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High pressure effects on the excitation spectra and dipole properties of Li, Be$^+$, and B$^{2+}$ atoms under confinement

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ABSTRACT

Properties of atoms and molecules undergo significant changes when subjected to spatial confinement. We study the excitation spectra of lithium-like atoms in the initial $1s^22s$ electronic configuration when confined by an impenetrable spherical cavity. We implement Slater’s $X$-a method in Hartree–Fock theory to obtain the excitation spectrum. We verify that as the cavity size decreases, the total, $2s$, $2p$, and higher excited energy levels increase. Furthermore, we confirm the existence of crossing points between $ns$–$np$ states for low values of the confinement radius such that the $ns \rightarrow np$ dipole transition becomes zero at that critical pressure. The crossing points of the $s$–$p$ states imply that instead of photon absorption, one observes photon emission for cavities with radius smaller than the critical radius. Hence, the dipole oscillator strength associated with the $2s \rightarrow 2p$ transition becomes negative, and for higher pressures, the $2s \rightarrow 3p$ dipole oscillator strength transition becomes larger than unity. We validate the completeness of the spectrum by calculating the Thomas–Reiche–Kuhn sum rule, as well as the static dipole polarizability and mean excitation energy of lithium-like atoms. We find that the static dipole polarizability decreases and exhibits a sudden change at the critical pressure for the absorption-to-emission transition. The mean excitation energy increases as the pressure rises. However, as a consequence of the critical transition from absorption to emission, the mean excitation energy becomes undetermined for higher pressures, with implications for material damage under extreme conditions. For unconfined systems, our results show good to excellent agreement with data found in the literature.

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I. INTRODUCTION

Confined quantum systems exhibit significant changes to their structure, stability, reactivity, binding interactions, dynamics, and spectra as a consequence of modifications to the spatial boundary conditions in the presence of an extreme environment. Atoms or molecules within cavities, organic/inorganic host–guest complexes, quantum dots, fullerenes, and nanotubes are examples of real quantum confined systems. The main objective when studying confined quantum systems is to construct an accurate theoretical model that takes into account changes in the electronic wavefunction and energy levels due to the boundary conditions imposed by the surrounding environment. In this respect, theoretical calculations can be realized by adopting a suitable choice of boundary conditions. The pioneering work of Michels et al. provided the first model of a hydrogen atom confined in an impenetrable spherical cavity to simulate the effect of pressure. In recent years, the topic of confined atoms has attracted much attention and has become a very active field of research. Reviews with detailed discussion of the progress in this field can be found in Refs. 2–6 and references therein.

To describe the electronic structure and interactions of a multi-electron system, a variety of theoretical methods have been developed, including, among others, Hartree–Fock (HF) theory and density functional theory (DFT), and these have had great success in different problems in atomic physics. Owing to the complexity of the $N$-body problem, some approximations have been implemented, in addition to having the system under confinement by spatial limitation of the electrons, which leads to...
complications in the one- and two-electron integrals. A widely used approach to the treatment of N-body systems is to consider a pseudopotential that describes the inner electronic structure of the atom. The basic idea of pseudopotentials is to take into account the multi-electron core interaction with a single valence electron by using a modified Coulomb potential.\textsuperscript{7,8,11} Such pseudopotential approaches have been used to describe the electronic spectra of confined systems.\textsuperscript{12,13} Lin and Ho\textsuperscript{12} used a pseudopotential for the lithium atom to simulate the core interaction with the single valence electron with optimized parameters. They calculated the photoionization cross section of the 2s shell electron under confinement by a power exponential potential due to an endohedral cavity and found that multiple Cooper resonances emerged.\textsuperscript{13} Their results show the importance of cage thickness and a smooth shell boundary in the photoionization cross section. Another example is due to Sarsa et al.,\textsuperscript{13} who studied the effects of confinement on the outer valence electrons for the ground state configurations of carbon and iron atoms. In standard HF theory, the main complication that arises when dealing with quantum confined systems is the treatment of the one- and two-electron integrals, particularly the electron exchange integral, as shown by Ludeña.\textsuperscript{15} Fortunately, Slater\textsuperscript{16} proposed a simplified approach to treat the electron exchange operator in the HF method by replacing it by a term proportional to the charge density of the inner electrons. This approach has been fruitful in treating problems in atomic and molecular structure with satisfactory results,\textsuperscript{17} particularly in the development of DFT theory. However, to the authors’ knowledge, there have not been any studies of the effects of confinement on the excitation spectra of a multi-electron system in the context of HF theory by means of Slater’s X-α approach.

The goal of this work is to apply Slater’s X-α approach to the ground and excited states of Li-like atoms confined in an impenetrable spherical cavity. To show the strength of Slater’s X-α approach to the calculation of the excitation spectrum of atoms, we take as a benchmark example the ground states of lithium-like atoms in the initial electronic configuration 1s\(^2\)2s\(^1\), adopting a restricted HF approach. We focus on the dipole oscillator strength (DOS) and derived properties such as the static dipole polarizability and the mean excitation energy.

