The Effect of Confinement on the Electronic Energy and Polarizability of a Hydrogen Molecular Ion

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The electronic energy and the polarizability of a confined hydrogen molecular ion in the ground state and the first excited state, for cavities of different volumes, are calculated using the variational method. In the treatment adopted an alternative molecular wave function is introduced with only one variational parameter and based on wave functions used for confined atoms. © 2016 Wiley Periodicals, Inc.

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Introduction

Studies on the effect of confinement on atomic and molecular systems are being applied in various fields such as the development of Organic Light Emitting Diodes (OLEDs),[1] in protein folding thermodynamics[2] and the development of new carbon adsorbents.[3]

Atomic and molecular systems under high pressure are gaining prominence in the scientific community because of their anomalous behavior. These unusual behaviors can be applied to new technologies. In several recent experimental studies,[3–5] molecules subject to confinement have been analyzed from different viewpoints. In the work of Zerr et al.,[4] the authors decompose hydrocarbons under high pressure and high temperature obtaining hydrogen molecules and diamonds. In the article by Mao and co-workers,[5] results are presented involving the dissociation of H_2O molecules under high pressure using X-rays to form a solid mixture of H_2 and O_2. The experimental work of Gallego et al.[3] confines hydrogen in carbon nanopores and the results obtained can be used as a guide to develop new carbon adsorbents.

Theoretical papers have also been important in the study of high pressure systems. Cottrell[6] made one of the first studies addressing confined molecular systems. Using the variational method, the energy of the orbital of the confined hydrogen molecular ion is calculated for different eccentricities of impenetrable prolate spheroidal boxes. The author used two variational parameters in the trial wave function. In Ref. [7], Ley-Koo and Cruz study some energy levels of the confined H atom and the confined H_2^+ and HeH^{++} molecules. The Schrödinger equation is solved using wave functions written in terms of a series of functions. In calculating the energy for different confinement volumes, they study the hyperfine structure of the confined H atom and the confined H_2^+ molecule. In the work of LeSar and Herschbach,[8] the electronic energy, polarizability, the pressure and the quadrupole moment of the confined hydrogen molecular ion and confined neutral hydrogen molecule for different eccentricities of the confinement area are studied. The variational method was used to get the energy eigenvalues and the trial wave function used in the

confined H_2^+ molecule approach is the same as that presented in Ref. [6]. The results indicate that the smaller the size of box, the lower the values of the polarizability and the quadrupole moment.[8]

Recently, different mathematical methods have been used to address confinement in order to expand the mathematical treatment in the study of such a system. In Ref. [9], the authors use the asymptotic iteration method to get the exact solution of the energy levels of confined hydrogen-like atoms. Cruz and Colín-Rodríguez[10] calculate, using the variational method, the electronic energy levels under confinement of an electron in an H atom and also the H_2^+ and HeH^{++} molecules. The trial wave function used has three variational parameters and is shown to be adaptable to molecular and atomic systems. The energy of the ground state of the molecular orbital of the H_2 molecule for different cavity eccentricities, as well as the vibrational properties of this molecule, is also analyzed by these authors.[11] In Ref. [12], the perturbation method is used to calculate the energy of the He atom under confinement. In the work of Sarsa and Le Sech,[13] the energy of the confined H_2^+ molecule is calculated with a variational approach using the Monte Carlo method and the wave function used in the calculation contain four variational parameters. Kang et al.[14]

