

Ionization potentials of neutral atoms and positive ions in the limit of large atomic number

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The many-electron Schrödinger equation allows one to make predictions for the nonrelativistic ionization potentials of both highly charged positive atomic ions and neutral atoms in the limit of large atomic number Z . Beginning with theoretical configuration interaction data on both Li- and Be-like positive atomic ions by K.T. Chung *et al.* [Phys. Rev. A **45**, 7766 (1992); Phys. Rev. A **47**, 1740 (1993)], their nonrelativistic first ionization potentials I are plotted in the form of I/Z^2 versus $1/Z$. In these two sequences, it is then clear that $\lim_{Z \rightarrow \infty} (I/Z^2)$ remains finite and that this limit is approached essentially linearly. Interpretation is afforded by means of the so-called $1/Z$ expansion of atomic theory. The question of the behavior of the nonrelativistic ionization potentials for large Z is then addressed for neutral atoms. We perform density functional theory (DFT) calculations using the local density approximation with Dirac exchange and neglecting Coulomb correlation for the heavy actinides as well as for the rare gas and alkali atoms from $Z=10$ up to $Z=291$. Our results suggest that there is a nonzero value for $\lim_{Z \rightarrow \infty} I$ for both the noble gases and the alkalis, the second one implying that there is a lower bound of about 2.56 eV to the ionization potential of any nonrelativistic neutral atom. We also explore an alternative approach via the one-body potential $V(r)$ of DFT by calculating the eigenenergies of the highest occupied atomic orbital in neutral atoms. Finally, relativistic corrections needed to compare measured ionization potentials to the predictions from the Schrödinger equation are briefly considered.

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I. BACKGROUND AND OUTLINE

Eight decades since the discovery of the many-electron Schrödinger equation [1], it is now widely accepted that this equation embraces a great deal of atomic and molecular physics. Nevertheless, and not withstanding great progress in computational technology, it remains very difficult to obtain truly accurate theoretical predictions. If we specialize to one-center atomic problems, to obtain solutions transcending Hartree-Fock level for more than a few tens of electrons remains a formidable task.

If we denote the nonrelativistic ground-state energy of an atomic ion by $E(Z, N)$ for atomic number Z and number of electrons N , it has been known for a long time that simplifications exist both for Z large at fixed N (the so-called $1/Z$ expansion of atomic theory: see Sec. II below) and for both Z and N large and such that $0 < \frac{N}{Z} \leq 1$, in which limit the Thomas-Fermi (TF) [2,3] statistical method, the forerunner of modern density functional theory (DFT) [4], comes into its own. In particular, the TF limit of the ground-state energy $E(Z, N)$ has the important scaling property

$$E_{\text{TF}} = Z^{7/3} f(N/Z), \quad (1)$$

where the function $f(N/Z)$ is known numerically from once-for-all self-consistent field calculations [5,6].

However, when one needs more subtle properties of positive atomic ions or neutral atoms in this semiclassical TF

regime, one finds over-simplifications such as zero chemical potential μ for neutral atoms and the related property of the TF ground-state electron density that at large distances from the nucleus $\rho_{\text{TF}}(r) \propto r^{-6}$, whereas it is known that the correct fall-off from the Schrödinger equation has the form

$$\rho(r) = A r^\gamma \exp(-2\sqrt{2}Ir), \quad (2)$$

where the first ionization potential I is in units of e^2/a_0 with r in units of the Bohr radius $a_0 = \frac{\hbar^2}{me^2}$ (i.e., atomic units). The exponent γ is presently not known precisely as a function of Z .

The above considerations have prompted us to reopen the question as to the correct Schrödinger equation prediction for the first ionization potential I in heavy neutral atoms. Naturally, experimental values of I at large Z cannot answer the question as to the nonrelativistic Schrödinger equation prediction of $I(Z)$ as $Z \rightarrow \infty$, since evidently relativistic effects will become significant for large Z .

With the above as background, the outline of the paper is as follows. In Sec. II we take advantage of many-electron configuration interaction calculations of Chung *et al.* [7,8] on Li- and Be-like positive atomic ion sequences of nonrelativistic first ionization potentials as a function of atomic number Z . After proposing a way to plot their data to allow extrapolation to large Z , we interpret the results obtained by means of the $1/Z$ expansion already referred to. Section III is then

TABLE I. Coefficients $\epsilon_i(N)$ in $\frac{1}{Z}$ expansion (3) for $N=2, 3$ and 4 (extracted from [9]).

