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One-Electron Atom/Ions And Two-Electron Atoms/Ions: A QMC Study

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Abstract

This paper aimed at determining the ionization energies of some one-electron (hydrogen-like) atoms/ions and some two-electron (helium-like) atoms/ions. The Quantum Monte Carlo (QMC)-CASINO code or package was utilized in the computation, employing the Variational Monte Carlo (VMC) and Diffusion Monte Carlo (DMC) methods. The calculated values obtained were in close agreement with literature values.

Keywords: Ionization energy, CASINO-code, VMC, DMC.

1. Introduction

Understanding the chemistry of the elements in the periodic table and other fundamental concepts such as lattice energy of inorganic solids can be achieved from a sound knowledge of their ionization energies [1]. With the development of quantum theory, the two-particle problem can be solved exactly and the kinetic energy of the electron in a hydrogen atom can be calculated using the Schrodinger equation;

$$i\hbar\frac{\partial\varphi}{\partial t} = H\varphi \qquad (1.1)$$

Since this Schrodinger equation does not take account of relativistic effects, Dirac [2] produced an equation which included a relativistic correction for the electron energy levels. However, Lamb and Retherford [3-5] in a series of experiments showed that there is a small shift in the energy levels of the hydrogen atom not accounted for by Dirac equation. This energy shift is now commonly called the Lamb shift. Theoretical atomic energy levels were calculated from a nonrelativistic model, and then relativistic and quantum electrodynamic effects were accounted for by treating them as perturbation corrections.

The advent of powerful computers, have aided highly complicated theoreticalcalculations of the energy levels and ionization energies of hydrogen-like ions [6] and helium-like ions [7] to be performed. These sophisticated equations for one-electron atomic ions and two-electron atomic ions, which need complex computer routines to compute, include corrections for variations of mass with velocity, reduced mass, mass polarization and Lamb shift. Also, corrections for interactions between the two-electrons in the case of the two-electron ions.

Updated theoretical ionization energies and Lamb shifts for one-electron atomic ions and two-electron atomic ions have been published and are generally accepted as very accurate [8,9]. These recent results differ very little from the earlier computed values of [5] and [6]. However, Lang and Smith [10] and Sabir et al [11] in their various publications devised a simple empirical equation to reproduce literature values for the ionization energies of one-electron atomic ions and two-electron atomic ions respectively with very good agreement.

The extensive publications by Moore [12-15] contain detailed tables of atomic energy levels in reciprocal wavelengths (cm^{-1}), ionization reciprocal wavelengths also in $cm^{-1}$and values converted from wave numbers to electron volts (eV) for atoms and atomic ions with estimated experimental errors and references to original work. This remains the most extensive survey of ionization energies.
In this paper, the ionization energies of some one-electron atomic ions and some two-electron atomic ions were calculated using the QMC-CASINO code. The VMC and DMC methods were employed in the code to determine the energies for each method and the unit is given in Hartree atomic unit (a.u).

2. Methodology

In calculating for the ionization energies of the studied one-electron and two-electron atomic ions, the QMC-CASINO code [16] was used, applying both VMC and DMC methods. VMC expectation values of operators such as the Hamiltonian are calculated with an approximate many-body trial wave function φ, and the integrals are evaluated using a Monte Carlo technique. The functional form of φ is chosen to contain a number of parameters whose values are obtained by stochastic optimization. Higher accuracy is achieved in the DMC method by evolving wave functions in imaginary time so that it decays towards the ground state, while the fixed-node approximation is used to maintain the fermionic symmetry [17].
Our trial wave function consists of a multi determinant expansion which describes near degeneracy or static correlation, a Jastrow factor which captures dynamic correlation and a back flow transformation which allows further variations in the nodal surface.

3. Results and Discussion

The ionization energies of the one-electron atomic ions and that of the two-electron atomic ions obtained from both VMC and DMC methods are presented in Table 3.1 and Table 3.2 respectively. The results therein are compared with experimental results published in the CRC Handbook of Chemistry and Physics [18]. This handbook presented an extensive authoritative data of ionization energies with reference to Moore and other up to date works [19].
The results of the ionization energies from the VMC and DMC methods of the QMC-CASINO code compare favorably with published experimental results in [18]. This is illustrated in the graphs in Fig. 3.1 and Fig. 3.2 as both graphs collapse into the graph obtained from experimental ionization energy values.

Table 3.1: VMC and DMC Values of the Ionization Energies of Some One-Electron Atom/Ion and their Corresponding Experimental Values.

Atom/Ion	Atomic No.	VMC (a.u)	DMC (a.u)	Exp. (a.u)
H	1	0.4999	0.4998	0.4997
He^{+}	2	1.9923	2.0006	1.9998
Li^{2+}	3	4.4926	4.4997	4.5001
Be^{3+}	4	7.9876	7.9998	8.0010
C^{5+}	6	17.9845	17.9986	18.0069
N^{6+}	7	24.4901	24.5015	24.5135
O^{7+}	8	31.9970	31.9998	32.0237
F^{8+}	9	40.5026	40.5005	40.5388
Ne^{9+}	10	49.9336	50.0000	50.0599

Table 3.2: VMC and DMC Values of the Ionization Energies of the Some Two-Electron Atom/Ions their Corresponding Experimental Values.

