Dipole sum rules of an endohedral confined hydrogen atom: Effects of the cavity discontinuity

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Abstract

In this work, the effects of an endohedral cavity on the hydrogen dipole oscillator strength sum rule, $S_k$, and its logarithmic version, $L_k$, are studied. The approach is based on a finite-differences numerical solution to the Schrödinger equation for the hydrogen atom spectrum under a cavity confinement model. Endohedral effects are accounted for by means of a shell-like cavity of inner radius $R_0$ and thickness $\Delta$ with a penetrable potential height $V_0$. To analyze the cavity discontinuity, a Woods-Saxon potential is used for different values of the smoothness at the inner and outer cavity radii. Small values of the smoothness parameter allows one to emulate the discontinuity of a square-well model potential. The dipole oscillator strength sum rules $S_k$ and $L_k$ are investigated as a function of the cavity potential depth $V_0$. We use the values of $R_0$ and $\Delta$ that describe a fullerene cage. One finds that the sum rules are fulfilled within the numerical precision for low potential height conditions. However, when the well depth is $V_0 = 0.7$ a.u., corresponding to the first avoiding crossing between the $1s$ and $2s$ state, the sum rule differs from its closure relation and it is this well depth for which the effects of the potential discontinuity are strongest. As the $S_{-2}$ sum rule is the static dipole polarizability, the results are compared to available data in the literature showing excellent agreement. We also show that inclusion of all bound and continuum excited states in the sum over states are necessary in order to obtain accurate sum rules.

Keywords: Endohedral, Cavity, Hydrogen atom, Sum rule, Logarithmic

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1. Introduction

Dipole oscillator strength (DOS) sum rules, $S_k$ with $k$ being an integer, as well as its logarithmic counterpart $L_k$, are important in many fields of physics and chemistry, as they contain information on the whole electronic spectrum of the system. For example: the Thomas-Reiche-Kuhn (TRK) sum rule describes the electric-dipole interactions \[1\,2\,3\]. The sum rule $L_0$, is related to Bethe’s mean excitation energy, $I_0$, and is important in the

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study of energy loss process of charged particles interacting with matter\cite{4}; The static dipole polarizability of an atom is given by the $S_\alpha$ sum rule; Sum rules also appear in the study of model systems in quantum mechanics\cite{5}; in atomic physics\cite{6,7} sum rules are related to the polarizability, dielectric and optical constants, photo-absorption cross-sections, spectral distribution and moments, light scattering, and refractive properties; In molecular physics\cite{8} the sum rule is used to study the rotational structure in the spectra of molecules; In solid state physics\cite{9,10,11} the sum rules are used to study the conductivity of superconducting films, the superconducting skin depth, and the interlayer conductivity of high-$T_c$ cuprates; In nuclear physics\cite{12} a sum rule is used to calculate the baryon self-energy in infinite nuclear matter; In particle physics\cite{13} the sum rule correlates the resonance properties of matter to a few vacuum-to-vacuum matrix elements in quantum chromodynamics; Recently, implications of sum rules in confined quantum systems have been reported for a hydrogen impurity confined by a penetrable spherical cavity\cite{14}. Consequently, the determination of the whole excitation spectrum of a quantum system is of fundamental importance in atomic and molecular physics, since the whole spectrum warrants the proper description of any physical quantity. In this regard, sum rule relations contain important information about both the energy spectrum and energy eigenfunctions of the system in a compact form, particularly regarding closure relations for the quantum state. Such relations rely on the fact that the solutions of the system under study form a complete set of states. This constrains the application of such sum rules to systems where both bound and continuum states are known, an open problem in many computational quantum physics applications\cite{15}.