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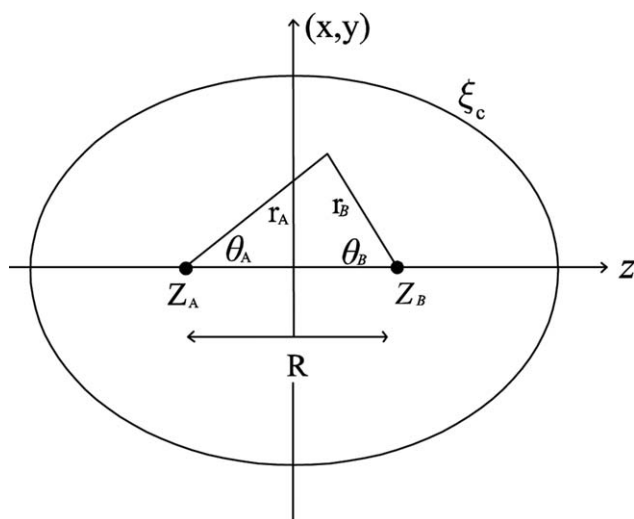
Figure 1. The H_2^+ molecule in an ellipsoidal cavity, where ξ_c is related to the eccentricity of the bounding cavity and Z_i is the atomic number of the atom that forms the molecule; r_i is the distance between the atomic nucleus and the electron; θ_i is the angle between r_i and the azimuth axis z; and R is the internuclear distance. The subscript i identifies the atom, ie., $i=a,b$.

analyze the energies of H_2^+-like impurities confined in spherical quantum dots.

In this article, we propose an approach that allows you to build eigenfunctions based on confined atomic wave functions[15] to be used in the variational method. We calculate the electronic energy and the polarizability of the confined ionized hydrogen molecule in the ground state and the first excited state for different values of cavity eccentricity.

The next section describes the theoretical methodology used in this work and the geometry of the studied molecule is also described. The third section shows the values of electronic energy and polarizability obtained for the H_2^+ molecule and these ground state results are compared to those found the literature.[7,8,10] Finally, the conclusions are in the last section.

Methods

This study looks at the electronic energy and polarizability of an H_2^+ molecule confined in an impenetrable prolate spheroidal cavity with the nuclei located at the focus of the confining surface. First, the geometry of the studied molecule (H_2^+) needs to be defined. It consists of three bodies: two protons and an electron, as shown in Figure 1.

The confinement parameter ξ_c in Figure 1 characterizes the ellipsoid of revolution that defines the enclosing cavity. The eccentricity of this cavity is given by $1/\xi_c$ and the major axis of the ellipsoid is given by multiplying ξ_c by R. To obtain the energy eigenvalues in this type of problem, the following Schrödinger equation must be solved:

$$H\Psi(r_a, r_b, \theta_a, \theta_b, \varphi) = E\Psi(r_a, r_b, \theta_a, \theta_b, \varphi),$$

where H is the Hamiltonian, Ψ is the molecular wave function and E is the energy of the system.

The Schrödinger equation for this problem has no analytical solution, therefore to find a solution we have to use some approximations. The first is the Born-Oppenheimer approach, which uncouples the electron movement from the nuclear movement. Thus, the description related to electrons can be taken considering the fixed nuclei.[16] Using the Born-Oppenheimer approximation, the Hamiltonian of the molecule H_2^+ is written, in atomic units, as:

$$H = -\frac{1}{2}\nabla^2 - \frac{Z_a}{r_a} - \frac{Z_b}{r_b} + \frac{Z_aZ_b}{R} + V, \tag{2}$$

where r_a and r_b are respectively the distances between nucleus a and the electron and between nucleus b and the electron and where Z_a is the atomic number of atom a and Z_b is the atomic number of atom b. In this case, we are studying the hydrogen molecule, so $Z_a = Z_b = 1$. R is the internuclear distance and V describes the system confinement.

For problems involving confined atomic systems, usually the cavities are spherical.[9,15,17,18] In the study of confined molecular systems both spherical cavities[13,19] and ellipsoidal cavities[10,11] have been used. In this work, the confinement system is described as an impenetrable prolate spheroidal cavity. Such confinement may be represented by a potential of the type:

$$V(\xi) = \begin{cases} 0, & 1 < \xi < \xi_c \\ \infty, & \xi > \xi_c \end{cases}, \tag{3}$$

where ξ_c define the size and eccentricity of the confining prolate spheroidal box. Prolate spheroidal coordinates (ξ, η, φ) are used to deal with the system:

$$\xi = \frac{r_a + r_b}{R}, \tag{4a}$$

$$\eta = \frac{r_a - r_b}{R} \tag{4b}$$

and φ is the same as the spherical coordinates.

