Physics Letters A 377 (2013) 2955–2958

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Semiempirical fine-tuning for Hartree–Fock ionization potentials of atomic ions with non-integral atomic number

Nicolás A. Cordero [a,*], Norman H. March [b,c], Julio A. Alonso [d]

[a] Departamento de Física, Universidad de Burgos, C Villadiego s/n, E-09001 Burgos, Spain
[b] Department of Physics, University of Antwerp (RUCA), 171 Groenenborgerlaan, B-2020 Antwerp, Belgium
[c] Oxford University, Oxford, UK
[d] Departamento de Física Teórica, Atómica y Óptica, Universidad de Valladolid, E-47011 Valladolid, Spain

ARTICLE INFO

Article history:
Received 9 July 2013
Accepted 6 September 2013
Available online 16 September 2013
Communicated by V.M. Agranovich

Keywords:
Ionization potentials
Hartree–Fock
Coulomb correlation
Z-expansion

ABSTRACT

Amovilli and March (2006) [8] used diffusion quantum Monte Carlo techniques to calculate the non-relativistic ionization potential $I(Z)$ in He-like atomic ions for the range of (fractional) nuclear charges Z lying between the known critical value $Z_c = 0.911$ at which $I(Z)$ tends to zero and $Z = 2$. They showed that it is possible to fit $I(Z)$ to a simple quadratic expression. Following that idea, we present here a semiempirical fine-tuning of Hartree–Fock ionization potentials for the isoelectronic series of He, Be, Ne, Mg and Ar-like atomic ions that leads to excellent estimations of Z_c for these series. The empirical information involved is experimental ionization and electron affinity data. It is clearly demonstrated that Hartree–Fock theory provides an excellent starting point for determining $I(Z)$ for these series.

1. Introduction

Some recent studies in relation to current practice in Density Functional Theory (DFT) [1] have argued for the importance of correctly fitting one-electron excitations in any quantitative 'correlated' orbital theory [2,3] and for the relevance of Z-expansions (Z being the atomic number) for atomic ionization potentials [4]. In relation to the above, the present authors [5,6] have semiempirically modified Hartree–Fock (HF) theory to allow for the correct asymptotic electron density, having the non-relativistic exponential form (in atomic units) [7]

$$\rho(r) \propto \exp(-2\sqrt{2I}r); \quad r \to \infty, \tag{1}$$

where I is the exact non-relativistic first ionization potential. In [5], Eq. (1), which in the HF method replaces the exact I by the approximation I_{Koopmans}, was enforced empirically using measurements of I (corrected for relativistic effects) for the four neutral spherically symmetric atoms Be, Ne, Mg and Ar.

In a fairly recent study of Amovilli and March [8], the long-range asymptotic behavior of the ground-state electron density in two-electron He-like ions was studied as a function of atomic number Z. The non-relativistic ionization potential $I(Z)$ was then obtained quantitatively from diffusion quantum Monte Carlo (DMC) calculations. In Fig. 1 of that article, a plot was then presented of the DMC ionization potential of such He-like atomic ions in the range of nuclear charges lying between the critical value $Z_c = 0.911028$, at which $I(Z)$ tends to zero, and $Z = 2$. Amovilli and March could usefully represent their DMC result for $I(Z)$ by the quadratic fit, given in atomic units:

$$I(Z) \simeq 0.218(Z - Z_c) + 0.507(Z - Z_c)^2. \tag{2}$$

Our aim is to test the validity of this kind of fit for heavier closed-shell ions using the Hartree–Fock model by fitting the ionization potential of an ion with N electrons and nuclear charge Z with a three parameter form generalizing Eq. (2) for the He-like ions to read

$$I(Z, N) \simeq a(N)\big[Z - Z_c(N)\big] + b(N)\big[Z - Z_c(N)\big]^2, \tag{3}$$

where Z_c is a function of N because this equation is intended to be applied to isoelectronic series of ions having a common value of N and varying nuclear charge Z. That is, Z_c should be different from one isoelectronic series to another.