N	ϵ_0	ϵ_1	ϵ_2	ϵ_3
2	-1	0.625	-0.15766	0.008699
3	-1.125	1.0228	-0.40837	-0.0230
4	-1.25	1.5593	-0.8819	

devoted to analyze how the nonrelativistic first ionization potentials will extrapolate to a large Z limit. In Sec. IV, we focus on the role of the self-interaction correction to the one-body potential $V(r)$ in DFT via some specific large Z examples. Section V briefly considers the estimation of relativistic corrections to allow measured ionization potentials in heavy atoms to be brought into contact with nonrelativistic Schrödinger theory. Finally, Sec. VI constitutes a summary.

II. TRENDS OF FIRST IONIZATION POTENTIAL FOR ISOELECTRONIC SERIES

The so-called $1/Z$ expansion of atomic theory states that the nonrelativistic energy of an ion with atomic number Z and N electrons can be written in the form (see, e.g., [9])

$$E(Z,N) = Z^2 \left[\epsilon_0(N) + \frac{\epsilon_1(N)}{Z} + \frac{\epsilon_2(N)}{Z^2} + \dots \right], \quad (3)$$

where ϵ_i are known coefficients (see Table I) and convergence is guaranteed for large enough Z [10]. If we limit ourselves to the second order in the expansion, we can express the ionization potential of an ion with atomic number Z and N electrons, $I(Z,N) = E(Z,N-1) - E(Z,N)$, in the following way:

$$\begin{aligned} \frac{I(Z,N)}{Z^2} &= [\epsilon_0(N-1) - \epsilon_0(N)] + [\epsilon_1(N-1) - \epsilon_1(N)] \frac{1}{Z} \\ &+ [\epsilon_2(N-1) - \epsilon_2(N)] \frac{1}{Z^2} + O\left[\frac{1}{Z^3}\right], \end{aligned} \quad (4)$$

the values of $\epsilon_i(N)$ with i small taken from [9] being recorded in Table I.

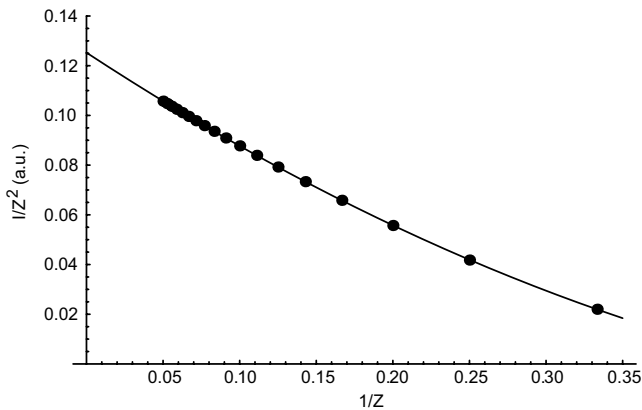


FIG. 1. Ionization potentials of the Li isoelectronic series calculated by Chung *et al.* [7] as a function of the inverse of the atomic number. The curve is a fit to Eq. (5).

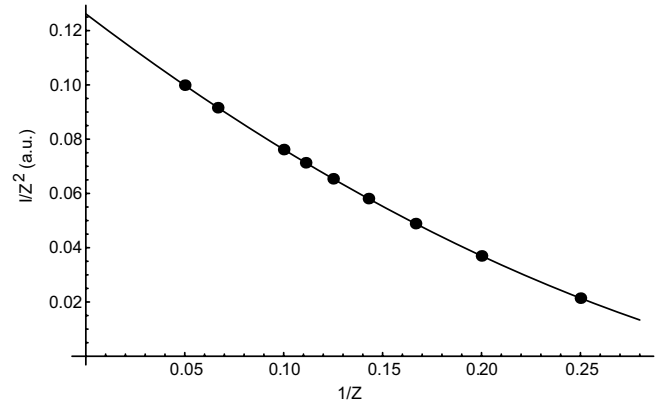


FIG. 2. Ionization potentials of the Be isoelectronic series calculated by Chung *et al.* [8] as a function of the inverse of the atomic number. The curve is a fit to Eq. (5).