In the new coordinates, the Hamiltonian (2) is rewritten as:

$$H = -\frac{1}{2}\frac{4}{R^2(\xi^2-\eta^2)}\left[\frac{\partial}{\partial\xi}(\xi^2-1)\frac{\partial}{\partial\xi} + \frac{\partial}{\partial\eta}(1-\eta^2)\frac{\partial}{\partial\eta}\right.$$
$$\left. + \frac{\xi^2-\eta^2}{(\xi^2-1)(1-\eta^2)}\frac{\partial^2}{\partial\varphi^2}\right] - \frac{Z_a}{r_a} - \frac{Z_b}{r_b} + \frac{Z_aZ_b}{R} + V(\xi), \tag{5}$$

where

$$r_a = \frac{R(\xi+\eta)}{2}, \tag{6a}$$

$$r_b = \frac{R(\xi-\eta)}{2}. \tag{6b}$$

The Schrödinger equation resulting from the Hamiltonian of eq. (5) is immediately separated on the azimuth axis around the coordinate φ. However, the same cannot be said for the coordinates ξ and η. Thus, the molecular wave Ψ_β function can be written as

$$\Psi_\beta(\xi, \eta, \varphi) \propto \psi_\beta(\xi, \eta)e^{im\varphi}, \qquad (7)$$

where the quantum number m has the values $m=0, \pm1, \pm2, \cdots$

The mathematical problem of finding eigenvalues and eigenfunctions for the Hamiltonian (5) can be solved by using approximation methods. This article uses the variational method.[20] The approximation method here is to choose an appropriate wave function $\Psi_\beta(\xi, \eta, \varphi)$ to get an energy eigenvalue greater than or equal to the exact energy (E_{exact}). In summary, the variational principle states that:

$$E_{exact} \leq \frac{\int_V \Psi_\beta^*(\xi, \eta, \varphi)\hat{H}\Psi_\beta(\xi, \eta, \varphi)dV}{\int_V \Psi_\beta^*(\xi, \eta, \varphi)\Psi_\beta(\xi, \eta, \varphi)dV} = E_\beta, \qquad (8)$$

where E_{exact} is the exact energy of the problem, $\hat{H}$ is the Hamiltonian operator (5) and $\Psi_\beta(\xi, \eta, \varphi)$ is the chosen wave function. The integral is performed on the total volume the system occupies ($1 < \xi < \xi_c$; $0 < \eta < 1$; $0 < \varphi < 2\pi$) and $dV = (\xi^2 - \eta^2)(R^3/8)d\xi \, d\eta \, d\varphi$. The variational method allows the addition of adjustable variational parameters (β). These parameters are used to minimize the expression of the mean energy $_\langle E_\beta\rangle$, leading to a more refined result. In this work, only one variational parameter was used on the suggested trial wave function. Thus, to further refine the result, the mean energy E_β is minimized with respect to the parameter β:

$$\frac{dE_\beta}{d\beta} = 0. \qquad (9)$$

Due to the features of this problem and the approach taken to construct the molecular orbital, the confined molecule H_2^+ was studied in two states. First, the molecule in state $1\sigma_g$, that is, in the ground state, was analyzed and then the excited state $1\sigma_u$ was analyzed. In both cases, the molecule has symmetry around the azimuth coordinate φ, and consequently, the magnetic quantum number is zero ($m=0$) for both states. Thus, the molecular wave function in this case ($m=0$) is independent of φ and set to $\psi_\beta(\xi, \eta)$.

To solve the integral (8), an appropriate trial wave function is needed. There are different types of trial wave functions that can be used in this case, such as functions which are composed of infinite series[7] and functions obtained by the Linear Combination of Atomic Orbitals (LCAO).[10] Here, based on the results obtained for atomic systems,[15] a new trial wave function for the problem was introduced that combines simplicity and good numerical results.