2. Results and discussion

We have first calculated the HF ionization potentials for two-electron ions with non-integer nuclear charge Z using a slightly modified version of the Froese-Fischer HF code [9] to allow for non-integer atomic numbers [5]. In each case, the ionization potential was calculated as the difference between the total energies of the species with 1 and 2 electrons (in general, $N-1$ and N electrons). The results are shown as open circles in Fig. 1. The fitting of these results to Eq. (3) appears in the figure as a solid line.

* Corresponding author.

0375-9601/$ – see front matter
http://dx.doi.org/10.1016/j.physleta.2013.09.014

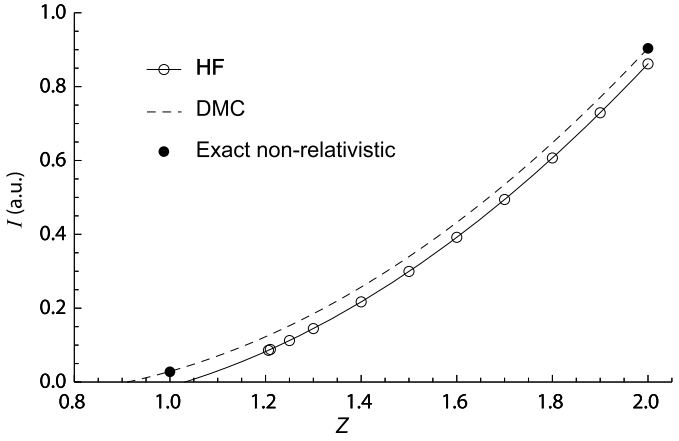

Fig. 1. Hartree–Fock (HF), diffusion Monte Carlo (DMC) and exact non-relativistic ionization potentials (in a.u.) for ions with nuclear charge Z and two electrons.

Table 1
Parameters obtained from the fitting of Eq. 3 to Hartree–Fock ionization potentials.

Ion	N	$a(N)$	$b(N)$	$Z_c(N)$
He-like	2	0.405	0.501	1.032
Be-like	4	0.169	0.140	3.029
Ne-like	10	0.505	0.146	8.902
Mg-like	12	0.162	0.091	11.028
Ar-like	18	0.331	0.076	16.729
Ca-like	20	0.134	0.062	19.027
Kr-like	36	0.310	0.052	34.709
Sr-like	38	0.125	0.053	37.025
Xe-like	54	0.263	0.042	52.656
Ba-like	56	0.116	0.042	55.031
Rn-like	86	0.256	0.032	84.651
Ra-like	88	0.109	0.040	87.026
Uuo-like	118	0.234	0.028	116.628
Ubn-like	120	0.104	0.034	119.031

Table 2
Experimental ionization potential for ions with N electrons and non-relativistic ionization potential corrected for finite nucleus size (in a.u.). Experimental values are taken from [13] unless otherwise noted.

Ion	N	I_{expt}	I_{NR}
H^-	2	0.0277[a]	0.0277
He	2	0.9036	0.9037
Li^-	4	0.0227[b]	0.0227
Be	4	0.3426	0.3426
F^-	10	0.1250[c]	0.1270
Ne	10	0.7925	0.7945
Na^-	12	0.0201[b]	0.0199
Mg	12	0.2810	0.2807
Cl^-	18	0.1328[d]	0.1358
Ar	18	0.5792	0.5822

[a] From Lykke et al. [14].
[b] From Lias et al. [15].
[c] From Blondel et al. [16].
[d] From Berzinsh et al. [17].

