on the result from the literature (7), we can get

$$\varepsilon_{aa} = \frac{1}{R} - \left(\alpha + \frac{1}{R}\right) exp(-2\alpha R) \quad (1)$$

$$\varepsilon_{ab} = (\alpha^2 R + \alpha) exp(-\alpha R) \quad (2)$$

$$S_{ab} = \left(\frac{\alpha^2 R^2}{3} + \alpha R + 1\right) exp(-\alpha R) \quad (3)$$

$$H_{aa} = \frac{1}{2}\alpha^2 - \alpha + \frac{1}{R} - \varepsilon_{aa} \quad (4)$$

$$H_{ab} = \left(\frac{1}{2}\alpha^2 - \alpha\right) S_{ab} + \frac{1}{R} S_{ab} - \varepsilon_{ab} \quad (5)$$

$$E_+ = \frac{H_{aa} + H_{ab}}{1 + S_{ab}} \quad (6)$$

$$E_- = \frac{H_{aa} - H_{ab}}{1 - S_{ab}} \quad (7)$$

Mathematically, we should check

$$\frac{\partial E_+}{\partial \alpha} = 0 \text{ and } \frac{\partial E_+}{\partial R} = 0 \qquad \text{or equivalently,}$$

$$\frac{\partial E_-}{\partial \alpha} = 0 \text{ and } \frac{\partial E_-}{\partial R} = 0 \quad (8)$$

where, $\frac{\partial E_+}{\partial \alpha} = \frac{H'_{aa} + H'_{ab}}{1 + S_{ab}} - \frac{H_{aa} + H_{ab}}{(1 + S_{ab})^2} S'_{ab}$ (9)

$$\frac{\partial E_+}{\partial R} = \frac{H'_{aa} + H'_{ab}}{1 + S_{ab}} - \frac{H_{aa} + H_{ab}}{(1 + S_{ab})^2} S'_{ab} \quad (10)$$

Then we get two equations for two variables, α and R.

From the equations for E_+, we know that there are many pairs of α and R meet the requirement of $\frac{\partial E_+}{\partial \alpha} = 0$ and $\frac{\partial E_+}{\partial R} = 0$, but only one pair of α and R , meet the requirement of experimental data. The whole process to determine these pairs of α and R is too complicated and time tedious, therefore, we neglect the detail here and only need to know the determined α and R, which are α=1.98a.u. and R=1.90a.u., respectively. Therefore,

$$\varphi_{1s+} = 0.6404(1s_a + 1s_b) \tag{11}$$

$$\varphi_{1s-} = 0.802(1s_a - 1s_b) \tag{12}$$

Where $1s_a = \frac{1}{\sqrt{\pi}} exp(-1.98r_a)$, $1s_b = \frac{1}{\sqrt{\pi}} exp(-1.98r_b)$. Both of them are not exact the electron 1s orbital of hydrogen atom but electron 1s-like orbital of hydrogen atom instead. Fig.2 is E~R and Fig.3 is the density distribution of electron in the hydrogen molecular ion. Based on φ_{1s+}, we get the energy eigenvalue is -0.10345a.u.(-0.1026a.u.) and bond length R=1.90a.u. (2.0097a.u.), in bracket is the experimental data.