The necessity for the development of refined theoretical models to account for the electronic and optical properties of novel quantum systems has arisen with the appearance of new technologies for the synthesis of material structures with low-dimensionality or in extreme conditions. In this regards, models of quantum confinement have proved to be appropriate (see for example Refs.\cite{16,17,18,19,20} for reviews in the field). There has given rise to an increasing interest in the study of dipole optical transitions of low-dimensional systems, e.g. the study of color centers in alkali-halides\cite{21}, where one or two electrons are trapped in anion vacancy sites in the ionic lattice. Recently, the electronic properties of the hydrogen atom confined by hard\cite{22,23,24,25,26} and soft\cite{27,28} spherical cavities have been reported. Similar studies on the optical absorption of hydrogenic impurities in semiconductor quantum dots\cite{29} have been communicated as well as the effects of electric fields of a confined hydrogen impurity in a quantum dot\cite{30}. Regarding dipole transitions, the work of Dutt et al.\cite{31}, Laughlin\cite{24}, Stevanovic\cite{26}, and Montgomery and Sen\cite{27} for the case of a hydrogen atom within an impenetrable spherical cavity have been reported for the study of the static dipole polarizability.

For the case of a hydrogenic system under endohedral confinement, exact analytical solutions for the whole excitation spectrum do not exist. Thus, the aim of this work is to construct the excitation spectrum of an endohedral confined hydrogen atom through numerical solutions by means of a finite-differences (FD) approach in order to study the sum rules as well as the bound and continuum contributions to them. This is done for as many discrete states as can exist inside a numerical box that contains the confining endohedral cage for a given potential well depth $V_0$, as well as for a commensurable number of states in the continuum (pseudo-continuum). The corresponding wave-functions and DOS are calculated for different endohedral cavity conditions and are used to analyze the effect of the endohedral cavity boundary at the inner and outer radii on the sum rules
and their closure relations. Where available, the results of this work are compared with other theoretical approaches.

The work is organized with the following structure: In Sec. 2, an overview of the DOS and their sum rule relations is provided, as well as for the numerical methodology employed to calculate them. The numerical results obtained in this work for the hydrogenic system are given in Sec. 3, where also a discussion is presented. In Sec. 4, the conclusions are reported. Atomic units are used throughout unless otherwise specified.

2. Theory

2.1. Sum rules and closure relations

The dipole oscillator strength sum rule, \( S_k \), for a quantum system for transitions from an initial state, \( n_0 \), to a final state, \( n \), is defined as

\[
S_k = \sum_{n \neq n_0} (E_n - E_{n_0})^k f_{nn_0} + \int E_k \frac{df}{dE} dE .
\]

(1)

Here the sum is over the discrete spectrum and the integral over the continuum states of the system, with \( f_{nn_0} \) and \( \frac{df}{dE} \) being the dipole oscillator strength (DOS) and dipole oscillator strength density for the discrete and continuum excitations, respectively. The DOS are defined as

\[
f_{nn_0} = \frac{2}{\langle \Psi_n | V | \Psi_{n_0} \rangle^2} ,
\]

(2)

where \( r \) is related to the dipole moment of the quantum system, \( \hat{\epsilon} \) is the polarization unit vector of the incident radiation or the direction of the momentum transferred, and \( \Psi_n \) and \( \Psi_{n_0} \) are the initial and final state from which the transition occurs, respectively.

When the excitation spectrum is complete, closure relations allow one to write the sum rule in terms of initial \( n_0 \) state properties of the system (closure relations). For example, Bethe and Jackiw \[32\] have shown that

\[
S_{-1} = 2\langle n_0 | r^2 | n_0 \rangle \\
S_0 = N_e \\
S_1 = 2\langle n_0 | p^2 | n_0 \rangle = 4\langle E_{n_0} - \langle n_0 | V | n_0 \rangle \rangle \\
S_2 = \langle n_0 | \nabla^2 V | n_0 \rangle \\
S_3 = 2\langle n_0 | (\nabla V)^2 | n_0 \rangle
\]

which are the quadrupole moment, the TRK sum rule, the momentum square, the force times momentum, and the force square \[32\]. Here \( N_e \) is the number of electrons in the system. Consequently, these sum rules allow one to test the excitation spectrum by comparing their sum-over-states values to the values obtained from the closure relations. Note that for a purely Coulombic interaction, \( S_3 \) diverges \[32\].

