Atomic charge states in a weakly coupled plasma environment

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The relative stability of various charge states of a number of selected elements has been studied as a function of increasing screening due to a weakly bound plasma represented by the statically screened Coulomb potential of the Yukawa-type. Elements with positive electron affinity in a vacuum are predicted to undergo a sequential electron detachment process from anionic state to the cationic one as the inverse screening length of plasma increases. Conversely, elements with negative electron affinity in a vacuum present only two charge states, neutral and positive. At small screening the neutral is the most stable charge state, and as the screening increases the cation develops as the most stable charge state. Values of the inverse screening length for each of the transitions have been calculated and discussed.

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I. INTRODUCTION

Almost all elements do have stable ground-state anions [1–5]. Remarkable exceptions are beryllium, nitrogen, magnesium, cadmium, and zinc. He and Ne rare gas atoms that cannot form stable negative ions in their ground states, but the possibility of the existence of stable, or at least long lived, anions of Ar, Kr, and Xe is still under debate. Haberland *et al.* have found tentative experimental evidence for Xe^- bound states [6].

Most of the research done until now has considered ions placed in a vacuum, but recently significant advances have been made in the study of atoms [7–12], molecules [13,14], and dipole-bound electrons [15,16] in model plasma environments represented by the statically screened Coulomb potential. Such screened potential has been customarily used to describe the effects of weakly coupled plasmas [17,18] on the electronic structure of test systems embedded in its interior.

The appropriateness of such a potential to describe the effective interaction potential and, therefore, the energies of bound states in a weakly coupled plasma has been revised recently by Brydges and Martin [19], who have demonstrated that the equation of state of a classical hydrogen plasma approaches that of the statically screened theory, independent of Planck's constant, as the plasma becomes weakly bound.

Additionally, Hahn [20] has used the statically screened potential to account for the anomalous enhancement of the radiative free-electron-ion recombination rate observed in several recent experiments with merged ion beams from storage rings [21,22], and Shukla [23] has reconsidered the statically screened potential to describe the screening effects of plasmas on dust particles.

The lowering of the threshold energy for the ionization reactions,

$$X^n \rightarrow X^{n+1} + e \quad \text{with} \quad n = -1,0 \tag{1}$$

of the anion $n=-1$, and of the neutral $n=0$, is one of the gross effects expected due the presence of the plasma environment. However, it has been previously found that screening affects differently not only to the various electronic states of the same charge state of one element [10–12], but also to the electronic ground states of the various charge states of the same element [7,9,14].

Therefore, in a plasma environment, the possibility arises for a different stability order, as compared to a vacuum, of the various charge states of the elements. Thus, it is to provide data concerning the behavior of the charge states with respect to the increasing screening parameter, under physically relevant weakly coupled plasma conditions we present the following study on the stability of the ground states of the anions, neutrals, and cations of a number of selected elements.

II. METHODS

Accurate calculation of the electron affinity (EA), as the energy difference between the neutral element and its anion, is a very challenging task [24]. In particular, elements with fully occupied pseudoshells (Mg, Ca, Sr, etc.) require the most sophisticated quantum mechanical procedures to obtain values for EA comparable with experiment [25].

Hence, we adopt a configuration interaction (CI) approach to calculate the minimum energy of the ground-state electron configuration of the cation, the neutral, and the anion of the selected elements in this investigation.

We have built our basis sets starting from the compilation of Roos and co-workers [26,27] For Li and B, the triple-zeta $(14s,12p,5d,4f)$ basis set contracted to $(5s,4p,3d,2f)$ was used. However, for Be-N, the $(5s,4p,3d,2f)$ basis set of Roos was augmented to $(6s,5p,4d,3f)$. The added functions were optimized to yield a good estimate of the electron affinity. For Na, the $(6s,5p,3d,2f)$ contraction of the $(17s,12p,5d,4f)$ basis set of Roos and co-workers was used as published [27], and for Mg we have further augmented the original basis set up to $(6s,6p,4d,2f)$, with extra p and d functions optimized for the EA. Finally, for K, the double-zeta basis $(6s,5p,3d)$ [26] was used.