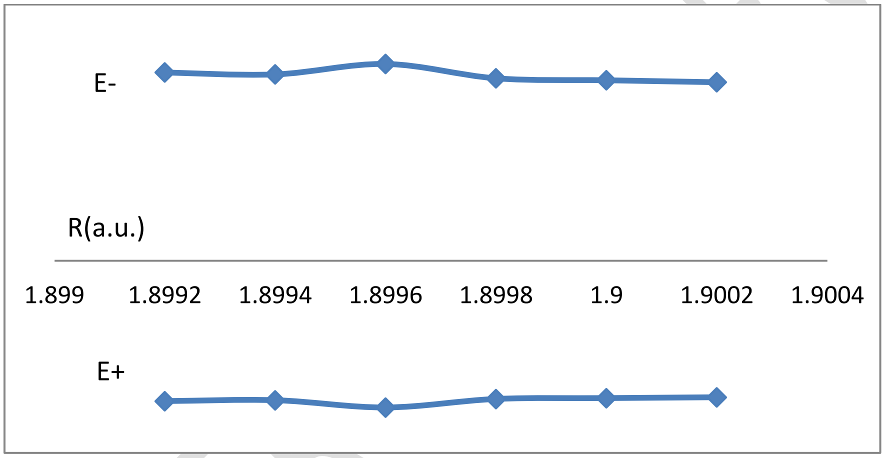

Fig.2 E~R Relation Illustration

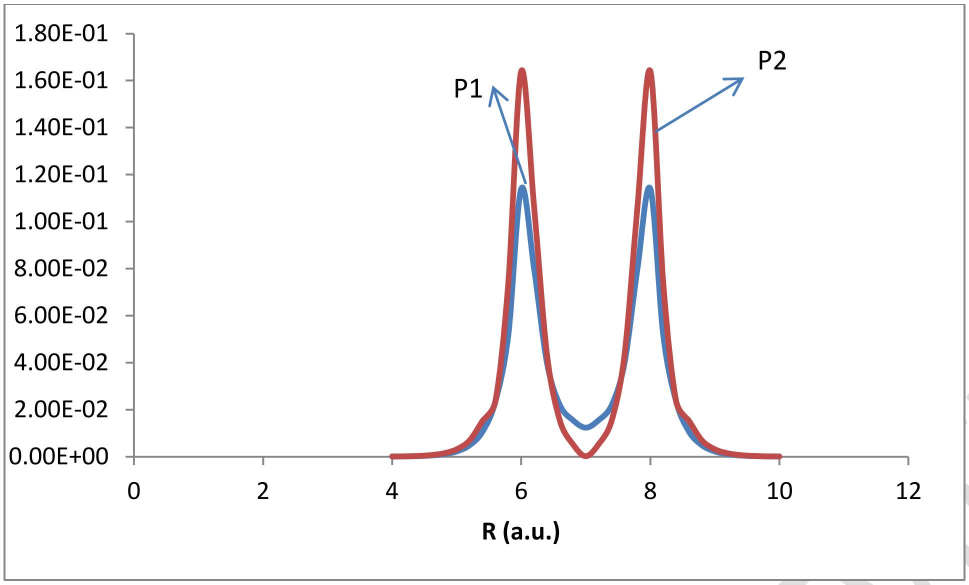

Fig.3 The Electron Density Distribution For $\varphi_{1s+}\ (P_1)$ and $\varphi_{1s-}\ (P_2)$ With R (a.u.)

3. Result and Discussion

From the result above, first we notice that $1s_a$ or $1s_b$ is the electron 1s-like orbital of hydrogen atom but the α (1.98a.u.) means the electron movement in hydrogen molecular ion is restricted due to the existence of second proton, just like the electron 1s orbital of hydrogen atom is compressed due to the existence of the second proton. In our previous work, the physical meaning of α is the compressing factor, which is totally different from the parameters used in literatures (19-24). As we discussed in the previous work, the effect of compressing electron 1s orbital will cause the energy of system increasing. Some researchers describe this case as screening effect from the rest electron, therefore, in calculation we should use "effective atomic number" instead of real atomic number. However, this screening mechanism can't convince us in that for hydrogen molecular ion, only one electron exists, so, the screening explanation doesn't exist, therefore invalid here.

Compared to the "effective atomic number" mechanism, the rationality of our strategy is obvious by introducing the compressing factor (α) in our calculation. The most important is that we can keep the physical picture of electron orbital of hydrogen molecular ion unchanged and at the same time get the consistent calculation result with the experimental data. That is, the hydrogen molecular ion has electron orbital which is composed of electron 1s-like orbital of hydrogen but due to the existence of the second proton, the movement of electron is restricted, not like the electron in orbital of free hydrogen atom. The compressing factor α demonstrates this case. It looks like the orbital of electron in hydrogen molecular ion is compressed (see our previous work (25)), therefore, the electron keep moving in hydrogen 1s like orbital but energy eigenvalue increases instead. Consequently, the bonding energy of electron in the hydrogen molecular ion is much smaller than that in free hydrogen atom (Fig.2 and Fig.3).This situation is correctly described by introducing the compressing factor (α) in our calculation.

Traditionally, the solution between the physical picture of orbital and inconsistency with the experimental data is to expand the electron orbital of hydrogen molecular ion to the complete basis set in calculation instead of just using electron 1s orbital of hydrogen atom. By including complete basis set in calculation, we do get the consistent calculation result with the experimental data but the computer time increases sharply. The tedious computer time restricts the application of quantum mechanics in complexity system. Some researchers developed different semi–empirical method by introducing more variational parameters in quantum calculation, these kinds of semi-empirical methods make the uncertainty in the quantum mechanics calculation increases, therefore, the reliability of the property prediction on the atom/molecule, based on the semi-empirical quantum mechanics calculation, decreases.

This situation is just like at the beginning, we use the function is too bad to describe the movement of electron/molecule, then, we introduce more function into the orbital to modify the orbital of the electron movement and finally, we can get the orbital which is the closest to the correct orbital or real orbital to describe the movement of electron in atom/molecule.

Our Strategy is that at the beginning, we try to use the wave function which is the closest to the true orbital of system, to describe the true movement of electron in atom/molecule, then find out the correct wave function by the optimizing the variational parameter and use this correct optimized wave function in calculation. The benefit to do so is 1.saving the computer time; 2.keeping the physical picture of orbital of atom/molecule very clear; 3.keeping the consistency between the calculation result and experimental data. Our calculation result of hydrogen molecular ion verifies our strategy is succeeded.