The logarithmic counterpart of the sum rule is defined as

\[
L_k = \sum_{n \neq n_0} (E_n - E_{n_0})^k f_{nn_0} \ln(E_n - E_{n_0}) + \int E_k \frac{df}{dE} \ln(E) dE .
\]

(4)

In this case, there is no closure relation for any value of \( k \) to the authors’ knowledge. However, the relation \( L_k = dS_k/dk \) connects \( L_k \) to the \( S_k \) closure relations when considering \( k \) as a continuum variable.
2.2. Dipole Oscillator strength

According to Fano [6], the atomic oscillator strength, averaged over the orientations of the polarization unit vector, for a transition \( n_0l_0 \rightarrow nl \) is given by

\[
f_{n_0n} = \frac{2}{3} (E_n - E_{n_0}) \frac{l_0 + l + 1}{2(l_0 + 1)} \frac{\langle n_0|l_0|n|nl\rangle^2}{\langle s_0|l_0|s|nl\rangle^2},
\]

(5)

The factor \((l_0 + l + 1)/2(l_0 + 1)\) arises from the average over \( m_0 \) and \( m \) quantum numbers.

Selection rules restrict \( l \) to the values of \( l_0 \pm 1 \) and the factor \( 1/3 \) arises from the spherical symmetry average.

In this work, results are presented for the initial state \( n_0 = 1, l_0 = 0 \) (1s−state) and thus only final states with \( l = 1 \) are considered.

Once the ground and excited states have been obtained, we proceed to evaluate the sum rules.

2.3. Endohedral confined hydrogen atom

In order to obtain the electronic spectrum of the system under endohedral confinement conditions and thus, determine the DOS and the sum rules, it is required to solve the stationary one-electron Schrödinger equation

\[
\left\{-\frac{1}{2} \nabla^2 - \frac{Z}{r} + V_c(r)\right\} \Psi = E \Psi.
\]

(6)

where \( Z \) is the nuclear charge, \( r \) is the electron-nucleus separation, and \( V_c \) is the confining model potential for the endohedral cage.

Due to the spherical symmetry of the confining potential, spherical coordinates are used to simplify the 3-dimensional equation. Thus, one rewrites the eigenfunctions of Eq. (6) as \( \Psi(r, \theta, \phi) = u_{nl}(r)Y^m_l(\theta, \phi)/r \), where \( Y^m_l(\theta, \phi) \) are the spherical harmonics associated with the orbital and magnetic quantum numbers \( l \) and \( m \), respectively. The functions \( u_{nl}(r) \) satisfy the radial equation

\[
\left\{-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} + V_c(r)\right\} u_{nl} = Eu_{nl}.
\]

(7)

This equation is a 1-dimensional self-adjoint equation for the radial function.

In our case, the endohedral confined hydrogen atom is modeled by placing the atom inside a penetrable confining spherical shell cavity represented by the Woods-Saxon potential \[33, 34\] defined as

\[
V_c(r) = \frac{V_0}{1 + e^{-(r-(R_0+\Delta))/\gamma}} - \frac{V_0}{1 + e^{-(r-R_0)/\gamma}},
\]

(8)

with inner radius \( R_0 \), width \( \Delta \), potential depth \( V_0 \), and \( \gamma \) a smoothing parameter. The Woods-Saxon potential does not have a discontinuity at \( r = R_0 \) and \( r = R_0 + \Delta \), as does a square-well potential. However, to see the effects of a discontinuity, one varies the value of \( \gamma \) to emulate such behavior. Thus, this work studies the effects of the discontinuity at the inner and outer radii in the sum rules for three different values of \( \gamma \), as shown in Fig. [I].
Figure 1: (Color on-line). Woods-Saxon model potential for three different values of the smoothing parameter $\gamma = 0.01, 0.05,$ and $0.1$, where one observes that $\gamma = 0.01$ emulates a square-well potential and $\gamma = 0.1$ has a smoother slope at the inner and outer shell cavity radii. For discussion see text.

In our approach, the only acceptable numerical solutions are those consistent with the boundary condition requirements $u_{nl}(r = 0) = 0$ and $u_{nl}(r \rightarrow \infty) = 0$ which connect smoothly at the potential boundaries $r = R_0$ and $r = R_0 + \Delta$. The solution to this problem, within the finite-differences method, has already been reported by one of the author in Ref. [28]. Thus, only a summary of the method is provided here.

One discretizes the function $u(r) \rightarrow u_k$ at the point $r \rightarrow r_k$, known as the $k$-th point on a numerical grid. One type of computational grid consists of a set of fixed coordinate positions $r_k$, which may or may not be uniformly spaced. Thus, $k = 0$ represents $u_0$ and $k = N + 1$ represents $u_{N+1}$ which are the boundary conditions of the system, respectively, and thus the wave function $u_k$ is solved for $N$ points in the grid.