In order to test Eq. (4), we have plotted $I(Z,N)/Z^2$ versus $1/Z$ using the nonrelativistic ionization potentials calculated by Chung *et al.* for the Li [7] and Be [8] isoelectronic series using configuration interaction methods. We have also fitted the data in [7,8] to a second order polynomial of $\frac{1}{Z}$

$$\frac{I(Z,N)}{Z^2} = a_0 + a_1 \frac{1}{Z} + a_2 \frac{1}{Z^2}. \quad (5)$$

In Fig. 1 we present the values for the Li (i.e., $N=3$) series. Figure 2 shows the data for the Be (i.e., $N=4$) series. Comparison of equations (4) and (5) shows that a_0 should be equal to $[\epsilon_0(N-1) - \epsilon_0(N)] = \frac{1}{8}$, a_1 equal to $[\epsilon_1(N-1) - \epsilon_1(N)]$ and a_2 equal to $[\epsilon_2(N-1) - \epsilon_2(N)]$. We have confronted these predictions with values extracted from the quantum chemical data in Tables II and III. The predictions of a_2 , as expected, are the most sensitive to the truncation of the $\frac{1}{Z}$ series as in Eq. (5).

We can see that in the limit $Z \rightarrow \infty$, $\frac{I(Z,3)}{Z^2}$ goes to 0.12526 while $\frac{I(Z,4)}{Z^2}$ goes to 0.12616. Both values are in excellent agreement with the $\frac{1}{8}$ prediction of Eq. (4). But this agreement is not limited to the leading term governing the asymptotic behavior, it is also quite remarkable for higher order coefficients as can be seen from Tables II and III.

III. FIRST IONIZATION POTENTIALS OF NEUTRAL ATOMS

Having related the nonrelativistic numerical findings of Chung *et al.* for positive atomic ions to the basic $1/Z$ expansion

TABLE II. Comparison of coefficients in equations (4) and (5) for the Li isoelectronic series ($N=3$).

i	$\epsilon_i(2) - \epsilon_i(3)$	a_i
0	0.125	0.12526
1	-0.3978	-0.40358
2	0.24621	0.28090

TABLE III. Comparison of coefficients in equations (4) and (5) for the Be isoelectronic series ($N=4$).

i	$\epsilon_i(3) - \epsilon_i(4)$	a_i
0	0.125	0.12616
1	-0.5365	-0.55333
2	0.47813	0.53746

sion of atomic theory, we turn to the question of whether we can understand the first ionization potentials of neutral atoms when $Z \rightarrow \infty$.

Since we know from corrected Thomas-Fermi statistical calculations [9] that, in atomic units,

$$E(Z, N)|_{N=Z} = -0.7687Z^{7/3} + \frac{1}{2}Z^2 - 0.26Z^{5/3} + \dots \quad (6)$$

which, as March and Parr [11] demonstrated, fits Hartree-Fock numerical data very well at the 3 term level of Eq. (6), it is necessary to sum to infinity partial subseries of the $1/Z$ expansion in Eq. (3). In the neutral atoms, this leads to the series for E in Eq. (6) in which clearly the basic expansion parameter is now $1/Z^{1/3}$ at large Z .

Seco *et al.* [12] have rigorously derived from the Schrödinger equation an upper bound to the nonrelativistic ionization potential of an ion with atomic number Z and N electrons when $Z \leq N \leq N_c(Z)$; $N_c(Z) < 2Z + 1$

$$I(Z, N) \leq CZ^{4/3(1-\alpha)}. \quad (7)$$

In the body of their paper they give the value $\alpha = \frac{9}{56}$, but in a note added in proof and in [13] they give an optimal value of $\alpha = \frac{2}{7}$. If we put this number in (7), we get

$$I(Z, N) \leq CZ^{20/21}. \quad (8)$$

We have found no systematic Thomas-Fermi data to help us analyze the behavior of the ionization potential of a neutral atom as the atomic number increases. So we have had recourse to modern density functional theory and solved the Kohn-Sham equations within the spin-dependent nonrelativistic local density approximation (LDA) [14] without taking into account Coulomb correlation for the neutral atom and the positive ion (as shown previously by some of the authors [15] correlation provides a small contribution). The reason for using a local approximation is that the LDA becomes exact as the atomic number tends to infinity not only for the exchange energy in neutral atoms [16,17] but also for other systems and components of the energy [18].