4. Potential Application

Following our strategy discussed above, we can extend our method to the multi electrons system, such as the atom after the hydrogen and molecule system. Here we would like listing some examples to show how to use our method in calculation but we wouldn't go into the detail here.

(1). Hydrogen Molecule/He Atom

If we apply our method onto the hydrogen molecule instead of the hydrogen molecular ion, there are two electrons and protons. But the molecular orbital of hydrogen molecule should come from the electron 1s orbital of hydrogen atom in the quantum calculation. However, from the literatures, the calculation results deviate too much from the experimental data. As we discussed above, the error comes from the fact that we use electron 1s orbital of hydrogen atom which is exact the same as we get from the solution of Schrodinger's equation. As we point out above, the electron 1s orbital of hydrogen atom deviates too much from the real state of electron in hydrogen molecule. Correctly, we should use the variational parameter to modify the electron 1s orbital of free hydrogen atom and optimize this variational parameter to make the energy of system minimized. Then using this electron 1s-like orbital of hydrogen atom in calculation we can get consistent result with the experimental data. The advantage of our method for hydrogen molecule is in that we only need one parameter to modify the electron 1s orbital of hydrogen atom in our calculation, then we can call this modified electron 1s orbital of hydrogen atom as the electron 1s-like orbital of hydrogen atom instead of just the electron 1s orbital of hydrogen atom. It is obvious that for Helium atom, we will have the same advantage as for hydrogen molecule.

(2). Li Atom

For Li atom, it has two 1s electrons and one 2s electron. For two 1s electrons, we can use one variational parameter (α_1) to modify the electron 1s orbital of hydrogen atom and one variational parameter (α_2) to modify the electron 2s orbital of hydrogen atom. That means all together we only need two parameters (α_1 and α_2) in our calculation for Li atom. Consequently, the calculation will become very efficient and more important is that we can keep the physical picture of electron orbital very clear.

(3) Heterogeneous Atomic Molecule

Taking LiH as an example, we should use one variational parameter (α_1) to modify the electron 1s orbital of hydrogen atom, one variational parameter (α_2) to modify the electron 1s orbital of hydrogen atom as the electron 1s orbital for Li and one variational parameter (α_3) to modify the electron 2s orbital of hydrogen atom as the electron 2s orbital for Li. That means altogether we only need three parameters in our calculation for LiH molecule. Compared to the Li atom, the number of parameters increases which will cost more computer time in calculation but still much less than the traditional method, such as the complete basis set or other semi-empirical methods. For our method, we keep the physical picture of orbital very clear and pretty easy to interpret the calculation result.

(4). Other Complicated System, Such As Solid Material System

Our method makes the quantum calculation becomes easy and efficient. Therefore, our method may extend to the more complicated system, such as solid materials. At present, most of researchers use the band theory to explain the experimental data from the solid materials. Due to the simplicity, our method may find wide application in these fields in the future.

5. Conclusion

In this paper we demonstrate how the concept of the compressing factor of electron orbital works in quantum calculation. Compared to the electron movement in free hydrogen atom, the electron movement in multi-electron system is restricted, just like the electron orbital being compressed. Our strategy correctly reflects this situation, therefore, in the quantum calculation of hydrogen molecular ion, we can get very good energy eigenvalue, bond length and the electron density distribution.

Summarily, our method has three advantages: 1. Keeping the physical picture of electron orbital very clear, therefore, easy to interpret the quantum calculation result; 2. Don't need too much parameters in quantum calculation but the precision of quantum calculation is greatly improved and tedious computer time in calculation can be avoided; 3. The reliability of the quantum calculation can be guaranteed because the least parameters are used in quantum calculation. We can predict that the concept of the electron orbital compressing factor will find wide application in the scientific fields.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

6. Reference

(1) M. Planck; "Ѐber eine Verbesserung der Wienschen Spektralgleichung". Verhandlungen der Deutschen Physikalischen Gesellschaft, 2:202-204 (1900a).

"Zur Theorie des Gesetzes der Energieverteilung im Normalspectrum". Verhandlungen der Deutschen Physikalischen Gesellschaft, 2:237 (1900b).

"Entropie und Temperatur Strahlender Wärme". Annalen der Physik, 306(4):719-737 (1900c).

"Ѐber irreversible Strahlungsvorgänge". Annalen der Physik, 306(1):69-122 (1900d).

(2) A. Einstein; "Ѐber einen die Erzeugung und Verwandlung des Lichtes Betreflenden Heuristischen Gesichtspunkt". Annalen der Physik, 322(6):132-148 (1905).