The remainder of this paper is organized as follows. In Sec. II, we present the theoretical approach used to study the influence of a spherical confinement field on lithium-like atoms. In Sec. III, we discuss our results and findings. In Sec. IV, we give our conclusions and perspectives. Note that we use atomic units (a.u.) throughout, unless physical units are explicitly stated.

II. THEORY

A. Slater’s X-α approach in Hartree-Fock theory

In this section, we present the HF method to obtain the 1s\(^2\)2s ground state energies of Li, Be\(^{+}\), and B\(^{2+}\) atoms, incorporating confinement conditions.

In an HF approach, the total wavefunction is defined as a Slater determinant \(\Psi(r) = N \det[\psi_i]\), where \(N\) is a normalization constant. The general restricted HF approach\textsuperscript{18} considers the two electrons in the 1s\(^2\) core to be in the same orbital. To simplify the calculation of the excitation spectra, we assume that the inner electrons do not see the outer electrons. This approach is known as the frozen-core approximation, which is usually treated within a pseudopotential approach.\textsuperscript{7,8,11} However, here we do not use any specific pseudopotential formula to describe the interaction of the inner electrons, since this is calculated explicitly for every confinement configuration in a self-consistent manner. Then, for the ground state of a lithium-like atom, the HF equations are

\[
\hat{h}_1(r)\psi_1(r) = e_1\psi_1(r),
\]

\[
\hat{h}_2 + 2\hat{J}_1 - \hat{K}_1 \psi_2(r) = e_2\psi_2(r),
\]

where \(e_j\) are the eigenvalues, \(\psi_j\) are the eigenfunctions, \(\hat{h}_j\) are the one-electron operators, and \(\hat{J}_j\) and \(\hat{K}_j\) are the two-electron Coulomb and exchange operators, respectively. These operators are defined as

\[
\hat{h}_j(r) = -\frac{1}{2}\nabla_j^2 - \frac{Z}{r} + V_c(r),
\]

\[
\hat{J}_j(r)\psi_j(r) = \left[ \int dr_2 \frac{\psi_j^*(r_2)\psi_j(r_2)}{r_{12}} \right] \psi_j(r),
\]

\[
\hat{K}_j(r)\psi_j(r) = \left[ \int dr_2 \frac{\psi_j^*(r_2)\psi_j(r_2)}{r_{12}} \right] \psi_j(r),
\]

where \(r_{12} = |r - r_2|\). The one-electron operator, Eq. (3), includes the confinement potential \(V_c(r)\) (see below). The total ground state energy of the confined system is given by

\[
E_{HF} = 2\hat{h}_1 + \hat{h}_2 + \hat{J}_1 + 2\hat{J}_2 - \hat{K}_2.
\]

It can be seen that Eq. (1) is in eigenvalue form, so the excitation spectra of the core electron can be readily obtained. However, Eq. (2) is not, owing to the presence of the exchange operator, Eq. (5). To have an eigenvalue equation, we resort to Slater’s X-α approach,\textsuperscript{16,19} in which the exchange operator is replaced by

\[
\hat{K}_1(r)\psi_1(r) = \alpha_x \rho_1^{1/3}(r)\psi_1(r),
\]

where \(\alpha_x\) is a parameter, and \(\rho(r)\) is the charge density due to the 1s\(^2\) inner electrons\textsuperscript{1} and is given by

\[
\rho_1(r) = 2|\psi_1(r)|^2,
\]

with \(\psi_1(r)\) the eigenfunction of the core electrons. To solve the HF equations (1) and (2), we implement a finite-difference numerical approach within a self-consistent field (SCF) procedure to obtain the eigenvalues, eigenfunctions, and dipole-dependent properties. For each iteration, we calculate Eq. (5) explicitly and determine Slater’s X-α constant as\textsuperscript{19,20}

\[
\alpha_x = \frac{\langle \psi_1(r)|\hat{K}_1(r)|\psi_2(r)\rangle}{\langle \psi_1(r)|\hat{J}_1(r)|\psi_2(r)\rangle},
\]

finding the excitation spectrum of the 2s electron. The procedure is repeated until Eq. (6) has reached self-consistency within a 10\(^{-6}\) error difference for the total ground state energy.

Owing to the spherical symmetry of the system, we assume \(\psi(r) = R_\ell(r)Y^\ell_m(\theta, \phi)\) and \(R_\ell(r) = u_\ell(r)/r\), where \(Y^\ell_m\) are spherical harmonics. This is done for both core and valence wavefunctions.
We consider the lithium-like atoms to be confined by an impenetrable spherical cavity, so the confinement potential is given by
\[ V_c(r) = \begin{cases} 0, & r < R_0, \\ \infty, & r \geq R_0. \end{cases} \]
(10)
where \( R_0 \) is the confinement radius of the cavity and is commensurate with the confinement pressure (see below).