The Hamiltonian operator of our systems will be

$$\hat{H} = \hat{T} + \hat{V} \tag{2}$$

with

$$\hat{T} = -\frac{1}{2}\sum_{i=1}^{\mathcal{N}} \hat{\nabla}_i^2 \tag{3}$$

and

$$\hat{V} = -Z\sum_{i}^{\mathcal{N}} \frac{e^{-\lambda r_i}}{r_i} + \sum_{i>j}^{\mathcal{N}} \frac{e^{-\lambda r_{ij}}}{r_{ij}}, \tag{4}$$

where $\mathcal{N}=Z-1$ for the cation, $\mathcal{N}=Z$ for the neutral, and $\mathcal{N}=Z+1$ for the anion; with Z being the atomic number of the element of interest. λ is the screening parameter, (which is proportional to $\sqrt{n_o/T}$), n_o being the plasma density, and T its temperature. The details of the CI can be found elsewhere [28]. As usual the wave function will be expanded as a linear combination of configurational state function built with a finite set of k spin orbitals $\{\chi_a\}_{i=1}^{k}$. The χ_a spin orbitals are now expanded in terms of Gaussian basis set functions, for which a closed-form analytical solution for all the required basis integrals is available [29]. Finally, we have made sure that all the calculated wave functions satisfy the quantum mechanical virial theorem for the screened Coulomb potential of Eq. (4), namely,

$$2\langle \hat{T}\rangle = -\langle \hat{V}\rangle + \lambda\left[Z\left\langle \sum_{i=1}^{\mathcal{N}} e^{-\lambda r_i}\right\rangle - \left\langle \sum_{i>j}^{\mathcal{N}} e^{-\lambda r_{ij}}\right\rangle\right], \tag{5}$$

where $\langle \hat{O}\rangle$ stands for the quantum mechanical average of the operator $\hat{O}$ over the electron coordinates.

All the calculations has been performed with a locally modified version of the GAMESS [30] suite of programs, which includes the screened basic molecular integrals package [29].

The screened potential $\exp(-\lambda r)/r$ used in Eq. (4) has been demonstrated to be appropriate for the modeling of weakly coupled plasmas in local thermal equilibrium [31,32]. Indeed, since the screening parameter is proportional to $\sqrt{n_o/T}$ each value of λ represents a set of plasma parameters and so, a range of plasma conditions. For instance, $\lambda = 0.1$ bohr^{-1}, corresponds to a typical set of values of $n_o \sim 10^{22}$ cm^{-3} and $T \sim 10^6$ K, appropriate for high temperature laboratory plasmas.

Thus, the lowering of the ionization limit, the so-called ionization potential depression (IPD), caused by laser-produced Al plasmas has been recently estimated [33] using a crude statically screened first-order perturbation theory as

$$\Delta\phi = \langle\psi|\left(-\frac{Ze^{-\lambda r}}{r} + \frac{Z}{r}\right)|\psi\rangle \sim \langle\psi|Z\lambda|\psi\rangle = Z\lambda, \tag{6}$$

where ψ is the normalized highest occupied orbital of the ion, which is assumed to become hydrogenlike as the principal quantum number increases. These IPD values are required to solve the Saha equation that gives the population distributions of various ionizations stages of the ions of the plasma. We will show below that the ionization potential depression is not linear in λ and hence, it is expected that distributions of the ionizations stages calculated by our improved IPD values will yield a more accurate description of the x-ray transmission experiments through weakly bound plasmas [34].

Hence, our approach relies on the test-particle method [35], which is extremely useful to calculate properties associated with discrete nature of particles in plasmas. Nevertheless, it should be mentioned at this point that many other important properties, in particular, those ascribed to the electronic spectra of plasmas are dominated by plasma fluctuations [36] and not accounted for in the test-particle method.