(3) N. Bohr; "I. On the Constitution of Atoms and Molecules". Philosophical Magazine and Journal of Science, 26(151):1-25 (1913).

(4) W. Heisenberg; "Ѐber den Anschaulichen Inhalt der Quanten Theoretischen Kinematik und Mechanik". Zeitschrift fὒr Physik (in German), 43(34):172-198 (1927).

(5) E. Schrödinger; "Quantisierung als Eigenwertproblem". Annalen der Physik, 384(4):273-376 (1926).

(6) John P. Lowe; "Quantum Chemistry". Second Edition, Academic Press, Inc. (1993). 1250 Sixth Ave, San Diego, CA92101-4311.

(7) T. E. Peacock; "Foundations of Quantum Chemistry". Univ. Queensland, Australia, John Wiley & Sons Inc., New York, (1969).

(8) Ajit J. Thakkar; “Quantum Chemistry”. Morgan & Claypool Publishers (2017). Print ISBN:978-1-6817-4636-4.

(9) E. A. Hylleraas; Z. Phys., 54, 347 (1929).

(10) Charles M. Werneth, et al.; “Variational Method Using Basis Functions”. J. Phys. A: Math. Theor., 43 (2010).

(11) James S. Sims; Stanley A. Hagstrom; “High Precision Variational Calculations for the Born-Oppenheimer Energies of Ground State of the Hydrogen Molecule”. J. Chem. Phys., 124 (2006).

(12) Wang Qing; Chen Tianlun; “A New Principle to Determine the Variational Parameter for the Variational-Cumulant Expansion”. Commun. Theor. Phys., 31 (1999).

(13) J. Pople; “Theoretical Models for Chemistry”. Proceedings of the Summer Research Conference on Theoretical Chemistry Structure and Reactivity. New York, John Wiley and Sons (1973).

(14) W. Kohn; “Nobel Lecture: Electronic Structure of Matter-Wave Functions and Density Functionals”. Review of Modern Physics, Vol.71, No.5, pp.1253-1266 (1999).

(15) Richard L. Lihoff; “ Introductory Quantum Mechanics”, Fourth Edition, Cornell Univ., Addison Wesley; May 04 (2003). 1301 Sansome St., San Francisco, CA 94111.

(16) E. N. Economou; “Green’s Functions in Quantum Physics”. Third Edition; Springer (2006).

(17) Holgate, Sharon Ann; “Understanding Solid State Physics”. CRC Press. pp.177-178, (2009). ISBN:978-1-4200-1232-3.

Van Zeghbroeck, B.; “Section2.3: Energy Band”. Principles of Semiconductor Devices. Electrical, Computer, Energy Engineering Dept., Univ. Of Colorado at Boulder (2011).

(18) Wei-Xing Xu; “The Behavior of the Hydrogen Atom under Different Potential Well``. Optics and Photonics Journal, 9 (2019).

(19) S. C. Wang; “The Problem of the Normal Hydrogen Molecule in the New Quantum Mechanics”. Phys. Rev., 31 (1928). Here we should give a note: In this reference, the author used the same equation as we used but the explanation about the parameter of the physical meaning is totally different. As the explanation from the author, the parameter in his paper is following the same idea as E. A. Hylleraas (see reference 7 in this work for detail). This can be illustrated for φ_{2s}. In our case, φ_{2s} will be:

$$\varphi_{2s} = \frac{1}{4(2\pi)^{1/2}}(2-\alpha r)e^{-\alpha r/2}$$

But in Wang’ case, φ_{2s} will be:

$$\varphi_{2s} = \frac{1}{4(2\pi)^{1/2}}(2-r)e^{-\alpha r/2}$$

Therefore, the equations for φ_{1s} in both work looks the same by accident and the physical meaning are totally different.

(20) W. B. Somerville; “An Extension of the Hylleraas Expansion for the Helium Ground State”. JournalDe Physique, Tome 31, Nov.-Dec., pp. C4-107 (1970).

(21) I. Hornyak and A. T. Kruppa; “Hylleraas- and Kinoshita-type Wave Functions with Correct Cusp Conditions”. Phys. Rev. A96, 052506 (2017).

(22) Frederick W. King, et al.; “Hylleraas-type Calculations of the Relativistic Corrections for the Ground State of the Lithium Atom”. Phys. Rev. A, Vol.58 (5), (1998).

(23) Takeshi Mukoyama; “Electronic Wave Functions for Helium-Like Atoms”. Bull. Inst. Chem. Res., Kyoto Univ., Vol.58(1), (1980).

(24) Carl W. David; “Compact Singlet S Helium Wave Functions (Corrected)”. Chemistry Education Materials, 30, (2006).

(25) Wei-Xing Xu; ``The Fundamental Mechanism for the Collision/Pressure Induced Optics Effect”. Optics and Photonics Journal, 8 (2018).