By using the finite-differences definition for derivative and integration [35], and by making a vector array $\vec{u} = \{u_k\}$, one finds that Eq. (7) is rewritten in matrix form as $H\vec{\phi} = E\vec{\phi}$ where $H$ is a tridiagonal matrix. The elements of $H$ are given in Ref. [28], as is the relation between $\vec{\phi}$ and $u$. So, the eigenvalue problem has been reduced to matrix algebra with the advantage of having a tridiagonal matrix which can be solved by LU decomposition [36].

The only limitation of the finite differences approach is the size of the numerical box, such that $r \rightarrow \infty$ is replaced by $r_{max}$ and the numerical precision controlled by the spacing between the adjacent points. A suitable choice of $r_{max}$ renders a sufficiently large number of eigenvalues and eigenfunctions for several sets of confinement conditions ($R_0$, $\Delta$, and $V_0$) and for each value of the angular momentum $l$. An advantage of this method
is that it can efficiently compute as many states as necessary, both in the discrete as well as in the continuous spectrum (pseudo-continuum). Thus, the continuum states are, in this model, represented by a finite number of discrete states placed in the continuum.

The grid box used to solve Eq. (6) extends from \( r = 0 \) to \( r_{\text{max}} = 500 \) a.u. with a total number of points \( N = 2000 \) spaced logarithmically in this range. Thus, the small increments are in the region of small \( r \), providing a good cusp representation of the wavefunction for \( r \to 0 \). The number of eigenvectors (and eigenvalues) is given by the number of grid points, \( N \), for each value of \( l \). As mentioned before, the precision requirements are controlled by \( \Delta r \) or by \( N \), the number of points. Our choice for \( N \) and \( r_{\text{max}} \) is a compromise between good precision, computer memory, and computation time.

Calculations were performed for values of the confining radius \( R_0 = 5.8 \) a.u., \( \Delta = 1.89 \) a.u., that characterize a C\(_{60}\) endohedral cavity \[34\]. We use the values of \( \gamma = 0.01, 0.05, \) and \( 0.1 \) a.u., this last value is suggested by Dolmatov et al. \[34\] for the smoothing parameter. For the potential barrier heights, the values of \( V_0 = 0 \) to 2 a.u. in steps of 0.1 a.u. were used. In particular, the value of \( V_0 = 0.380 \) a.u. has been considered since it characterizes a H@C\(_{60}\) cavity \[34\].

The method has been implemented in a Fortran 95 code that generates the solutions and calculates the DOS sum rules. The eigenvectors and eigenvalues were obtained via tested LAPACK subroutines \[37\].

2.4. Sum rules for endohedral cavities

We will now consider how the sum rules closure relations of equation \[8\] are modified by the presence of the endohedral cavity. By taking into account the hydrogen Coulombic interaction potential and the Woods-Saxon endohedral potential of Eq. (8), the sum rules become

\[
S_{-1} = 2\langle n_0 | r^2 | n_0 \rangle \\
S_0 = N_e \\
S_1 = 4(E_{n_0} - \langle n_0 | V | n_0 \rangle) \\
S_2 = Z |R_{1s}(0)|^2 + \langle u_{1s} | V_0 | u_{1s} \rangle \\
S_3 = 2 \langle u_{1s} | Z f_2(r, R_0 + \Delta) - f_2(r, R_0) \rangle \langle u_{1s} \rangle
\]

where

\[
f_2(r, \Gamma) = \left( \frac{2r}{\Gamma} - \frac{r^2}{\Gamma^2} \right) e^{-(r-\Gamma)/\gamma} + \frac{2(\xi)}{(1 + e^{-(r-\Gamma)/\gamma})^3}
\]

and

\[
f_3(r, \Gamma) = \frac{V_0}{\gamma} e^{-(r-\Gamma)/\gamma} \left( 1 + e^{-(r-\Gamma)/\gamma} \right)^2
\]