TABLE I. Properties of selected elements with positive electron affinity. λ_1 and λ_2 correspond to the points at which $E(X^-)=E(X)$ and $E(X)=E(X^+)$, respectively. λ_c corresponds to $E(X^-)=E(X^+)$. All λ's are given in bohr^{-1} and $\Delta E_c = E(X) - E(X^-) = E(X) - E(X^+)$ in eV. EA is electron affinity in eV.

Element	EA	λ_1	λ_2	λ_c	ΔE_c
Li	0.6157	0.3042	0.4330	0.3990	−0.1068
B	0.2546	0.1269	0.4084	0.3560	−0.6286
C	1.2631	0.2970	0.5394	0.4880	−0.5537
Na	0.5293	0.2304	0.3748	0.3290	−0.1507
K	0.4565	0.1639	0.2797	0.2560	−0.1438

III. RESULTS

The relative energies of the anions and the cations with respect to their corresponding neutral elements, have been calculated as a function of the inverse screening length λ, for the elements of the first row from Li to N, and for Na, Mg, and K.

In Tables I and II, our calculated EA's for $\lambda = 0$ are shown to compare with the best values collected from the literature. Ionization potentials of each of the elements have also been calculated at $\lambda = 0$. It is found, as expected from good wave functions for the EA [25], that our predicted values (not shown) lie within 1 meV or less from the experimental mark.

Inspection of Table I reveals that the CI method, along with the selected extended one-electron basis sets, used in the present investigation does a good job at predicting positive electron affinities. In particular, it is worth noting that our calculated electron affinities, $\mathcal{E}$, for Li and C, agree well with the results of Gdanitz [37] for Li, $\mathcal{E} = 0.6183$ eV, as well as with those of de Oliveira *et al.* [24] for carbon, $\mathcal{E} = 1.2629$ eV. Naturally, these numbers lie close to their cor-

TABLE II. Properties of selected elements with negative electron affinity. λ_2 corresponds to the point at which $E(X)=E(X^+)$. λ_c corresponds to $E(X^-)=E(X^+)$. All λ's are given in bohr^{-1} and $\Delta E_c = E(X) - E(X^-) = E(X) - E(X^+)$ in eV. EA is electron affinity in eV.

Element	EA	λ_2	λ_c	ΔE_c
Be	−0.2905	0.6782	0.5580	−0.4770
N	−0.3470	0.6872	0.5570	−1.6046
Mg	−0.3466	0.5003	0.3500	−1.0012

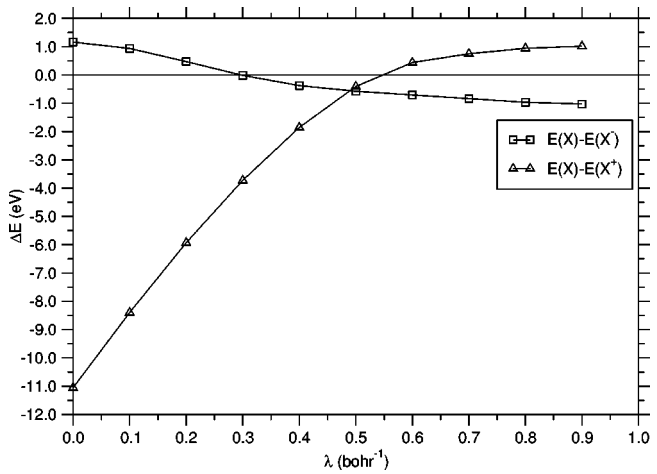

FIG. 1. Energy differences of the carbon's anion and cation with respect to the neutral of species as a function of the screening parameter.