1. Finite-difference approach

As the finite-difference approach has been reported previously by Cabrera-Trujillo and Cruz,\(^1\) here we just summarize our implementation to find the eigenvalues and eigenfunctions of Eqs. (1) and (2). The finite-difference approach consists in discretizing the function \( u(r) \rightarrow u_k \) and \( r \rightarrow r_k \), known at the kth point on a numerical grid, with \( k = 0 \) corresponding to \( u_0 \) and \( k = N + 1 \) to \( u_{N+1} \), which are the boundary conditions of the system.\(^2\) In our case, for the impenetrable cavity, \( u_{N+1} = 0 \) and \( r_{N+1} = R_0 \). We implement the finite-difference approach centered at the midpoint. With this, Eqs. (1) and (2) are rewritten as
\[ \vec{H}\phi = \vec{E}\phi, \]
(11)
where \( \vec{H} \) is a tridiagonal symmetric matrix with \( N \) eigenvalues and eigenfunctions, and \( \phi \) is related to \( \vec{u} \) by a linear transformation.\(^3\)

We solve Eq. (11) in a grid box that extends from \( \vec{r} = 0 \) to \( \vec{r} = R_0 \), with a total of \( N = 2000 \) points spaced logarithmically in this range as a function of the confinement radius \( R_0 \). This logarithmic grid allows us to give a better description of the wavefunction up to the origin and a good number of continuum states. We have found that \( N = 2000 \) satisfies the Thomas–Reiche–Kuhn (TRK) sum rule up to five decimal digits. The accuracy of our finite-difference approach can be controlled by the number of points in the grid and their spacing; for example, for the free lithium atom, we obtain eigenvalues with precision up to the fifth decimal place. This approach gives a total of \( N \) excited states to describe the DOS electronic properties for each spherical cavity with radius \( R_0 \) per electron. The values of \( R_0 \) are chosen between 0.5 a.u. and 100 a.u. Our approach is implemented in a Fortran 95 code that calculates the eigenvalues, eigenfunctions, and physical properties of the system.

B. Physical properties

1. Dipole oscillator strengths

The DOS accounts for the transition probability from an initial state to a final excited state and is defined as
\[ f_{i\alpha} = \frac{2}{3} \left( \langle \phi_i | \hat{r} | \phi_{\alpha} \rangle \right)^2, \]
(12)
where \( i \) stands for electron \( i = 1 \) (core electron transitions) or \( i = 2 \) (valence electron transitions). To confirm that our numerical approach has rendered a complete set of states, the TRK sum rule,\(^2\) the sum of all dipole oscillator strengths. Consequently, it can be rewritten as
\[ f_{i\alpha} = 2\alpha_i^s + \alpha_i^p, \]
(15)
where \( \alpha_i^s \) is the contribution from the core \( (i = 1) \) or the valence \( (i = 2) \) electron. For photon absorption, the polarizability is positive, but for photon emission, it becomes negative.

2. Static dipole polarizability

The static dipole polarizability is defined through the DOS [Eq. (12)], and is given by
\[ \alpha_i = \sum_n \frac{f_{i\alpha}}{(E^{(n)}_\alpha - E^{(0)}_i)^2} = \sum_n \frac{f_{i\alpha}^N}{(\varepsilon_n^i - \varepsilon_n^\alpha)^2}, \]
(14)
where it exhibits an explicit dependence on the single-electron dipole oscillator strengths.

3. Mean excitation energy

A parameter that characterizes the amount of energy loss when a swift heavy ion penetrates a target is provided by the mean excitation energy \( I_{\alpha} \), as defined by Bethe:\(^26\)
\[ \ln I_{\alpha} = \frac{\sum_{n} f_{i\alpha} \ln (E^{(n)}_\alpha - E^{(0)}_i)}{\sum_{n} f_{i\alpha}^{N}} \]
(16)
Using the TRK sum rule,\(^2\) Eq. (16) can be rewritten as
\[ 3\ln I_{\alpha} = 2 \sum_{n} f_{i\alpha}^{1s} \ln (\varepsilon_n^{1s} - \varepsilon_n^{i}) + \sum_{n} f_{i\alpha}^{1s} \ln (\varepsilon_n^{1s} - \varepsilon_n^{2s}) \]
\[ = 2 \ln I_1^{1s} + \ln I_2^{1s}, \]
(17)
which is the orbital decomposition or Bragg rule for the mean excitation energy, as used by Oddershede and Sabin\(^-\) in energy loss deposition studies.