We note that the expressions for \( S_k, k = 1, 2, \) and 3 are modified explicitly due to the presence of the confining potential. However, as \( |n_0| \) depends on \( V_0 \) also \( S_k \), for \( k < 0 \) will depend on \( V_0 \). Again, one observes that \( S_3 \) diverges due to the presence of the Coulombic attraction at \( r \to 0 \). Consequently, we will only report results for \( k \leq 2 \).
Figure 2: (Color on-line). Dipole oscillator strength sum rules, $S_k$, as a function of the potential well depth $V_0$ for values of $k$ from -6 to 2 for the case of an endohedral confined hydrogen atom described by the Woods-Saxon potential. The lines represent the sum rules as obtained via the excitation spectrum from the FD approach for $\gamma = 0.01$ a.u., the (◻) symbols with the same line-color correspond to $\gamma = 0.05$ a.u., and (×) with the same line-color corresponds to $\gamma = 0.1$ a.u.. Fig. 2a) gives the contribution from the bound states. Fig. 2b) the contribution of the continuum states and Fig. 2c) the total sum rules are reported. For comparison, we show Ndengue’s values for $S_{-2}$ by the (∆) symbol [38], as well as the free hydrogen atom values for $S_k$ from Bethe and Jackiw [32] (○ symbols). For discussion see text.

3. Results

In Fig 2 the computed sum rule, $S_k$, as a function of the potential well depth $V_0$ is shown for values of $k$ from -6 to 2 for the endohedral atom described by the Woods-Saxon potential. The lines represent the results obtained via the sum over excited states for a value of $\gamma = 0.01$ a.u.. The (◻) symbols with the same color-line are the sum rules for $\gamma = 0.05$ a.u., and (×) for $\gamma = 0.1$ a.u.. The results shown in Fig. 2a) are the contribution from the sum over the bound states. Those of Fig. 2b) are the contributions to the sum rules from only the continuum states and those of Fig. 2c) are the total sum rule when all
Figure 3: (Color on-line). Dipole oscillator strength sum rule, $S_k$, as a function of the potential well depth $V_0$ for values of $k$ from -1 to 2 for the case of an endohedral atom described by the Woods-Saxon potential and its comparison to the closure relations.

Excitations are included, as obtained by the finite-differences method. For comparison, we present the results of Ndengue et al. \[38\] (Δ symbols) for the $S_{-2}$ sum rule which is the polarizability of the system, showing excellent agreement to our results, as well as the hydrogen free atom $S_k$ sum rules from Bethe and Jackiw \[32\] (○ symbols at $V_0 = 0$ a.u.). For all sum rules, we observe a sudden change in the sum rules around $V_0 \approx 0.7$, which correspond to the first avoided-crossing in the energy between the 1s and 2s states (see Fig. 6) for hydrogen confined in an endohedral cavity, where the effects of the potential discontinuity are more noticeable compared to at smaller or larger values of $V_0$. Furthermore, the largest effect occurs in the continuum spectrum for large values of $V_0$.

However, notice that according to the TRK sum rule, we have that $S_0 = 0.99999$ for all the cases considered, which means that we have a complete excitation spectrum.

In Fig. 3 the sum rule is given as a function of the potential well depth $V_0$ for $k = -1$ to 2. We also show values obtained from the closure relations. The lines are the sum rules as obtained from the sum over the excitation spectrum and the symbols with the same color-line are the results of the closure relations, Eq. (9). As observed, the results are almost identical, except at the avoiding crossing $V_0 \approx 0.7$ a.u. where a slight difference is observed. Note that there is a small difference in the sum rules for $V_0 > 0.7$ a.u., the value of the avoiding crossing, which is a consequence of the different excitation spectrum that results from the potential discontinuity at $r = R_0$ and $r = R_0 + \Delta$.

The previous conclusions are also present in the logarithmic sum rule, $L_k$, which is shown in Fig. 4 as obtained through the sum over the excitation spectrum, as a function...
of $V_0$ and for $k$ going from -6 to -1. Again the lines are the results for $\gamma = 0.01$ a.u., the (◻) symbols with the same color-line are for $\gamma = 0.05$ a.u., and (×) symbols with the same color-line correspond to $\gamma = 0.1$ a.u.. Note that we are plotting the negative value of $L_k$ for $k < 0$. Contrary to $S_k$, the values of $L_k$ decrease as the potential-well depth is increased. Again, the largest change in $L_k$ is found for a critical value of $V_0$, as a consequence of the avoided crossing in the energy eigenvalues between the 1s and the 2s states at around $V_0 = 0.7$ a.u..

