

Generalizations of Bohr model for diatomic and polyatomic molecules

I. MOTIVATION

Using Bohr-like model even for the simplest diatomic molecule H_2^+ is a formidable task [1]. Molecular problems are complicated because an effective potential for the electronic structure may acquire multiple minima or may have no minimum at all. In sections 1 - 4 we present an effective method to deal with these complications, and in the last section we list other possible improvements and modifications of the Bohr model.

A. Binding energies from complex dimensional scaling

Method of dimensional scaling together with analytic extension was applied earlier by a group of D. Herschbach for resonance states of atoms, for quasibound rovibrational states of hydrogen molecule, for Van der Waals interactions and for Stark effect resonances [2], [3]. Comparison with numerical integrations and other accurate methods show that the much simpler dimensional scaling method yields good results for wide range of atomic and molecular forces. Independently, J. Rost[4] used complex dimensional scaling for weakly bound three-body systems including a molecule of H_2^+ . He found that even if the effective potential surface does not exhibit a minimum, the extension of the method of dimensional scaling to complex numbers can theoretically handle this situation and gives good practical estimates for binding energies.

In present study, we extend the method of complex dimensional scaling to systems with multiple degrees of freedom like multiatomic molecules. We apply complex extension for an effective potential within nearest atom quantization approximation that gives accurate results for large atomic separations, but fails to give stable minimum due to collapse at short distances.

II. INTRODUCTION TO BOHR MODEL

Bohr model is one of possible semiclassical descriptions of a quantum system. It was used for the first time for a hydrogen atom, before the advent of quantum mechanics. The original model is no longer accurate for helium and lithium atoms. There was a renewed interest in Bohr model in recent years in connection with the method of dimensional expansion, where the Bohr model reappears from full quantum theory in the limit of large dimensionality. It was later used in combination with the method of dimensional scaling for many electron atoms. However, direct application of the model to a hydrogen molecule fails to predict a stable minimum.

In recent years, a completely new generalization of the method of dimensional scaling was successfully used for a hydrogen molecule and for simplest molecules[5]. For molecules with heavy atoms the method requires further tuning and modification in order to reproduce the energy accurately. The purpose of this study is finding generalizations of Bohr model that could introduce a simple insight into otherwise purely numerical quantum chemistry methods.

III. METHOD OF NEAREST NUCLEUS QUANTIZATION AND ITS ANALYTICAL EXTENSION

It was suggested[5] to describe an electronic ground state by a static configuration of electrons, with the kinetic energy expressed through electronic quantum numbers n_i and the distances from i -th electron to the nearest nucleus, r_i , as

$$T = \sum_{i=1}^N \frac{n_i^2}{2r_i^2}, \quad (1)$$

in atomic units.

For a single hydrogen atom, the method of nearest nucleus quantization is equivalent to classical Bohr model, with

$$E = \min_r \left(-\frac{1}{r} + \frac{1}{2r^2} \right) = -\frac{1}{2}. \quad (2)$$

For H_2 molecule, the method consists of minimization of the function

$$E = \min_{r_1, r_2} (V + V_c), \quad (3)$$

where V is the potential,

$$V = -\frac{1}{r_{a1}} - \frac{1}{r_{b1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}} + \frac{1}{R}, \quad (4)$$

and V_c is the kinetic energy,

$$V_c = \frac{1}{2r_{a1}^2} + \frac{1}{2r_{b2}^2}, \quad (5)$$

see Fig. 1 for notations. Local minimum in equation (3) exists for sufficiently large separation distances, $R > 2.77$. In the present study, we were able to analytically extend equation (3) into the region of $R < 2.77$, where the minimum transforms into an inflection point on the potential surface. This

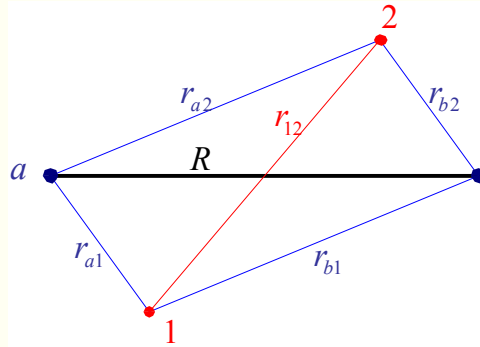


FIG. 1. Distances in H₂ molecule

model predicts the equilibrium separation distance $R_0 \approx 1.4$ with accuracy of less than 1%. The method somehow over-estimates binding energy, but it is more accurate than axis-quantization method which avoids the collapse, but considerably under-estimates the energy.

