DEVELOPMENT AND APPLICATIONS OF A QUANTUM MONTE CARLO METHOD TO SOLVE THE TIME INDEPENDENT SCHRÖDINGER EQUATION FOR SIMPLE SYSTEMS - PART II

Guilherme de Souza Tavares de Moraes and Rogério Custodio
Instituto de Química, Unicamp, Barão Geraldo, 13083-970 Campinas, São Paulo, Brazil

Abstract

An alternative numerical method to solve the Schrödinger equation independent of time was applied to study the ground state of different atoms exploring the q-exponential spacing of the radial wave functions with excellent performance.

Key words:

Schrödinger equation, Composite numerical method, Electronic Structure

Introduction

A numerical method was developed to solve the Schrödinger equation in the integral form called the Alternative Variational Monte Carlo. This method combines differentiation techniques, numerical integration and Schmidt orthonormalization¹ to calculate fundamental and excited states of quantum systems. This method can be combined with approximate methods to be applied to many-body problems, such as the Hartree-Fock approximation that determines eigenvalues and eigenfunction of stationary states. In this poster we will focus on the application of the method in the eigenvalues of the ground state of atomic systems, proving the efficiency of the method.

Results and Discussion

Applying the method to the hydrogen atom in three-dimensional space represented by cartesian coordinates were obtained relative errors of 0.2% for the ground state and 1.1% for the first excited state regarding the exact results. The character of the Coulomb potential led to the need for an exponential spacing in the coordinate grid for the calculation of the total energies. The solution of the radial equation for hydrogen and atoms with more than one electron was performed with a generalized exponential spacing known as q-exponential² and defined by the equation:

$$e_q^x = [1 + (1 - q)x]^{\frac{1}{(1-q)}} \quad 1$$

By performing a scan for numerical wave functions with different number of points and different values of the q-parameter, it was found that the calculations show a crossing point near the Hartree-Fock limit. Fig.1 shows that the energy values for a large number of points are independent of the q parameter. However, it is possible to define the numerical value of the total energy from its derivative with respect to the q parameter. The energy values for hydrogen, helium and some elements of the second period of the periodic table in the ground state are shown in Table 1. The procedure can be applied for the determination of more complex radial functions of multielectronic atoms. Tests are being conducted to verify the applicability of the same methodology for the study of

excited states of atoms or whether equivalent information can be obtained for simple molecules.

Image 1. q-exponential scan for wave functions with different point numbers for ¹H.

Table 1. Ground state energy values calculated for some atoms and a comparison with the literature values.

Atom	Energy Simulated (u.a.)	Energy Literature (u.a.)	Relative error(%)
Hydrogen	-0.50000292	-0.50000000	0.0006
Helium	-2.86167991	-2.86167999	0.000003
Lithium	-7.43272706	-7.43272693	0.000002
Beryllium	-14.5730230	-14.5730232	0.0000001

Conclusions

The developed method combined with the q-exponential spacing presents excellent performance and highlights an exclusive property of numerical character to reach the Hartree-Fock limit.

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¹ W. H. Press; Numerical recipes in C: the art of scientific computing, Cambridge, Cambridge University Press, 1992.

² C. Tsallis, Quim. Nova **17**, 468 (1994).