For the case $k \geq 0, 1,$ and 2, the $L_k$ sum rule is shown in Fig. 5. In this case, $L_0$ is negative for $V_0 < 0.7$ a.u. and becomes positive for $V_0 > 0.7$ a.u.. For $k = 1$ and 2 the bound contribution is negative for $V_0 < 0.7$ a.u while the continuum contribution is positive. Again, the largest effect of the boundary discontinuity is found for $V_0 > 0.7$ a.u..

In Table 1 some representative values of the $S_k$ sum rule for several values of $V_0$ and $k$ are provided for reference purposes as obtained from the sum over excited states within the FD approach for $\gamma = 0.1$ a.u.. Also, for comparison, the closure relations values for
the ground state are given in parenthesis when the closure relation exists.

In Table 2, some values of $L_k$ as a function of $V_0$ and $k$ are provided for reference for $k = -6$ to 2.

In order to better understand these results, Fig. 6 displays the energy values for the five lowest states (1s, 2s, 2p, 3s, and 3p) of the endohedral confined hydrogen system as a function of the potential well depth $V_0$. The lines are the results for $\gamma = 0.01$ a.u., the (◻) symbols with the same color-lines are the corresponding results for $\gamma = 0.05$ a.u. and the (×) symbols with the same color-lines are for $\gamma = 0.1$ a.u.. The first interesting result is the avoided crossing between the $ns$ and the $(n + 1)s$ states, characteristic of this system [34]. It is precisely this avoided crossing for the 1s and the 2s states that plays an important role in $V_0$ dependence of the sum rules. Particularly because it is the 1s state that changes from being localized at the nuclei of the hydrogen atom for $V_0 < 0.7$ and then being localized in the endohedral cavity for $V_0 > 0.7$. Around the avoided crossing, the 1s state is shared between the hydrogen atom and the endohedral cavity in agreement with Connerade’s findings [17].

These conclusions are confirmed by analyzing the wave-functions for the system. In Fig. 7, the wave-functions for the (a) 1s, (b) 2p, (c) 3p, (d) 4p, and (e) 5p states that are involved in the lower DOS transitions are shown for several values of $V_0$. The lines correspond to $\gamma = 0.01$ a.u., the (◻) symbols with the same color-line are for $\gamma = 0.05$ a.u.,
Table 1: Dipole oscillator strength sum rule, $S_k$, for several values of the confinement potential $V_0$ as obtained from the excitation spectrum of the Woods-Saxon endohedra cavity for $\gamma = 0.1$ a.u.. In parenthesis are shown the results from the closure relations. The notation $a(b)$ means $a \times 10^b$.

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<td>2.2156(6)</td>
<td>5.2330(4)</td>
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<td>4.1058(9)</td>
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<td>5.3073(4)</td>
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<td>0.4836</td>
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<td>5.3580(4)</td>
<td>1.2522(3)</td>
<td>29.472</td>
<td>0.5326</td>
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</tbody>
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Table 2: Logarithmic dipole oscillator strength sum rule, $L_k$, for several values of the confinement potential $V_0$ for a value of $\gamma = 0.1$ a.u. The notation $a(b)$ means $a \times 10^b$.

<table>
<thead>
<tr>
<th>$V_0$</th>
<th>$L_6$</th>
<th>$L_5$</th>
<th>$L_4$</th>
<th>$L_3$</th>
<th>$L_2$</th>
<th>$L_1$</th>
<th>$L_0$</th>
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<td>0.0</td>
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<td>-2.4396(1)</td>
<td>-9.5776(0)</td>
<td>-3.8103(0)</td>
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<td>-8.0419(1)</td>
<td>-2.9079(1)</td>
<td>-1.0740(1)</td>
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<td>-1.3898(1)</td>
<td>-4.6922(0)</td>
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<tr>
<td>0.6</td>
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<td>-1.3138(2)</td>
<td>-2.8869(1)</td>
<td>-7.0370(0)</td>
<td>-1.9938(0)</td>
<td>2.6655</td>
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<tr>
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<tr>
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<td>-8.4850(6)</td>
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<td>0.8719</td>
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Figure 6: (Color on-line). The five lowest energy level values of a hydrogen atom confined in an endohedral cavity, as obtained by Eq. (7). The lines represent the results obtained with the Woods-Saxon potential for \( \gamma = 0.01 \) a.u.. The (◻) symbols with same color-line are the corresponding values for the Woods-Saxon potential with \( \gamma = 0.05 \) a.u. and (×) symbols are for \( \gamma = 0.1 \) a.u.. Note the differences around the avoided-crossing for the three different values of the smoothing parameters. See text for discussion.