III. RESULTS

A. Unconfined lithium-like atoms

To show the reliability of our approach when applied to a multi-electron system, we present in Table I the results for the unconfined Li, Be\(^+\), and B\(^{2+}\) atoms. We show the core electron ground and excited orbital energies \( \varepsilon_0^{1s} \) and \( \varepsilon_0^{1p} \), the total HF energy \( E_{HF} \), the DOS \( f_{i\alpha}^{1s,p} \) for the first dipole transition, the polarizability \( \alpha_i^s \), and the mean excitation energy \( I_{\alpha} \). The same quantities are also reported for the valence (2s) electron. In the case of the \( 2s \) and \( 1s \) valence energy losses, the values for the Li, Be\(^+\), and B\(^{2+}\) atoms, we observe good agreement up to four-decimal precision when compared with the results of Froese-Fischer.\(^23\) For the Li atom mean excitation energy \( I_2^{1s} \), we observe a difference of less than 5% with respect to the value reported by Oddershede and...
TABLE I. Unconfined ground state properties for free Li, Be+, and B2+ atoms. We report values for the core (i = 1) and valence (i = 2) electrons for the ground (\(\epsilon_0\)) and excited (\(\epsilon_2\)) orbital energies, the total HF energy \(E_{\text{HF}}\), the DOS \(f_{1s}\), the static dipole polarizability \(\alpha_0\), and the mean excitation energy \(I_0\). Slater’s \(\alpha_0\) parameter, Eq. (9), takes the values \(\alpha_0^L = 0.5802\), \(\alpha_0^{Be} = 0.5263\), and \(\alpha_0^{B^2+} = 0.4992\).

|              | Core (1\(s^2\)) | Valence (2\(s^1\)) |
|--------------|-----------------|--------------------|
|              | Li              | Be\(^+\)           | B\(^{2+}\)          |
| \(\epsilon_0\) | -2.79232        | -5.66697           | -9.54158            |
| \(\epsilon_2\) | (-2.79236)\(^a\) | (-5.66711)\(^a\)   | (-9.54198)\(^a\)   |
| \(E_{\text{HF}}\) | -7.23633        | -13.6109           | -21.9834            |
| \(f_{1s}\)    | (13.6113)\(^a\) | (13.6113)\(^a\)    | (21.9862)\(^a\)    |
| \(\alpha_0\)   | 0.26119         | 0.30497            | 0.32965             |
| \(I_0\)       | 103.613         | 197.505            | 321.368             |
|               | (109.32)\(^c\) | ...                | ...                 |

|              | Li              | Be\(^+\)           | B\(^{2+}\)          |
| \(\epsilon_2\) | -0.20116        | -0.67282           | -1.39722            |
| \(\epsilon_2\) | (-0.19632)\(^a\) | (-0.66615)\(^a\)  | (-1.38985)\(^a\)   |
| \(E_{\text{HF}}\) | -7.43749        | -14.2838           | -23.3826            |
| \(f_{2s}\)    | (-14.2774)\(^a\) | (-23.3759)\(^a\)  | ...                 |
| \(\alpha_0\)   | 0.65127         | 0.41315            | 0.29963             |
| \(I_0\)       | 171.188         | 27.3836            | 8.9940              |
|               | (164.05)\(^d\) | (24.9646)\(^f\)    | ...                 |
|               | (3.29)\(^c\)   | ...                | ...                 |

\(^a\)From Ref. 28.
\(^b\)From Ref. 27.
\(^c\)From Ref. 29.
\(^d\)From Ref. 30.
\(^e\)From Ref. 31.
\(^f\)From Ref. 32.

Sabin.\(^{27}\) For the valence (2\(s\)) electron, we obtain orbital energy values of \(\epsilon_2^{Li} = -0.20116\) a.u., \(\epsilon_2^{Be} = -0.67282\) a.u., and \(\epsilon_2^{B^2+} = -1.39722\) a.u., for the Li, Be\(^+\), and B\(^{2+}\) atoms, respectively, with a difference of less than 3% in comparison with the results of Froese-Fischer.\(^{25}\) However, for the total HF energy, we obtain values with a difference of less than 1% with respect to the results of Froese-Fischer.\(^{27}\) For the dipole polarizability, we obtain \(\alpha_0^{Li} = 171.188\) a.u. and \(\alpha_0^{B^2+} = 27.3836\) a.u., in comparison with values of 164.05 a.u. and 24.9646 a.u. reported by Schwerdtfeger and Nagle\(^{31}\) and Tang et al.\(^{29}\), respectively.

Thus, our approach using Slater’s X-a allows us to account for the ground state properties \(\epsilon_0\) and \(E_{\text{HF}}\) of the Li, Be\(^+\), and B\(^{2+}\) atoms, with good agreement with available theoretical results.

In Fig. 1, we show the wavefunctions for the 1\(s\) and 2\(s\) orbitals as functions of position \(r\) for unconfined Li, Be\(^+\), and B\(^{2+}\) atoms. For comparison, we also show the results of Froese-Fischer.\(^{28}\) We observe excellent agreement for the 1\(s\) orbital for all ranges. For the 2\(s\) electron, we also obtain very good agreement for electron distances \(r > 1\) a.u. However, we observe that small deviations appear for the inner part of the wavefunction, \(r < 1\) a.u., compared with the Froese-Fischer results.