Atom/Ion	Atomic No.	VMC (a.u)	DMC (a.u)	Exp. (a.u)
He	2	0.9114	0.9031	0.9036
Li^{+}	3	2.7868	2.7805	2.7797
Be^{2+}	4	5.6633	5.6558	5.6556
C^{4+}	6	14.4205	14.4073	14.4089
N^{5+}	7	20.2800	20.2804	20.2883
O^{6+}	8	27.1568	27.1563	27.1684
F^{7+}	9	35.0268	35.0326	35.0556
Ne^{8+}	10	43.9407	43.9091	43.9459

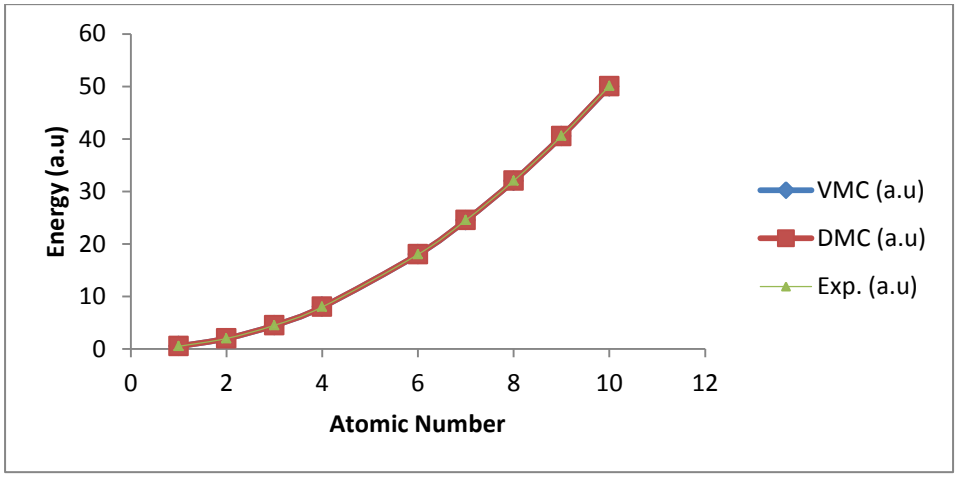

Fig. 3.1: A Combined Graph of VMC, DMC and Experimental Values of the Ionization Energies of the One-Electron Atom/Ions Plotted Against Atomic Number.

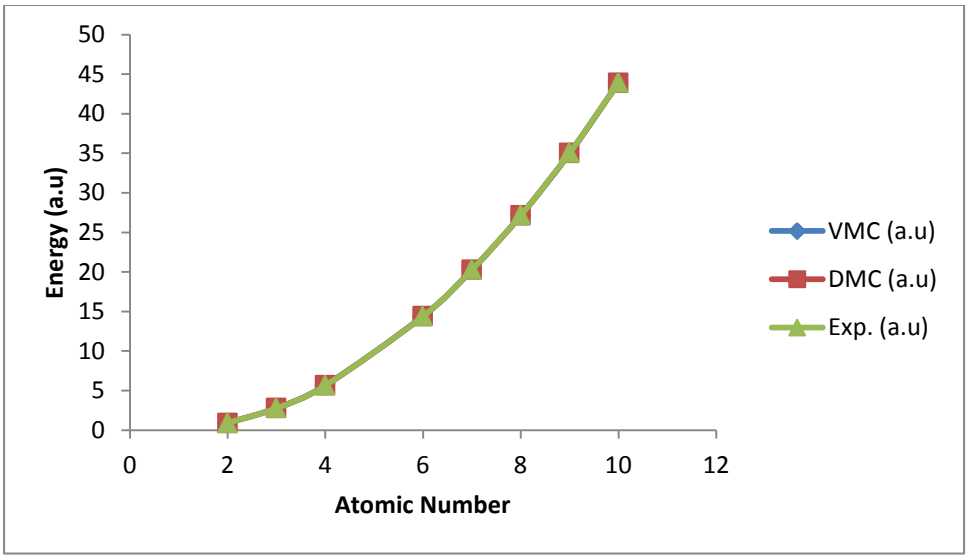

Fig. 3.2: A Combined Graph of VMC, DMC and Experimental Values of the Ionization Energies of the Two-Electron Atom/Ions Plotted Against Atomic Number.

Conclusion

With the QMC-CASINO package, the ionization energies of some one-electron atomic ions and two-atomic atomic ions were calculated employing the VMC and DMC methods and a plot of the ionization energies against the atomic numbers of the elements of the ions shows that as the atomic number increases, the ionization energies increase. This confirms the statement that ionization energies increase moving from left to right across the period in the periodic table.

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