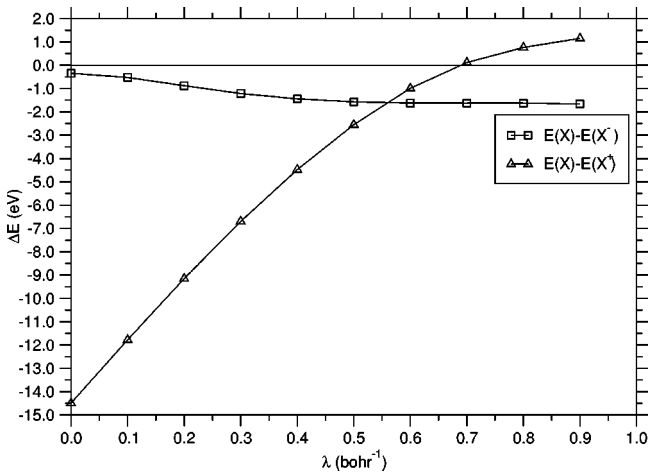

FIG. 2. Energy differences of the nitrogen's anion and cation with respect to the neutral species as a function of the screening parameter.

responding experimental estimates [5], $\mathcal{E}=0.6180$ eV and $\mathcal{E}=1.2621$ eV for Li and C, respectively. For boron, the experimental value [5] is $\mathcal{E}=0.2907$ eV. Our prediction of 0.2546 eV is slightly poorer than the best calculations of Gdanitz [37]: 0.2833 eV; de Oliveira *et al.* [24]: 0.2786 eV: and Gutsev *et al.* [38]: 0.271 eV. Finally, for sodium, our calculations yield an electron affinity of 0.5293 eV, only 18 meV lower with respect to the experimental mark of 0.5479 eV [5]. A recent measurement of the electron affinity of potassium [39] reports a value of 0.501 46 eV. Our value of 0.4565 eV is only 45 meV lower.

There are no precise experimental data available for the elements with negative electron affinity, other than the indication that the electron affinity is indeed negative. Nevertheless, Gutsev *et al.* [38] have recently calculated the EA's for Be, N, and Mg using both density functional theory (DFT) and molecular orbital (MO) based on theoretical procedures. Their data suggest that these EA's are very sensitive to the method. Our values, shown in Table II, lie between their DFT and MO estimates.

The performance of our method, discussed in the previous paragraphs, supports the point that it constitutes a reasonably well-balanced procedure for studying trends of the relative energies between charged elements and their corresponding neutrals in the statically screened Coulomb potential.

Since elements with positive EA in a vacuum, namely $\lambda=0$, behave differently with respect to the inverse of the screening length of the plasma, as compared to elements with negative EA, we will split the subsequent discussion accordingly.

A. Elements with $\mathcal{E}>0$ at $\lambda=0$

The relative stabilities of the anion, the neutral, and the cation of the elements with positive electron affinity in a vacuum are illustrated in Fig. 1, that shows the energy of the anion $E(X^-)$ and the energy of the cation $E(X^+)$, relative to the energy of the neutral species $E(X)$, as functions of the inverse screening length for carbon. Plots for the remaining elements with $\mathcal{E}A>0$, considered in this work, are similar and, will be not shown for the sake of brevity.

Three regions are clearly identified by inspection of Fig. 1. Thus, at small λ, i.e., $\lambda<\lambda_1$, the anion is the most stable charge state. As the screening parameter increases, the relative energy of the anion with respect to the neutral species decreases steadily, as shown in Fig. 1. At the same time, the relative energy of the cation with respect to the neutral species increases as λ increases, so that for large enough values of $\lambda>\lambda_2$, the most stable species is found to be the cation. Naturally, at intermediate values of the screening parameter $\lambda_1<\lambda<\lambda_2$, the neutral species is predicted to be the most stable species.

The values of λ that determine each of the three regions alluded to in the preceding paragraph are given in Table I. Also, in Table I are shown the values of the critical inverse screening length λ_c at which the energy of the cation and the anion are equal. Recall that at these critical points, where the Mulliken's electronegativity vanishes, the neutral species constitutes the most stable charge state of the element.