B. Confined total and orbital HF energies

In Fig. 2, we show the 1\(s\), 2\(s\), 2\(p\), 3\(s\), and 3\(p\) energy levels for Li, Be\(^+\), and B\(^{2+}\) atoms confined by an impenetrable spherical cavity as a function of the confinement radius \(R_0\). For comparison, we also show the results of Weiss\(^{31}\) for the free atom energy levels at \(R_0 = 30\) a.u. We can see that the energy levels increase, reaching the continuum, as the confinement radius decreases. Furthermore, we observe the appearance of crossing points for the 2\(s\) and 2\(p\) energy levels, as well as for the 3\(s\) and 3\(p\) levels, which are highlighted by circles for better visualization. Our results confirm the energy level behavior and crossing already reported from other approaches.\(^{1,3,5}\) Figure 2(a) shows the 3\(s\) and 3\(p\) states of the Li atom. We find that the energy levels reach the continuum for cavities with \(R_0 < 10\) a.u. and \(R_0 < 12\) a.u., respectively. Here, the 3\(s\) energy level is deeper than the 3\(p\) state. As the confinement radius decreases, the 3\(s\) and 3\(p\) energy levels increase until a crossing point around \(R_0 \sim 2\) a.u. For values of \(R_0 < 6\), the 3\(p\) energy is lower than the 3\(s\) energy. For the 3\(s\) and 3\(p\) states of the Be\(^+\) and B\(^{2+}\) atoms, we find a similar trend as for the Li atom. We can see that the crossing points between the 3\(s\) and 3\(p\) states of the Li, Be\(^+\), and B\(^{2+}\) atoms are in the positive spectrum. For the Be\(^+\) atom, we find that the crossing point occurs at \(R_0 \sim 4.6\) a.u.

In Fig. 2(b), we show the 2\(s\) and 2\(p\) energy levels, and we can again see an energy increase and the emergence of crossing points as \(R_0\) decreases. We find that the 2\(p\) energy level of the lithium atom
becomes positive for \( R_0 < 4.6 \text{ a.u.} \) and the 2s energy level becomes positive for \( R_0 < 4.4 \text{ a.u.} \). In this case, the crossing point is present for \( R_0 \sim 3.4 \text{ a.u.} \). This cavity size corresponds to a pressure of 85 GPa (see below), which is lower than the 210 GPa reported by Rahm et al. The discrepancy is attributed to the different confinement models.

The increase in energy is explained as follows. For an impenetrable cavity, the electrons remain localized within the cavity. As the pressure increases, so does the electron kinetic energy (as a consequence of the Heisenberg uncertainty principle), and the total energy can become positive for a critical pressure, as we have just shown, but the system is still bounded.

In Fig. 3, we show the results for the total HF energy for the Li, Be\(^+\), and B\(^{2+}\) atoms for the initial 1s2s configuration, confined by an impenetrable spherical cavity, as functions of the confinement radius. For comparison, we also show, in the case of Li, the theoretical results of Sañu-Ginarte et al., Le Sech and Banerjee, Sarsa and Le Sech, and Sarsa et al., and we can see that there is excellent agreement. In addition, the HF results for the unconfined atoms obtained by Weiss are shown at \( R_0 = 5 \text{ a.u.} \). For the free case, when \( R_0 \to \infty \text{ a.u.} \), we obtain total energy values of \( E_{\text{HF}}^{\text{Li}} = -7.437 \, 49 \text{ a.u.} \), \( E_{\text{HF}}^{\text{Be}} = -14.283 \, 8 \text{ a.u.} \), and \( E_{\text{HF}}^{\text{B}} = -23.382 \, 6 \text{ a.u.} \), in good agreement with the values reported by Froese-Fischer and Sañu-Ginarte et al. As the confinement radius decreases, the HF energy increases, for all atoms, as previously reported by Connerade et al. For the Li, Be\(^+\), and B\(^{2+}\) atoms, we observe in Fig. 3 that the effect of the cavity is minimal for \( R_0 > 7.3 \text{ a.u.} \), \( R_0 > 5.5 \text{ a.u.} \), and \( R_0 > 2.5 \text{ a.u.} \), respectively. For the Li atom, for \( R_0 < 1.3 \text{ a.u.} \), the HF energy becomes positive. A similar situation occurs for the Be\(^+\) and B\(^{2+}\) atoms for \( R_0 < 0.94 \text{ a.u.} \) and \( R_0 < 0.75 \text{ a.u.} \), respectively.

From Figs. 2 and 3, we conclude that the effect of the confinement cavity is stronger on the valence electrons that on the core electrons.

