Journal of Electrostatics 71 (2013) 1029–1035

Contents lists available at ScienceDirect

Journal of Electrostatics

journal homepage: www.elsevier.com/locate/elstat

Correspondences between the classical electrostatic Thomson problem and atomic electronic structure

Tim LaFave Jr. *

University of Texas at Dallas, Department of Electrical Engineering, Richardson, TX 75080, USA

ARTICLE INFO

Article history:
Received 6 November 2012
Received in revised form
2 July 2013
Accepted 1 October 2013
Available online 11 October 2013

Keywords:
Electrostatics
Thomson problem
Shell-filling
Atomic structure
Quantum dots
Ion traps

ABSTRACT

Correspondences between the Thomson problem and atomic electron shell-filling patterns are observed as systematic non-uniformities in the distribution of potential energy necessary to change configurations of $N \leq 100$ electrons into discrete geometries of neighboring $N-1$ systems. These non-uniformities yield electron energy pairs, intra-subshell pattern similarities with empirical ionization energy, and a salient pattern that coincides with size-normalized empirical ionization energies. Spatial symmetry limitations on discrete charges constrained to a spherical volume are conjectured as underlying physical mechanisms responsible for shell-filling patterns in atomic electronic structure and the Periodic Law.

1. Introduction

Quantum mechanical treatments of electrons in spherical quantum dots, or "artificial atoms" [1], routinely exhibit correspondences to atomic-like shell-filling patterns by the appearance of abrupt jumps or dips in calculated energy or capacitance distributions as electrons are added to or removed from the system [2–10]. Additionally, shell-filling is observed in ion trap models in which ions are subjected to a spherical harmonic potential [11–14]. An understanding of physical mechanisms responsible for shell-filling is useful to the engineering of tailorable electronic properties of quantum dots and ion traps as well as a better understanding of atomic electronic phenomena.

Electron shell-filling behavior has been observed in two-dimensional classical electrostatic models using a parabolic potential [15]. However, electrostatic treatments of three-dimensional artificial atoms have fallen short of yielding any observable shell-filling patterns [2]. Recently, similarities between classical electrostatic properties of spherical quantum dots and the distribution of empirical ionization energies of neutral atoms were reported for $N \leq 32$ electrons [16,17] when evaluated using the discrete charge dielectric model [18]. The present paper builds on this previous work by identifying numerous correspondences between the electrostatic Thomson problem of distributing equal point charges on a unit sphere and atomic electronic structure.

Despite the diminished stature of J.J. Thomson's classical "plum-pudding" model [19] among more accurate atomic models, the Thomson problem has attracted considerable attention since the mid-twentieth century [20]. The Thomson problem has found use in practical applications including models of spherical viruses [21], fullerenes [22,23], drug encapsulant design [24], and crystalline order on curved surfaces [25]. Numerical solutions for many-N electron systems have emerged in the last few decades using a variety of computational algorithms [26–36]. The Thomson problem is now a benchmark for global optimization algorithms [34,35], yet its general solution remains an important unsolved mathematics problem [37].

A symmetry-dependent electrostatic potential energy distribution is obtained using numerical solutions of the Thomson problem for $N \leq 100$ electrons residing strictly on a unit sphere. This distribution exhibits many disparities ("jumps" and "dips") that appear to be randomly distributed. However, upon closer inspection these disparities appear in a "systematic" [38] pattern shown here to be consistent with the pattern of atomic electron shell-filling as found in the form of the modern Periodic Table. A derivation of the symmetry-dependent potential energy distribution is given. A detailed description of its many correspondences with atomic electronic structure is provided in support of the conjecture

* Tel.: +1 319 512 9909.
E-mail addresses: tim.lafavejr@utdallas.edu, tjlafave@yahoo.com.

0304-3886/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.elstat.2013.10.001

that spatial symmetry limitations on discrete charges constrained to a spherical volume of space, as within a spherical dielectric or the central field of a nucleus, are underlying physical mechanisms responsible for electron shell-filling in quantum dots, ion traps, and atomic electronic structure. Additionally, a pattern of the largest energy disparities is shown to coincide with size-normalized empirical ionization energy data with discussion concerning relevant topological features of N-charge solutions and correspondence to shell-filling in atoms and ion traps. The systematic pattern of classical electrostatic symmetry-dependent energies consistent with atomic electron shell-filling is anticipated given the variety of neighboring geometric electron orbital shapes obtained from quantum mechanics (s, p, d, and f orbitals).

For ease of verification, the reported results are based on data collected in an interactive database of numerical solutions of the Thomson problem hosted by Syracuse University [39] which may be compared with numerous other published sources [26–36].

2. Discrete symmetry changes

In the absence of a positively-charged spherical volume, electrons in the "plum pudding" model repel each other in such a manner that they naturally form solutions of the Thomson problem [40]. These solutions are obtained by minimizing the total Coulomb repulsion energy

$$U(N) = \sum_{i<j}^{N} \frac{1}{|r_i - r_j|} \tag{1}$$

of each N-electron system with r_i and r_j constrained to the surface of a unit sphere. An example of the 5-electron solution is shown in Fig. 1a. The minimum energy is obtained with an electron at each "pole" of the unit sphere, and the remaining three electrons are located at vertices of an equilateral triangle about the "equator". Herein, the geometric configuration of each N-electron system is denoted in square brackets, $[N]$.