Therefore in Fig. 3 we have plotted the ionization potential for the rare gas neutral atoms. The corresponding numerical values appear in the fourth column of Table VIII. The nonrelativistic ionization potential for this series decreases monotonically and seems to tend to a nonzero constant value for large atomic number. In order to test if this also occurs for other series, we have considered the heavy actinides (those with the outermost f shell at least half filled) that have a $\ell=0$ highest occupied atomic orbital in the nonrelativistic case. The results in Fig. 4 show that in this case there is a monotonous behavior too, but I increases with Z

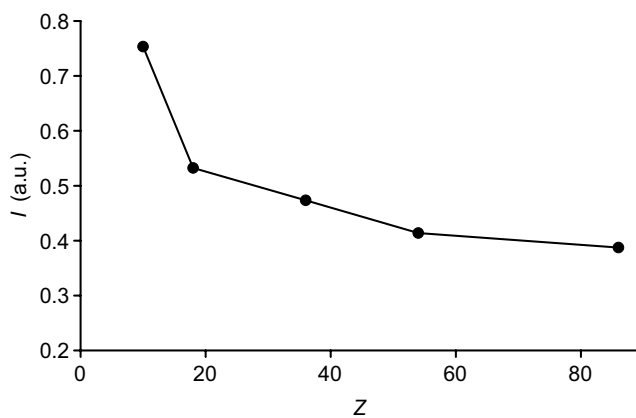


FIG. 3. Ionization potentials of neutral rare gas atoms as a function of the atomic number calculated with the LDA approximation to DFT neglecting relativistic and correlation effects. The line is merely a guide for the eye.

and the existence of an asymptotic finite value does not seem so clear (nevertheless one has to take into account the difference in energy scales in Figs. 3 and 4). The fact that I increases across the actinide series is not surprising. This is the usual behavior when an atomic shell is progressively filled [15]. Then I drops after the shell has been completely filled and the occupation of the next shell begins. In the case of the heavy actinide atoms the $5f$ shell is progressively filled as Z increases, and becomes filled at $Z=102$. Nevertheless there is a difference between the actinides and lighter atoms with partially filled shells. In the actinides the highest occupied atomic orbital (HOAO) is not an orbital of the partially filled $5f$ shell but one of the fully occupied $6s$ shell. A similar feature involving the $4f$ and $5s$ orbitals has been previously found for the lanthanides [19,20].

Equation (8) provides an upper bound for the nonrelativistic ionization potential of an ion, but there is no similar inequality giving a lower bound for the nonrelativistic ionization potential of a neutral atom. Figures 3 and 4 show that there are different trends in the ionization potentials of atoms depending on the selected atom series. In order to study if a lower bound exists, we have calculated the ionization poten-

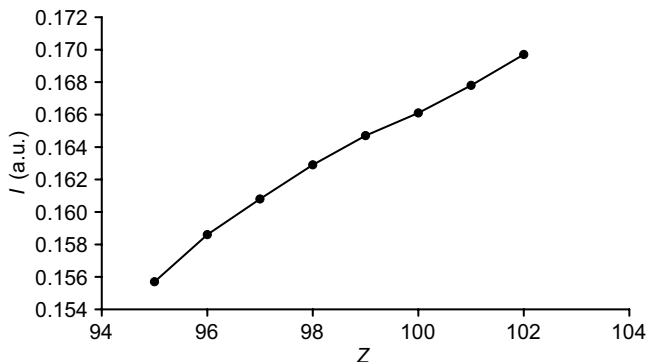


FIG. 4. Ionization potentials of heavy actinides as a function of the atomic number calculated with the LDA approximation to DFT neglecting relativistic and correlation effects. The line is merely a guide for the eye.

TABLE IV. Ionization potential in atomic units for the rare gas and alkali atom series in the $10 \leq Z \leq 291$ range, calculated using the LDA approximation neglecting Coulomb correlation.

Noble gases			Alkalis		
Atom	Z	IP	Atom	Z	IP
Ne	10	0.7535	Na	11	0.1789
Ar	18	0.5322	K	19	0.1485
Kr	36	0.4734	Rb	37	0.1407
Xe	54	0.4138	Cs	55	0.1274
Rn	86	0.3873	Fr	87	0.1232
Uuo	118	0.3624	Uue	119	0.1141
Uho	168	0.3405	Uhe	169	0.1125
Buo	218	0.3267	Bue	219	0.1061
Ben	290	0.3148	Beu	291	0.1033

tials of the noble gas and alkali metal atoms using the non-relativistic LDA approximation with Dirac exchange and neglecting Coulomb correlation. Since we are interested in the large atomic number limit, we have calculated both natural and artificially created atoms as well as theoretical atoms up to $Z=291$. These two series of atoms have the highest and lowest ionization potentials in the periodic table, respectively, and, therefore, represent the limiting cases for all the neutral atoms ionization potentials. The results of these calculations appear in Table IV and Fig. 5. For both series there is a monotonous decrease in the ionization potential when the atomic number increases and there seems to be a nonzero asymptotic ionization potential value.