B. Elements with $\mathcal{E}<0$ at $\lambda=0$

For these elements the negative anion is found to be less stable that the neutral species for all values of the screening parameter scanned in this research. Figure 2 shows the results obtained for nitrogen, which are qualitatively equal to those of beryllium and magnesium, the other two elements with negative EA, considered in this paper. Consequently, the behavior with respect to λ can be characterized by two salient values of λ, namely, λ_2 the value of the screening parameter at which the energies of the neutral and the cation become equal and λ_c the value of the screening parameter at which the energies of the anion and the cation become equal.

The predicted values of λ_2 and λ_c for Be, N, and Mg are shown in Table II.

IV. SUMMARY AND DISCUSSION

The relative stability of various charge states of a number of selected elements has been studied as a function of in-

creasing screening due to a weakly bound plasma represented by the statically screened Coulomb potential.

It is observed that elements with positive electron affinity in a vacuum are most stable in their corresponding anionic form at small screening and as the screening increases they ionize sequentially one electron at a time. For large enough screening parameter values, but still small enough for the Yukawa potential to be physically meaningful, the cation is found to be their most stable charge state.

Conversely, elements with negative electron affinity in a vacuum present only two charge states, neutral and positive. At small screening the neutral is the most stable charge state, and as the screening increases the cation develops as the most stable charge state.

Values of the screening parameter, which determine each of the regions described above have been calculated and found to lie within the physically meaningful range associated with weakly coupled plasmas.

It is also worth mentioning that each element has a characteristic critical screening parameter at which the electron affinity equals the negative of the ionization potential and hence, the Mulliken electronegativity becomes zero. Recall that if the critical energy ΔE_c of some element was positive, it means that this particular element will ionize two electrons simultaneously at λ_c, for its charge will suddenly change from -1 to $+1$ at λ_c. Namely, we would have a simultaneous pressure-induced ionization of two electrons at these critical plasma conditions. According to our calculations this seems not to be the case. Thus, elements with positive EA will change their charge state smoothly from the anionic form to neutral at λ_1, and finally to the cationic form at λ_2. Conversely, elements with negative EA are predicted to remain neutral until $\lambda=\lambda_2$, where one electron will ionize.

Recall that the simultaneous ionization of two electrons from the same subshell has been predicted by Winkler and ourselves to occur from the $1s^2$ ground states of both H^- [8,14] and He [9,10]. Notice, nevertheless, that the critical values at which the simultaneous plasma-induced ionization of two electrons occurs are very large, namely, $\lambda_c \sim 1.5$ bohr^{-1} for H^- and $\lambda_c \sim 2.3$ bohr^{-1} for He. Since, as indicated above, the screening parameter λ is proportional to $\sqrt{n_o/T}$ each value of λ represents a set of plasma conditions. However, small values of λ represent weak screening and large values of λ represent stronger screening.

Simultaneous ionization of the two $1s^2$ electrons of either H^- and He takes place at critical values of the screening parameter large enough as to raise serious doubts about the reliability of the statically screened potential model to describe the ionizations of test particles embedded in such a plasma.

Our calculations, however, indicate that such multielectron simultaneous ionizations cannot occur from higher either *s* or *p* subshells under weak screening conditions, as suggested by the smaller values of the λ_c's, shown in Tables I and II, for which the statically screened potential model is reliable [35], along with the fact the critical ΔE_c's are negative for all the elements investigated. Observe, in particular, that according to our calculations, the two *ns* electrons of Li^- $(n=2)$, Na^- $(n=3)$, and K^- $(n=4)$, will ionize sequentially as opposed to simultaneously. Also, simultaneous ionization of two electrons from the $2p$ subshell is predicted not to occur, at least for elements B to F of the first row.

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