For CH molecule, we consider 4 valence electrons of carbon and an electron of hydrogen atom, with the kinetic energy

$$V_c = \frac{2}{r_{a1}^2} + \frac{2}{r_{a2}^2} + \frac{2}{r_{a3}^2} + \frac{2}{r_{a4}^2} + \frac{1}{2r_{b5}^2}. \quad (6)$$

The obtained energy is shown on Fig. 2. It agrees well with exact quantum calculations.

For CH₄ molecule, we consider regular tetrahedron configuration of 4 valence electrons of carbon and 4 electrons of hydrogen atoms. The obtained energy agrees qualitatively with exact calculations, but it is somehow over-estimated at $R < 2.5$ and under-estimated at $R > 2.5$.

IV. CONCLUSION

The method of complex extension removes the main obstacle of using otherwise very accurate nearest-atom-quantization method for many-atom molecules. Without complex extension, the system collapses for physically

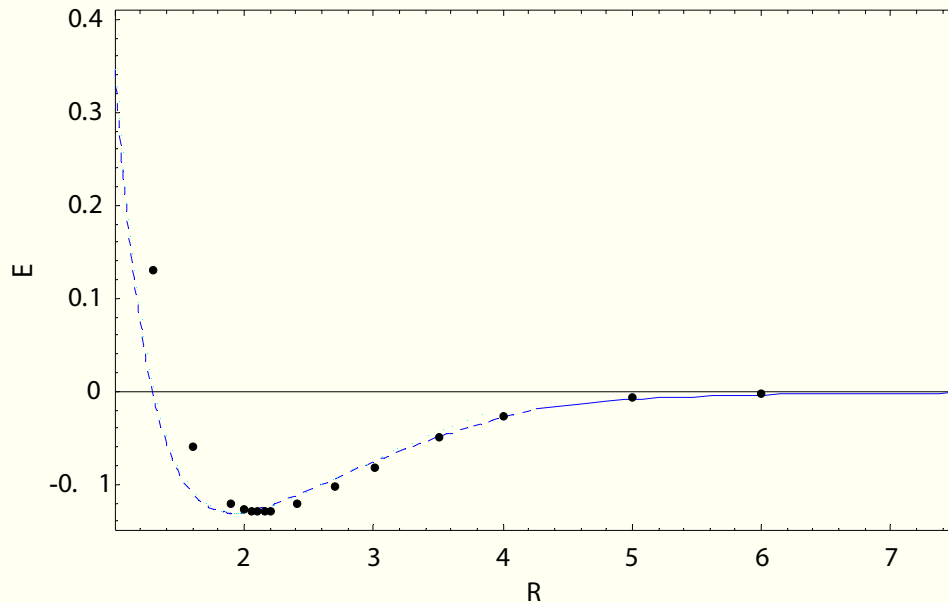


FIG. 2. Energy in nearest atom quantization model, solid line, and its analytic extension, dashed line, vs. exact energy, dots, for CH molecule.

important distances due to presence of Coulomb attraction terms. It was shown that complex extension offers a concept for the application of dimensional scaling to systems which had been excluded so far because their effective potential exhibits an inflection point rather than a minimum. The method is formulated for arbitrary number of degrees of freedom; it could be used for heavy molecules. This simple version of analytic extension leaves many possibilities for further improvement.

V. SUMMARY OF OTHER WAYS OF IMPROVEMENT OF BOHR MODEL

The study shows that there is no universal generalization that is valid for all kinds of chemical bonds like covalent, ionic or semipolar. Some variations of the Bohr model give surprisingly accurate results for one class of molecules, but less accurate for other molecules.

We studied many other generalizations of Bohr model, among them

- Hybrid variational Bohr approach
- Alternative constraints
- Combinations of Heitler - London model with Bohr model
- Use of Gaussian orbitals in derivation of effective potential
- Orthogonal configurations (Hartree - Fock like)
- H_2^+ -inspired constraints
- Classical configurations of higher dimensionality (more than 3)
- Combination of one electron two center Coulomb solutions with Bohr-like methods

Printed notes on these methods could be presented upon request. I am going to test the methods for a large set of diatomic molecules in order to give recommendations which of them are optimal for a given class of molecules.

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- [1] S. Kais, J. D. Morgan III, and D. R. Herschbach, *J. Chem. Phys.* **95**, 9028 (1991).
 - [2] S. Kais and D. R. Herschbach, *J. Chem. Phys.* **98**, 3990 (1993).
 - [3] T. C. Germann and Sabre Kais, *J. Chem. Phys.* **99**, 7739 (1993).
 - [4] J. M. Rost, *J. Phys. Chem.* **97**, 2461 (1993).
 - [5] A. A. Svidzinsky, S. A. Chin, M. O. Scully, *Phys. Lett. A* **355**, 373 (2006).