In Fig. 2(c), we show the 1s energy levels as functions of \( R_0 \). We find that the effect of the cavity on the 1s ground state energy is minimal for \( R_0 > 2 \text{ a.u.} \), \( R_0 > 1.5 \text{ a.u.} \), and \( R_0 > 1 \text{ a.u.} \) for Li, Be\(^+\), and B\(^{2+}\) atoms, respectively. For the Li atom, we observe a sudden change in the energy for \( R_0 < 2 \text{ a.u.} \) and it reaches a positive value for the 1s core state for \( R_0 < 0.77 \text{ a.u.} \). A similar situation occurs for the Be\(^+\) atom for \( R_0 < 0.555 \text{ a.u.} \) and for B\(^{2+}\) for \( R_0 < 0.427 \text{ a.u.} \).

The discrepancy is attributed to the different confinement models.

FIG. 2. Orbital energies for the 1s, 2s, 2p, 3s, and 3p states of Li, Be\(^+\), and B\(^{2+}\) atoms confined by a spherical impenetrable cavity as a function of the confinement radius \( R_0 \): (a) 3s and 3p states; (b) 2s and 2p states; (c) 1s ground state. The crossing points between the ns-np levels are highlighted by circles for better visualization. The curves without symbols are for the ns states, while the curves with symbols are for the np states. For comparison, the HF results of Weiss for the unconfined atom energy levels are also shown at \( R_0 = 30 \text{ a.u.} \).

FIG. 3. Total HF energy, Eq. (6), as a function of cavity radius \( R_0 \) for Li, Be\(^+\), and B\(^{2+}\) atoms. In the case of Li, the symbols show the theoretical results from Sañu-Ginarte et al. (×), Le Sech and Banerjee (○), Sarsa and Le Sech (□), and Sarsa et al. (△). The HF results for unconfined atoms as reported by Weiss are shown at \( R_0 = 5 \text{ a.u.} \).
C. Pressure

The order of magnitude of the pressure that the cavity exerts on the atomic system as \( R_0 \) is shrunken is given by the static pressure

\[
P = -\frac{\partial E_{\text{eff}}}{\partial v} = -\frac{1}{4\pi R_0^2} \frac{\partial E_{\text{eff}}}{\partial R_0}
\]

where \( v \) is the volume of the spherical cavity. In Fig. 4, we show the results for the pressure as a function of the spherical cavity radius \( R_0 \) for Li, Be\(^+\), and B\(^{2+}\) atoms. For comparison, we show some characteristic pressures found in nature. We first note that for the same cavity radius, the pressure is lowest for B\(^{2+}\), increases for Be\(^+\), and is highest for Li. This is a consequence of the ionic character of the system. The lithium atom is more diffuse in its 2\( s \) orbital, so the same cavity radius induces a higher pressure, while, owing to the high nuclear charge, the boron ion has already compacted its 2\( s \) electron, so the same cavity radius induces a smaller pressure on the ionic system. The figure also shows the cavity size and pressure for which the 2\( s \) \( \rightarrow \) 2\( p \) transition occurs in our approach. For Li, we find it at 85 GPa (\( R_0 \approx 3.4 \) a.u.), for Be\(^+\) at 350 GPa (\( R_0 \approx 2.5 \) a.u.), and for B\(^{2+}\) at 690 GPa (\( R_0 \approx 2.1 \) a.u.). These results are within an order of magnitude of those reported by Rahm et al., \(^\dagger\) which were obtained using a different confinement model, thus confirming the suitability of our approach. Rahm et al. reported a higher pressure, probably because their model considers penetrable confinement conditions.

D. Dipole oscillator strength

In Fig. 5(a), we show the DOS for the electronic transitions 1\( s \) \( \rightarrow \) 2\( p \) (core excitations) and 2\( s \) \( \rightarrow \) 2\( p \) (valence excitations) for Li, Be\(^+\), and B\(^{2+}\) atoms confined by an impenetrable spherical cavity as a function of the confinement radius \( R_0 \). In the case of the Li atom, for \( R_0 < 15 \) a.u., \( f_{1s2p}^{ls} \) begins to decrease, showing a change near \( R_0 \approx 9 \) a.u., where we find a value of \( f_{1s2p}^{ls} = 0.588 \) 95 a.u. At \( R_0 = 6.5 \) a.u., we obtain a DOS of 0.460 46 a.u., and at \( R_0 = 3.5 \) a.u. a value of \( f_{1s2p}^{ls} = 0.023 \) 20 a.u., near the radius for which the crossing point occurs. For the Be\(^+\) atom, we observe similar behavior. The DOS for the transition decreases rapidly near \( R_0 \approx 5 \) a.u., with \( f_{1s2p}^{ls} = 0.357 \) 81 a.u., and then reaches a value of \( f_{1s2p}^{ls} = 0.015 \) 23 a.u. at \( R_0 = 2.6 \) a.u., which is near the crossing point. For the B\(^{2+}\) atom, we observe the same DOS reduction as \( R_0 \) is decreased until the crossing point at \( R_0 = 2.1 \) a.u. When \( R_0 \) is decreased, the DOS for the valence electron excitation, \( f_{1s2p}^{ls} \), is reduced until the 2\( s \) electron reaches the crossing point between the 2\( s \) and 2\( p \) energy levels, so that at that pressure the DOS become zero (\( \epsilon_{1s} = \epsilon_{1p} \)).