To change the electrostatic electron configuration of a given $[N]$ solution of the Thomson problem to the configuration of its neighboring $[N-1]$ solution such that the total number of electrons remains unchanged, a single electron is moved from the unit sphere to its origin. In general, the resulting electron distribution is one electron, q_0, at the origin, and the remaining $N-1$ electrons distributed on the unit sphere having the $[N-1]$ solution of the Thomson problem. This centered configuration may be denoted by $[N-1^+]$, in which "+" indicates the presence of q_0. The total energy

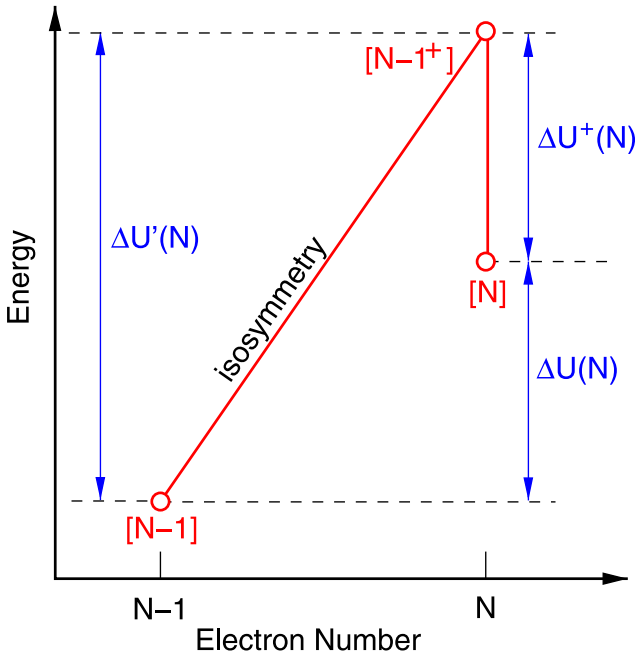

Fig. 2. Discrete spatial symmetry changes in the Thomson problem. Changing the symmetry of a given $[N]$ configuration to the symmetry of its neighboring $[N-1]$ configuration while maintaining all N electrons involves an intermediate $[N-1^+]$ centered configuration. This transition represents the symmetry-dependent component, $\Delta U^+(N)$, of the energy needed to remove a single electron. The remaining transition from $[N-1^+]$ to $[N-1]$ is the isosymmetric component whose energy, $\Delta U'(N)$, is linearly dependent on N.

of any transformed system may be expressed as a function of $U([2])$, the energy of the two-electron solution of the Thomson problem,

$$U\left(\left[N-1^+\right]\right) = U([N-1]) + 2(N-1)U([2]) \tag{2}$$

where the last term accounts for the interaction of q_0 with all $N-1$ electrons residing on the "Thomson sphere".

The $[4^+]$ solution shown schematically in Fig. 1b, consists of four electrons at vertices of a regular tetrahedron about q_0 at the origin. Symmetrically, the $[4^+]$ point group configuration is identical to the $[4]$ point group configuration [12] of the Thomson problem as q_0 interacts identically with all $N-1$ charges on the Thomson sphere. Using Eq. (2), the energy difference as shown in Fig. 2

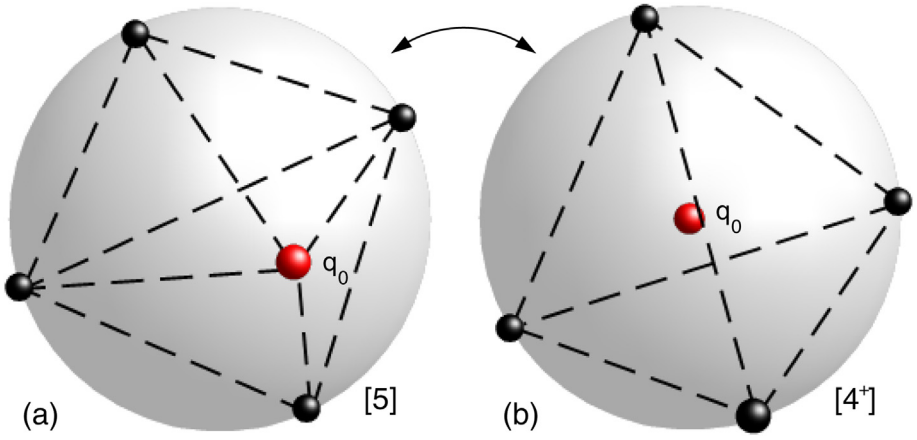

Fig. 1. Discrete spatial symmetry changes. The 5-electron solution of the Thomson problem on (a) a unit sphere transforms into (b) the centered $[4^+]$ configuration having one charge, q_0, at the origin surrounded by the Thomson solution for 4-electrons on the unit sphere.