Combining confined atomic orbitals built with the help of the formalism of supersymmetric quantum mechanics,[15] the following eigenfunction for the state $1\sigma_g$ is used:

$$\psi_\beta(\xi, \eta) \propto \left(N_a(\beta)(\xi_c - \xi)e^{-\frac{R}{2\beta}(\xi + \eta)} + N_b(\beta)(\xi_c - \xi)e^{-\frac{R}{2\beta}(\xi - \eta)}\right). \quad (10)$$

For the state $1\sigma_u$ the following trial wave function is used:

$$\psi_\beta(\xi, \eta) \propto \left(N_a(\beta)(\xi_c - \xi)e^{-\frac{R}{2\beta}(\xi + \eta)} - N_b(\beta)(\xi_c - \xi)e^{-\frac{R}{2\beta}(\xi - \eta)}\right). \quad (11)$$

The terms $(\xi_c - \xi)$ require that the wave function is zero in $\xi = \xi_c$, ξ_c defining the confining cavity, the exponentials corre-

spond to the wave functions of the H atom in the ground state and β is the variational parameter. $N_a(\beta)$ and $N_b(\beta)$ are the constants of atomic normalization of the confined atoms that make up the studied molecule and have the following values:

$$N_a(\beta) = \left(\int_0^{2\pi} \int_{-1}^1 \int_1^{\xi_c} (\xi_c - \xi)^2 e^{-\frac{R}{\beta}(\xi + \eta)}\left(\xi^2 - \eta^2\right)\left(R^3/8\right)d\xi \, d\eta \, d\varphi\right)^{-1}, \qquad (12a)$$

$$N_b(\beta) = \left(\int_0^{2\pi} \int_{-1}^1 \int_1^{\xi_c} (\xi_c - \xi)^2 e^{-\frac{R}{\beta}(\xi - \eta)}\left(\xi^2 - \eta^2\right)\left(R^3/8\right)d\xi \, d\eta \, d\varphi\right)^{-1}. \qquad (12b)$$

With the suggested eigenfunctions, the electronic energy and the average polarizability of the confined H_2^+ molecule in the ground state are calculated and compared to results obtained previously.[7,8,10] The electronic energy and the average polarizability of the same molecule in the excited state $1\sigma_u$ are also calculated. The average polarizability indicates how sensitive the molecule is with respect to being polarized by an external electric field.[20]

For the calculation of this property, the approximation presented by Kirkwood is used.[21] We know that the average polarizability (α) of a molecule is composed of a parallel polarizability component and of two perpendicular polarizability components[8]:

$$\alpha = \frac{\alpha_\parallel + 2\alpha_\perp}{3}, \qquad (13)$$

where $\alpha_\parallel$ is the polarizability parallel to an external electric field and $\alpha_\perp$ is the polarizability perpendicular to this field. These polarizabilities are related to the mean values of $\langle z^2\rangle$ and of $\langle x^2\rangle$ respectively, as follows:

$$\alpha_\parallel \equiv \alpha_{zz} = 4\langle z^2\rangle^2, \qquad (14a)$$

$$\alpha_\perp \equiv \alpha_{xx} = \alpha_{yy} = 4\langle x^2\rangle^2. \qquad (14b)$$

The polarizabilities are related to the average values of the position of the electron cloud of the molecule. As the coordinate system used in this work is that of prolate spheroidal coordinates, the Cartesian coordinates have to be related to the prolate spheroidal coordinates and this relationship is given in Ref. [8]:

$$x = \frac{R}{2}\sqrt{\left(\xi^2 - 1\right)\left(1 - \eta^2\right)}\cos\varphi, \qquad (15a)$$

$$y = \frac{R}{2}\sqrt{\left(\xi^2 - 1\right)\left(1 - \eta^2\right)}\sin\varphi, \qquad (15b)$$

$$z = \frac{R\xi\eta}{2}. \qquad (15c)$$

The average y^2 calculation is not necessary since both the x-axis and the y-axis are defined as axes perpendicular to the polarizability. From the eqs. (15a) and (15b), it can be seen that the mean values of x^2 and y^2 are equal for all confinement volumes.