The expression for the ionization potential $I(Z, N)$ given in Eq. (4) derived from the $1/Z$ expansion is not directly useful for analyzing the asymptotics of the ionization potential for the neutral atoms since in this case $N(=Z)$ is not a constant and the coefficients are then strictly nonconstant. Nevertheless, we can formally rewrite Eq. (4), obtain by truncation an expression similar to Eq. (5),

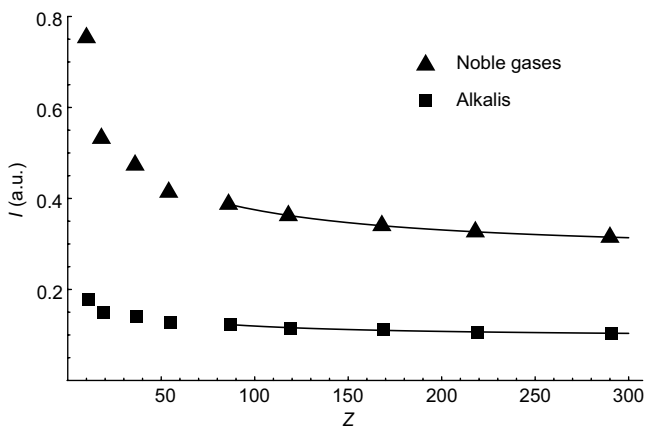


FIG. 5. Ionization potential in atomic units for the rare gas and alkali atom series in the $10 \leq Z \leq 291$ range, calculated using the LDA neglecting Coulomb correlation. The curves are fits to Eq. (10) for the heavy and ultra-heavy atoms in these series.

$$I(Z) \equiv I(Z, Z) = b_0 Z^2 + b_1 Z + b_2 + b_3 \frac{1}{Z} + b_4 \frac{1}{Z^2}, \quad (9)$$

and estimate the coefficients b_i from a fitting to the calculated data. The results of these fittings are reported in Table V. Recalling that the two selected series are the limiting cases for the ionization potential of any neutral atom, Eq. (9) with the b_i coefficients given in Table V for the noble gas atoms provides with an upper bound to the ionization potential of a neutral atom in the $10 \leq Z \leq 291$ range, while the same equation with the coefficients for the alkalis gives a lower bound. The upper bound to the ionization potential given in Eq. (8) is an increasing function of Z while the one we have obtained is a decreasing function of Z , but we have to take into account that the first is valid for any ionization potential $I(Z, N)$ while the second only holds for the first one $I(Z, Z)$.

From Table V it is clear that b_0 and b_1 are orders of magnitude smaller than the rest of the coefficients. We can then go one step further, assume that both of them are zero (i.e., that there is a nonzero asymptotic ionization potential value) and fit the ionization potentials in the two series to second order polynomials of $\frac{1}{Z}$,

$$I(Z) \equiv I(Z, Z) = c_0 + c_1 \frac{1}{Z} + c_2 \frac{1}{Z^2}. \quad (10)$$

In order to avoid the small oscillations of the ionization potentials for the light- and medium-weight atoms, we have

TABLE V. Fitted coefficients (in a.u.) to Eq. (9) for the noble gas and alkali atom series.

	Noble gases	Alkalis
b_0	2.19292×10^{-6}	6.76047×10^{-8}
b_1	-1.16925×10^{-3}	-8.40341×10^{-5}
b_2	0.471975	0.118818
b_3	-0.0650695	0.807804
b_4	29.8167	-1.82758

TABLE VI. Fitted coefficients (in a.u.) to Eq. (10) for the ultra-heavy noble gas and alkali atom series.

	c_0	c_1	c_2
Noble gases	0.275848	12.0738	-214.739
Alkalis	0.0942509	2.88699	-35.8156

only used for the fitting in this case the results for the heavy and ultra-heavy atoms with $Z \geq 86$. The results of the fittings appear in Table VI and are plotted in Fig. 5.

It is interesting to note that going from the the 5 term approximation of Eq. (9) to the 3 term approximation of Eq. (10) has a small effect on the value of the zeroth-order coefficient for the alkali atom series (c_0 is close to b_2). This is precisely the value of $\lim_{Z \rightarrow \infty} I(Z)$ for this series if we assume that Eq. (10) is valid. Taking into account that the ionization potential decreases monotonically as the atomic number increases for the alkali atom series, that this series is the one with the lowest ionization potentials in the periodic table and that there seems to be a nonzero asymptotic value, the calculated results suggest that there is a lower bound to the ionization potential of any nonrelativistic neutral atom in the LDA neglecting Coulomb correlation and that its value is approximately 0.094 a.u. \approx 2.56 eV.