The corresponding parameters are given in Table 1. The figure also shows the DMC fit given by Eq. (2). In order to test the accuracy of these two fits we have calculated the exact non-relativistic ionization potentials of He and H^-, i.e. the electron affinity of H. To do this we have started from the experimental values and subtracted the relativistic correction calculated by Chakravorty et al. [10] as well as the finite nuclear size correction using the same recipe we employed in a previous work [5]. Both experimental and non-relativistic ionization potentials are given in Table 2. The DMC fit given by Eq. (2) passes through the two exact values but the HF does not due to its lack of account for Coulomb correlation effects. This lack of Coulomb correlation leads to an overestimation of the critical nuclear charge at which an ion is no longer capable of binding two electrons: $Z_c \approx 1.032$ versus the exact value $Z_c = 0.911\,028$. Nevertheless there is a noticeable agreement between the curvatures of both fits $b \approx 0.501$ for HF and $b \approx 0.507$ for DMC.

Table 3
Critical atomic number Z_c at which a non-relativistic ion is no longer capable of binding N electrons.

Ion	N	HF	HF corrected	MRCI[a]	MRCI[b]
He-like	2	1.032	0.917	0.91	0.92
Be-like	4	3.029	2.859	2.85	2.86
Ne-like	10	8.902	8.737	8.74	8.74
Mg-like	12	11.028	10.875	10.86	
Ar-like	18	16.729	16.601	16.60	16.61

[a] Multireference Configuration Interaction results from Hogreve [11].
[b] Multireference Configuration Interaction results extracted by Sergeev and Kais [12] from Chakravorty et al. values of isoelectronic series [10].

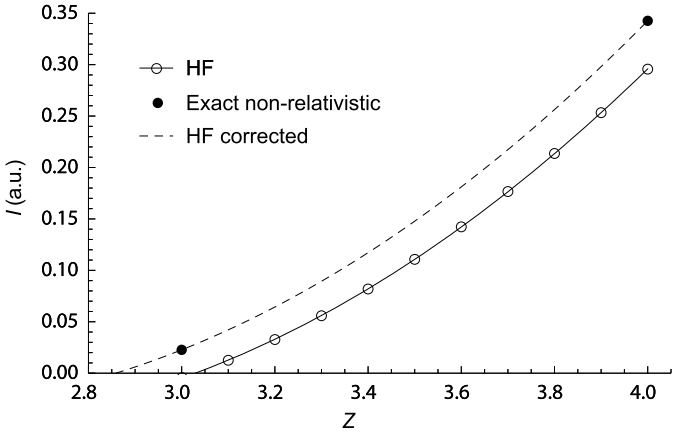

Fig. 2. Hartree–Fock (HF), corrected Hartree–Fock and exact non-relativistic ionization potentials (in a.u.) for ions with nuclear charge Z and four electrons.

This means that the HF approximation is capable of describing the deviation from linearity of the ionization potential with atomic charge. The reason is that the ionization potential is influenced importantly by the behavior of the exchange-correlation potential far from the nucleus. In this region the exchange effects are more important than Coulomb correlation interactions and, in fact, dictate the asymptotic decay of the exchange-correlation potential. We can therefore try to correct the error in the HF Z_c by simply using Eq. (3) with the HF value for the curvature b, imposing that the curve for $I(Z,2)$ passes through the two exact values and solving for Z_c. The result, given in the first row of Table 3, is $Z_c \approx 0.917$ in excellent agreement with the exact value and the results from Multireference Configuration Interaction (MRCI) calculations [11,12].

It has been known for some decades that the value of Z_c for non-relativistic atomic negative ions with N electrons and nuclear charge Z obeys the inequalities [18]:

$$N - 2 < Z_c < N - 1. \tag{4}$$

To test if HF is capable of properly describing the deviation from linearity of the ionization potential of heavier ions and satisfies these inequalities, we have studied the ionization potential at the HF level for other spherical ions with non-integer nuclear charge.

Fig. 2 shows the results for the four-electron ions. Open circles show HF ionization potentials and the solid line is the fit to Eq. (3). Full circles show exact ionization potentials for Be and Li^-, i.e. the electron affinity of Li. HF ionization energies underestimate exact ones and consequently this method overestimates $Z_c(4)$. If we keep the value for $b(4)$ and force the fit to pass through the exact ionization potentials we get the dashed line and the value of