and the (×) symbols with the same color-line are for \( \gamma = 0.1 \) a.u.. It is evident that the electron in the 1s state shown in Fig. 7a) evolves from having a large probability at the hydrogen nuclear position for small \( V_0 \) values to being found at the cavity shell. This also occurs for the 2p state. For example, the 2p state starts at the nuclei for \( V_0 < 0.7 \), and then it is shared between the hydrogen nuclei and the endohedral cavity at the avoided crossing, and finally for \( V_0 > 0.7 \) a.u. it is completely bounded by the endohedral cavity. Since this state produces the largest contribution to the DOS, from the transition from the 1s to the 2p state then the sudden change in the DOS and therefore in the sum rules occurs as the well depth goes through the avoided crossing. This means that there is a competition between the Coulombic potential and the endohedral well depth as \( V_0 \) deepens. Another interesting result is the effect of the discontinuity of the square-well potential for \( r = R_0 \) and \( r = R_0 + \Delta \) which is simulated by the Woods-Saxon potential for the smallest value of \( \gamma \). In Fig. 7 there is a small difference between the results for \( \gamma = 0.01 \) a.u. (lines) and the results for a smoother cavity (symbols with same color-line) at the position of the discontinuity of the endohedral shell. This is also reflected in the energy values for both potentials, as shown in Fig. 6. For small values of \( V_0 \)
the results are almost identical, but for values of $V_0$ around and larger than the first avoided crossing, the differences start to be noticeable. Another interesting property of the endohedral cavity is that for some states, a node in the wave-function gets trapped inside the endohedral cavity, as observed in Fig. 7 for the states 3$p$, 4$p$, and 5$p$, such that the probability of finding the electron within the cavity for large values of $V_0$ is small. Thus, the electron is confined either inside and outside of the endohedral cavity for $n > 2$ in a $np$ state excitation.

4. Conclusions

By considering the full excitation spectrum of a hydrogenic impurity confined in an endohedral cavity characterized by a radius $R_0$, thickness $\Delta$, and potential well depth
$V_0$, the dipole oscillator strength sum rules are calculated as a sum over all excited states, discrete as well as continuum. The work is complemented by studying the logarithmic sum rule, $L_k$. When the $S_k$ sum rules obey a closure relation in terms of the ground state average values, comparison are made between the computed sum rules and those obtained from the closure relations.

We find that as the cavity well deepens, i.e. increase of $V_0$, the $1s$ state initially confined at the hydrogen atom now becomes trapped by the endohedral cavity for $V_0 > 0.7$ a.u. Also, the $2p$ state becomes trapped by the endohedral cavity such that dipole oscillator strength from the $1s \to 2p$ transition increases as $V_0$ increases and becomes the dominant transition. Higher excitations into the $np$ states have a negligible probability of having the electron in the endohedral shell.

Thus when two interactions are competing in a quantum confined system, there will be a transition in the sum rule and its corresponding closure expression from one interaction to the other for a specific value in the parameter that defines the endohedral confinement, i.e. one interaction will take over from the other. Therefore, the oscillator strength, sum rules, and optical properties of impurity states in a spherical cavity are strongly affected by the confinement strength with implications in material science.

Our calculations also shows that it is necessary to include both bound and continuum states in the calculations in the $S_k$ and $L_k$ sum rules. For negative $k$ the bound state contribution dominates while the contributions from continuum (pseudo) states are by far the largest for positive $k$ (see Figs. 2-5). This conclusion is identical to what we have seen for non-confined hydrogen \[15\] as well as for dipole sum rules of a range of other non-confined atoms and molecules \[39, 40\].

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