IV. BOUND STATES IN NON-RELATIVISTIC NEUTRAL ATOM THOMAS-FERMI-LIKE POTENTIALS AT LARGE ATOMIC NUMBER

We turn now to what appears to be another potentially tractable approach to the estimation of $I(Z)$ for closed shell atoms from the one-body potential $V(r)$ of DFT. Essentially, one is utilizing here the route to I via the known asymptotic form (2) at large r of the ground-state density $\rho(r)$.

From the nonrelativistic theory of atoms at very large Z , with the corresponding TF energy given by the first term in Eq. (6), the natural starting point is the self-consistent TF potential given by

$$V_{\text{TF}}(r) = -\frac{Ze^2}{r} \phi(x) \quad (11)$$

with simple scaling properties shown in the relation between the distance r and the dimensionless variable x , namely,

$$r = bx; b = \frac{\alpha a_0}{Z^{1/3}};$$

$$\alpha = \frac{1}{4} \left(\frac{9\pi^2}{2} \right)^{1/3}. \quad (12)$$

$\phi(x)$ is a tabulated function (see, e.g., [21]) having the asymptotic form

$$\phi(x) = \frac{144}{x^3} \quad (13)$$

There is an approximate analytical expression for $\phi(x)$ calculated by Latter [22]. With $V_{\text{TF}}(r)$, therefore, proportional to r^{-4} at large r , it seems clear, in contrast to the bare Coulomb form $-\frac{Ze^2}{r}$, that the potential (11) will have a finite number of bound states.

Introduction of the self-interaction correction

It was already clear in the early days of Schrödinger wave mechanics that both exchange effects and the self-interaction correction were important in determining one-electron eigenvalues in neutral atoms. The first issue was addressed by Dirac [23], giving rise to the Thomas-Fermi-Dirac model, while the second was studied by several authors (see, for instance, [24]). A notable study of such one-electron eigenvalues for selected atoms within the Thomas-Fermi and Thomas-Fermi-Dirac potentials corrected for electron self-interaction by Latter [22] makes this quantitatively clear.

To gain orientation, we have interpolated Latter's Thomas-Fermi-Dirac eigenvalues for states with $\ell=0$, calculating the 6s one-electron eigenvalue for Rn, the 5s for Xe, etc., down to the 2s for Ne versus Z . The resulting values are shown in Table VII and plotted in Fig. 6. There is an overall decrease of the eigenvalue of the highest occupied s state with atomic number Z but with a strong oscillatory behavior. Comparison of Thomas-Fermi and Thomas-Fermi-Dirac results shows that taking into account exchange effects increases the binding energies but does not change the dependence on Z .

We have also interpolated from Latter's results for the self-interaction corrected Thomas-Fermi and Thomas-Fermi-Dirac models the highest occupied eigenvalues (i.e., $\ell=1$)

TABLE VII. Binding energies in a.u. of the highest occupied s and p states in the self-interaction corrected Thomas-Fermi (TF) and Thomas-Fermi-Dirac (TFD) potentials for the rare gas atoms (interpolated from [22]).

Atom	Z	s		p	
		TF	TFD	TF	TFD
Ne	10	1.436	2.100	0.616	1.263
Ar	18	0.595	1.051	0.213	0.548
Kr	36	0.793	1.348	0.327	0.782
Xe	54	0.398	0.794	0.161	0.425
Rn	86	0.443	0.890	0.184	0.500

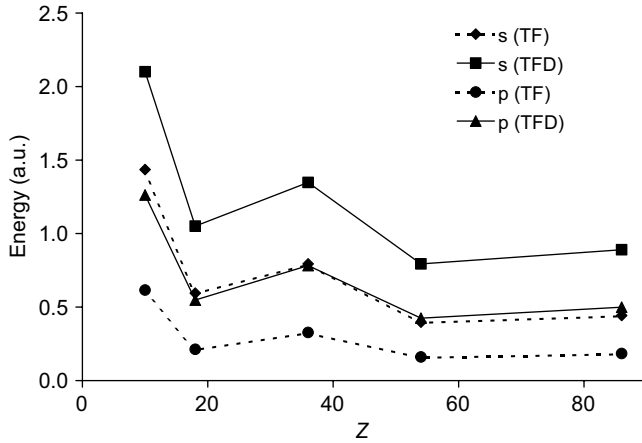


FIG. 6. Binding energies in a.u. of the highest occupied s and p states in the Thomas-Fermi (dashed lines) and Thomas-Fermi-Dirac (solid lines) potentials for the rare gas atoms (interpolated from [22]). The lines are only a guide for the eye.

from Rn ($6p$) through to Ne ($2p$). The corresponding numbers are given in the same table and figure as the $\ell=0$ results. The behavior is similar to that of the s states. These results are to be compared to the first ionization potentials (see Table VIII for experimental values). The highest occupied atomic orbital eigenenergies roughly follow the general trend of the experimental ionization potentials but the latter show a monotonic decrease while the former present the already mentioned oscillatory behavior.