Crossing occurs for confinement radii \( R_0 \approx 3.4 \) a.u., 2.4 a.u., and 2.1 a.u. for Li, Be\(^+\) and B\(^{2+}\) atoms, respectively. For confinement radii less than the crossing point, the 2\( p \) energy levels have lower values than those found for the 2\( s \) energy level, and there is photon emission induced by the pressure cavity. We should note here that in a sudden approximation perturbation, for a shrinking of the cavity from radius \( R_0 \) to \( R_0 + \Delta R_0 \), the probability of finding the system in the 2\( p \) state is zero owing to symmetry arguments (orthogonal states). Thus, there is a higher probability for the system to remain in the same symmetry state and then proceed to the 2\( p \) state by photon emission. Consequently, for a cavity radius lower than the critical crossing point, \( f_{1s2p}^{ls} \) becomes negative owing to photon emission, and some other transitions must increase its DOS value to satisfy the TRK sum rule. In Fig. 5(a), we also show the core results for the \( f_{1s2p}^{ls} \) transition, and we can see that the DOS increases as \( R_0 \) is reduced. \( f_{1s2p}^{ls} \) shows an abrupt change near \( R_0 \approx 5 \) a.u., 3.5 a.u., and 3 a.u. for the Li, Be\(^+\), and B\(^{2+}\) atoms, respectively. For lower values of \( R_0 \) the DOS transition increases, reaching values near 1 as consequence of confinement, thus becoming a dominant intensity line.
In Fig. 5(b), we show the $1s \rightarrow 3p$ and $2s \rightarrow 3p$ DOS for Li, Be', and B²⁺ atoms as functions of the cavity radius. As can be seen, for cavities with radius lower than the critical crossing point, $f_{2s}^{3p}$ becomes larger than unity, although the TRK sum rule is satisfied for all cavity radii. Thus, $2s \rightarrow 3p$ becomes the strongest transition, so there is a change in luminosity in the atom as the pressure increases, but in this case due to photon emission induced by the change in pressure, similar to piezoluminescence.

**E. Static polarizability**

In Fig. 6, we show the static dipole polarizabilities $\alpha_{2s}$ and $\alpha_{2p}$ for the valence and core states for Li, Be', and B²⁺ atoms confined by an impenetrable spherical cavity, as a function of the confinement radius $R_0$. The crossing points are highlighted by vertical lines. Note that owing to the small contribution of the core electrons, the total atomic polarizability is dominated by the valence contribution for all pressures. For comparison, Fig. 6(a) also shows the unconfined Li and Be' results as reported by Schwerdtfeger and Nagle, and Tang et al., and the crossing points are highlighted by vertical lines. From Fig. 6, we observe that as the confinement radius decreases, so does the polarizability, until the $s$-$p$ crossing point is reached. In Fig. 6(a) for the Li atom, for a cavity with radius $R_0 = 4.4$ a.u., the polarizability decreases to 54.2926 a.u., which is about 30% of the free value. As $R_0$ is reduced, the $2s$ and $2p$ energy levels become positive, and the $\alpha_{2s}$ polarizability increases, diverging at $R \sim 3.4$ a.u., which is at the critical crossing point of the $2s$--$2p$ energy levels. For lower values of $R_0$, $\alpha_{2s}$ becomes negative owing to the transition to photon emission. In the case of the Be' atom, at $R_0 = 6.5$ a.u., we observe a value of $\alpha_{2s}^{Be'} = 26.2083$ a.u., and then the polarizability decreases for lower values of the confinement radius until $R_0 \sim 3.4$ a.u., where a minimum value of $\alpha_{2s}^{Be'} = 16.3509$ a.u. is found. Then, for values of $R_0 < 3.4$ a.u., the polarizability increases rapidly, diverging at $R_0 \sim 2.4$ a.u., and it then becomes negative for lower values of $R_0$. A similar situation occurs for the Be²⁺ atom, but with a minimum value of 6.772 95 a.u. at $R_0 \sim 2.8$ a.u. and a divergence at the crossing point $R_0 \sim 2.1$ a.u. In Fig. 6(b), we show the results for the core contribution $\alpha_{2s}^{Be'}$, where...
F. Mean excitation energy

