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Relativistic calculations of screening parameters and atomic radii of neutral atoms

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ABSTRACT

Calculations of the effective nuclear charge for elements with $1 \leq Z \leq 118$ have been performed in a Dirac–Fock approach including all relativistic effects as well as contributions from quantum electrodynamics. Maximum charge density for every subshell of every element in the periodic table was also computed in the same framework as well as atomic radii based on the total charge density. Results were compared with the extensively cited works of Clementi et al., obtained in the 1960s with Roothan's self-consistent-field method.

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Contents

1. Introduction

The usefulness of simple analytical functions for describing the electronic orbitals has been demonstrated long ago [1], and even now, with very high computer processing power, some codes rely on them to obtain physical properties that range from g-factors [2] and crystallographic defect structures [3], electron–hole interactions in layered materials [4] to molecular equilibrium structures and force constants [5]. In fact, the materials science community has been very active in searching new materials with targeted properties using state-of-the-art codes that still rely on atomic radii calculated with Slater-type-orbitals (STO) [6]. Quantum chemistry program packages, for instance, rely heavily on these analytical functions, with libraries of basis sets that span over several types of wavefunctions, from single STO to linear combinations of Gaussian-Type functions [7]. Electron and photon scattering are some of the physical processes in which screening parameters are still very much in use [8], with several calculations relying on atomic radii obtained through the use of screened potentials [9]. Scattering cross sections of both neutral atoms and ions make use of the effective nuclear charge [10–12] and atomic form factors that can be evaluated in the independent particle model using screened hydrogenic wavefunctions [13]. Tong et al. [14], for instance, have investigated two-photon transitions in atomic inner shells by evaluating the relativistic and atomic-screening effects on the decay rates, and found that electron screening has a sizable effect in the two-photon decay rate by expanding the outer-shell wavefunctions, hence decreasing orbital overlap. Multielectron quantum electrodynamic (QED) computations still employ several approaches that rely on the screening of the nuclear potential in order to evaluate the electron's self-energy by providing a scaling factor to the hydrogenic expression [15–17]. Also, atomic and covalent radii are usually calculated on several codes with simple analytical expressions based on Z_{eff} [18,19], which also renders this method as a versatile tool for teaching periodic trends in the classroom [20].

The definition of atomic radii varies greatly within the literature (see [15] and references therein), dating back as far as the work of Slater which noticed a correlation between the maximum charge density of the outermost electron shell and ionic radius of an atom [21]. Other authors, however, have chosen either the simple [22] or weighted [23] mean radius of specific orbitals to infer the atom size, while others defined it as half the distance of the molecular single bond length in heteronuclear diatomic molecules [18,24]. One particular use of the atomic radii is in the measuring of drift times of atoms in gases, which are used in velocity filters, for example in the isolation of superheavy elements in buffer-gas traps [25,26]. Although the radii data of superheavy elements is scarce, the experimental results of the ionic radii of Am^+, Pu^+, Fm^+ and Cf^+ seem to favor a mean spherical radius description over the mean atomic radius based on the total electronic density [15].

The STO functions, which are still very useful, especially in codes that calculate solid state properties, due to the large number of evaluated orbitals, can be written as

$$\psi_{n,l,m} = Nr^{n-1}e^{-\frac{Z_{eff}}{n}r}Y_{l,m}(\theta,\phi), \tag{1}$$

where n, l, m are, respectively, the principal, orbital and magnetic hydrogenic quantum numbers, N is the normalization factor, and $Y_{l,m}(\theta,\phi)$ are the spherical harmonics, whereas the effective nuclear charge Z_{eff} is just the nuclear charge, Z, minus the screening constant $\sigma_{n,l}$

$$Z_{eff} = Z - \sigma_{n,l}. \tag{2}$$

Clementi et al. [27,28] performed a systematic calculation in the 1960s of the screening constants of all orbitals for neutral atoms with $1 \leq Z \leq 86$, using Roothan–Hartree–Fock (RHF) Self-Consistent-Method with STO, and their results are still a reference, as seen not only by the sheer number of citations of both papers (more than 3000), but also their substantial increase in the last decade. The fact that the STO, used in their HF computation, lack radial nodes by definition, will result in drastically different average radius and Z_{eff} for wavefunctions with one or more nodes.

In this work, we have calculated screening constants, effective nuclear charges and atomic radii for every shell of neutral atoms with $1 \leq Z \leq 118$, using the relativistic Multiconfiguration Dirac–Fock General Matrix Element (MCDFGME) program package [29,30] in the monoconfiguration mode. The effective nuclear charge is obtained through a routine that evaluates many-electron radiative corrections, being Z_{eff} deduced from the comparison of the mean value of the radius of the Dirac–Fock (DF) orbital with that of the hydrogenic one [31]. These QED contributions, such as the vacuum polarization and electron self-energy, contribute to the high reliability of this code in obtaining high precision level energies and radiative and radiationless transition rates [32,33]. The fact that our calculations are fully relativistic result in wavefunctions that, in some orbitals, deviates quite strongly from the non-relativistic calculations of Clementi et al. [27,28], which in turn results in different atomic radii and screening constants.

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