V. COMMENTS ON RELATIVISTIC CORRECTIONS

As the number of electrons in the atom increases, relativistic effects become more important and have to be taken into account to understand the asymptotic behavior of atomic ionization potentials. There are some very sophisticated formalisms to study both Schrödinger and relativistic Dirac-Coulomb equations like, for instance, the one developed by Nakatsuji *et al.* [25,26], but they have only been applied to systems with a small number of electrons.

In order to gain some insight into relativistic effects, we have performed spin-polarized self-consistent calculations within the modern DFT framework of Kohn-Sham equations [14], both at the nonrelativistic as well as at the scalar rela-

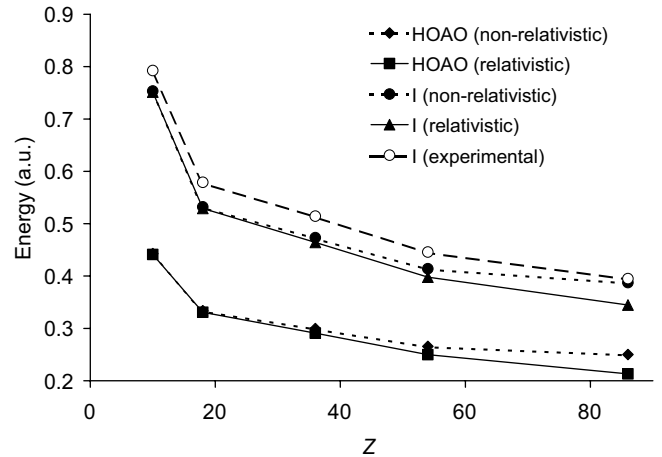


FIG. 7. Energy of the highest occupied atomic orbital (HOAO) and ionization potential (I) in absolute value and in atomic units for the rare gas atom series, calculated using the LDA neglecting Coulomb correlation both within the nonrelativistic (dashed lines) and the scalar relativistic (solid lines) approximations. Experimental ionization potentials from [30] are given for comparison. The lines are only a guide for the eye.

tivistic (i.e., solving relativistic equations for the radial part of the wave function but keeping its nonrelativistic angular part, using a computer code already tested for neutral as well as for ionized atoms in [15,27]) levels. A similar relativistic LDA formalism has been recently used to analyze the properties of some transuranium compounds [28]. We have limited ourselves to Dirac exchange, neglecting Coulomb correlation effects (see [29] for their relative importance when compared to relativistic effects), and made use of the LDA.

We have compared in Table VIII and Fig. 7 nonrelativistic to scalar relativistic values for the energy of the highest occupied atomic orbital as well as the ionization potential, for the rare gas atom series. Table IX and Fig. 8 show the same results for the heavy actinides.

If we compare the nonrelativistic results for the HOAO in Table VIII and the corresponding Thomas-Fermi-Dirac values (i.e., p energies) in Table VII, we can see that the oscillations in TFD HOAO energies disappear and that LDA results are much smaller and closer to the experimental ionization potentials. Relativistic corrections slightly decrease both HOAO energies and ionization potentials, wors-

TABLE VIII. Binding energy of the highest occupied atomic orbital (HOAO) and ionization potential (I) in atomic units for the rare gas atom series calculated using the LDA neglecting Coulomb correlation with and without relativistic corrections. Experimental ionization potentials from [30] are given for comparison.

Atom	Z	Nonrelativistic		Relativistic		Experimental I
		HOAO	I	HOAO	I	
Ne	10	0.443	0.753	0.441	0.752	0.792
Ar	18	0.334	0.532	0.331	0.529	0.579
Kr	36	0.300	0.473	0.291	0.464	0.514
Xe	54	0.266	0.414	0.250	0.398	0.446
Rn	86	0.250	0.387	0.213	0.345	0.395

TABLE IX. Energy of the highest occupied atomic s orbital (HOAO) and ionization potential (I) in absolute value and in atomic units for the heavy actinides calculated using the LDA neglecting Coulomb correlation with and without relativistic corrections. Experimental ionization potentials from [30] are given for comparison.