In Fig. 7, we show the mean excitation energies $I_0^{I_e}$, $I_0^{I_s}$, and $I_0$ for Li, Be$^+$, and B$^{2+}$ atoms confined by an impenetrable spherical cavity as functions of the confinement radius $R_0$. We can see that at $R_0 = 30$ a.u., the results for the free mean excitation energies are in good agreement with previous HF results from Oddershede and Sabin,\textsuperscript{27} Kamakura,\textsuperscript{41} and Dehmer et al.\textsuperscript{42} From Fig. 7(a), we can see that as $R_0$ decreases, $I_0^{I_s}$ increases, showing an abrupt change near $R_0 \approx 10$ a.u., and 4 a.u. for the Li, Be$^+$, and B$^{2+}$ atoms, respectively, with $I_0^{Li} = 3.879\, 67$ eV, $I_0^{Be^+} = 14.739\, 33$ eV, and $I_0^{B^{2+}} = 28.556\, 61$ eV. For the Li valence electron, we observe an increase of $\sim 40\%$ with respect to the free mean excitation energy at $R_0 = 4.4$ a.u. For Be$^+$, we find an increase of $\sim 11\%$, and for B$^{2+}$ an increase of $\sim 9\%$ for the same confinement. Figure 7(a) also shows $I_0^{I_e}$ for Li, Be$^+$, and B$^{2+}$ atoms, and we observe an increase in the mean excitation energy as $R_0$ is reduced. In Fig. 7(b), we show results for the total mean excitation energy $I_0$. We find $I_0 = 33.708\, 90$ a.u., in good agreement with the value of $34.004\, 13$ a.u. obtained by Oddershede and Sabin,\textsuperscript{27} Eq. (17), and the value of 34 a.u. reported by Dehmer et al.\textsuperscript{42} for Li atoms. Note that as a consequence of 2s–2p energy level crossing, the photon emission produces a negative energy transfer, so the logarithmic contribution is undetermined, as defined by Eqs. (12) and (13). This is observed in the $I_0^{I_e}$ contribution and in the total $I_0$ mean excitation energy for $R_0$ less than the critical cavity radius at the $s$–$p$ crossing energy levels. Thus, a different approach may be required to determine it, such as that proposed by Smith et al.\textsuperscript{13}

C. Slater’s X–α contribution

One advantage of Slater’s X–α approach is that we can estimate the electron exchange contribution to the energy for a confined quantum system through a single parameter. In Fig. 8, we show the behavior of Slater’s X–α parameter $\alpha_X$ as a function of the cavity confinement radius $R_0$. We find that the largest contribution occurs for the Li atom, followed by the Be$^+$ ion and then the B$^{2+}$ ion for low-pressure cavities. The contribution increases as $R_0$ decreases, reaching a maximum, and it then decreases as the cavity becomes small. For the ions, the 2s electrons are tighter and the electron exchange parameter is lower for large spherical cavities. However, this behavior is inverted as the cavity increases the pressure. For cavities whose radius is smaller than the critical radius, the $\alpha_X$ parameter is largest for B$^{2+}$, followed by Be$^+$, and then Li. So, electron exchange is important as long as the valence electrons remain bounded.

In Tables II and III, for reference purposes, we show the 1s, 2s, and 2p energy levels, the total HF energy, the first allowed DOS transition $2s \rightarrow 2p$, the dipole polarizability, the mean excitation energy, and Slater’s $\alpha_X$ parameter [Eq. (9)] for selected values of the confinement radius $R_0$ for Li, Be$^+$, and B$^{2+}$ atoms.
We have studied lithium-like atoms confined by an impenetrable spherical cavity of radius $R_0$. We find good to excellent agreement when comparing orbital and total energies, as well as when determining dipole transitions, static polarizability, and mean excitation energies for the unconfined systems. For the lithium atom, we find excellent agreement for confined ground state energies in comparison with available theoretical results.

We confirm that, as a consequence of the confinement, the system orbital and total energies increase as the pressure increases owing to a reduction in cavity size. However, the first allowed dipole transition, $2s \rightarrow 2p$, decreases, while $2s \rightarrow 3p$ increases. Consequently, as the pressure increases, the intensity of light emitted by the atom in the cavity is shifted. However, there is a crossing point (critical pressure) at which the $2s$ and $2p$ energy levels are inverted; consequently, the DOS for that transition becomes zero at that critical pressure. For higher pressures, the DOS becomes negative owing to photon emission. In addition, the $2s \rightarrow 3p$ DOS reaches values larger than unity for high pressures, and the $2s \rightarrow 2p$ DOS becomes negative. Thus, we can confirm that the static dipole polarizability is reduced as the pressure increases, as the electrons become highly localized within the cavity and less prone to be polarized, and diverges at the point of transition from photon absorption to photon emission. We also find that the mean excitation energy, which measures the ability of the atom to absorb energy due to excitations, increases as the pressure is increased, with implications for material damage under extreme conditions. As a result of the existence of the crossing point, the valence and total mean excitation energy become undetermined owing to a logarithmic indeterminacy, and thus a different approach may be required.

Our work shows the reliability of Slater’s X-$\alpha$ approach in the context of HF theory to study confined N-electron quantum systems. This approach has the advantage that it can be extended to larger systems to provide excitation spectra in different confinement environments, thus shedding light on the behavior of N-body quantum systems under extreme conditions.

**IV. CONCLUSIONS**

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