Atom	Z	Nonrelativistic		Relativistic		Experimental
		HOAO	I	HOAO	I	
Am	95	0.091	0.156	0.107	0.181	0.220
Cm	96	0.093	0.159	0.113	0.200	0.221
Bk	97	0.094	0.161	0.116	0.199	0.229
Cf	98	0.095	0.163	0.120	0.207	0.232
Es	99	0.097	0.165	0.123	0.211	0.236
Fm	100	0.098	0.166	0.127	0.217	0.239
Md	101	0.099	0.168	0.130	0.225	0.242
No	102	0.100	0.170	0.134	0.230	0.244

ening the agreement with experimental ionization potentials.

If we turn our attention to the ionization of the heavy actinides, there are two differences with the rare gases. The first one is that the electron is not removed from the highest occupied atomic orbital of the neutral atom (a $5f$ level), but from the $6s$ level. A similar behavior can be seen from the data of Kotochigova *et al.* for the lanthanides [19,20], involving the $4f$ and $5s$ levels. The reason is that removing one s electron from the neutral atoms leads to a reordering of the energies of the orbitals, stabilizing the $6s$ and especially the $5f$ levels. The second difference is that for the heavy actinides relativistic corrections increase both HOAO energies and ionization potentials, bringing relativistic results closer to the experimental ionization potentials.

VI. SUMMARY

We have studied the problem of ionization potentials in the large atomic number limit focusing first on the nonrela-

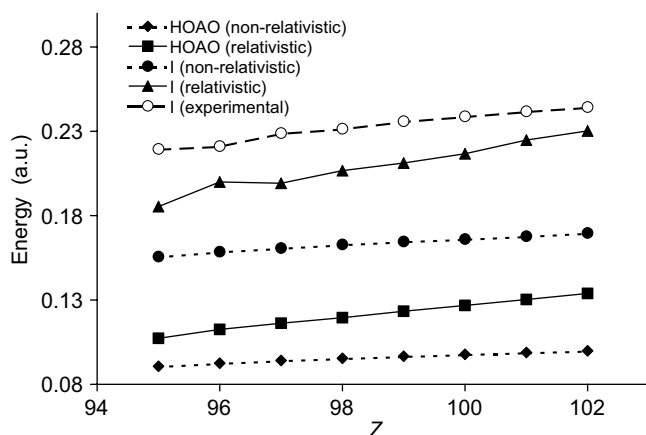


FIG. 8. Energy of the highest occupied atomic s orbital eigenenergy (HOAO) and ionization potential (I) in absolute value and in atomic units for the heavy actinides, calculated using the LDA neglecting Coulomb correlation both within the nonrelativistic (dashed lines) and the scalar relativistic (solid lines) approximations. Experimental ionization potentials from [30] are given for comparison. The lines are only a guide for the eye.

tivistic approximation and taking into account later scalar-relativistic corrections. We have made use of the $\frac{1}{Z}$ expansion of atomic theory to analyze theoretical configuration interaction results from Chung *et al.* [7,8] and shown that the limit $\lim_{Z \rightarrow \infty} (I/Z^2)$ for the Li and Be isoelectronic series is finite and that the asymptotic behavior is essentially linear (with the small deviations from linearity in excellent agreement to the second-order truncation of the $\frac{1}{Z}$ expansion). We have also calculated the LDA nonrelativistic ionization potentials of the noble gas and alkali atom series up to $Z=291$ with Dirac exchange and neglecting Coulomb correlation in order to understand the asymptotic behavior of the neutral atom ionization potential and shown that there is a lower bound of about 0.094 a.u. to the ionization potential of any neutral atom. We have then analyzed the role of self-interaction in noble gas atoms comparing the values of the eigenenergies of the s and p states in the Thomas-Fermi and Thomas-Fermi-Dirac potentials obtained by interpolating Latter's results [22]. Finally, we have performed nonrelativistic and scalar-relativistic calculations within the LDA approximation to DFT with Dirac exchange and neglecting Coulomb correlation for the rare gas atom series and for the heavy actinides in order to study the differences in the highest occupied atomic orbital eigenenergies as well as in the ionization potentials. We have shown that as previously found for the lanthanides, the highest occupied atomic orbital in the actinides is not an orbital of the partially filled f shell but one of the fully occupied s shell but, in spite of that, the behavior of the ionization potential is similar to that of lighter partially filled shell atoms.

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