Table 1. Numerical results of the energy eigenvalues (E_β) obtained for cavities of different eccentricities ($1/\xi_c$) and volume (V).

ξ_c	V	β	E_β	$E_{[7]}$	$E_{[10]}$	$\mid E_{[7]} - E_\beta \mid$	$\mid E_{[10]} - E_\beta \mid$
5.6924	749	1.0988	−0.6031	−0.6025	−0.6022	0.0006	0.0009
2.2237	36.8	1.7581	−0.2959	−0.2500	−0.2499	0.0459	0.0460
1.9934	24.8	1.8920	−0.0471	0.0000	0.0001	0.0471	0.0472
1.7434	14.9	2.1491	0.4890	0.5250	0.5258	0.0360	0.0368
1.6150	10.9	2.3958	0.9918	1.0000	1.0250	0.0082	0.0107
1.3621	4.88	3.3229	2.7210	3.0000	3.0214	0.2790	0.3004

The variational parameter β is used to minimize the amount of electronic energy. The values represented by $E_{[7]}$ and $E_{[10]}$ are eigenvalues given in Refs. [7] and [10], respectively. $\mid E_{[7]} - E_\beta \mid$ and $\mid E_{[10]} - E_\beta \mid$ are the absolute differences between the value from the literature and the value found in this work. The energies, volumes and internuclear distances are in atomic units.

Table 2. Numerical results of total electronic energy eigenvalues (E_β) for cavities with different sizes of major axis ($R\xi_c$) and internuclear distances R.

$R\xi_c$	R	V	β	E_β	$E_{[8]}$	$\mid E_{[8]} - E_\beta \mid$
12	2.024	879	1.086	−0.6013	−0.6021	0.0008
10	2.012	502	1.154	−0.6091	−0.6010	0.0081
8.0	1.955	252	1.261	−0.6129	−0.5937	0.0192
7.0	1.874	167	1.326	−0.6049	−0.5800	0.0249
6.0	1.731	104	1.389	−0.5764	−0.5455	0.0309
5.0	1.518	59.4	1.440	−0.4994	−0.4587	0.0407
4.0	1.248	30.2	1.470	−0.2988	−0.2369	0.0619
3.0	0.936	12.8	1.462	0.2676	0.3867	0.1191
2.0	0.601	3.81	1.385	2.2784	2.5901	0.3117

The column data $E_{[8]}$ are the electronic energy eigenvalues indicated in Ref. [8]. The absolute difference between the result obtained with the result from the literature is shown by $\mid E_{[8]} - E_\beta \mid$. The energies, volumes, and internuclear distances are in atomic units.

The results obtained for the electronic energy and average polarizability described in this section can be compared to data from the literature.[7,8,10] The average values are determined by using the suggested wave functions and the fixed value of β by minimization of eq. (9). These calculations were done for cavities of different eccentricities. For the numerical calculation, the software Wolfram Mathematica was used (Universidad de Valladolid license).

Results

The electron energy and the polarizability of the confined H_2^+ molecule in the ground state $1\sigma_g$ and the excited state $1\sigma_u$ were calculated for different volumes of cavities. First, the results for the molecule in the ground state $1\sigma_g$ are presented and then the results obtained for the excited state $1\sigma_u$. All energies are calculated numerically by the variational method. The energy, volumes and internuclear distances are in atomic units.

The confined H_2^+ molecule in the ground state

With the trial wave function (10) and the Hamiltonian (5), the electronic energy is calculated using the variational method (8). Then, comparing the energy eigenvalue obtained for each confinement parameter value (ξ_c) with results available in the literature (initially those in Refs. [7,10], then those from Ref. [8]). In the calculations performed and shown in Table 1, the value of the internuclear distance is fixed as two atomic units (a.u.), i.e. $R = 2\,a_0 = 2$ bohrs ($a_0 = 0.53$ Å). The size of the semi-major axis is calculated for different values of the parameter ξ_c and the volume of the confining cavity is estimated. Table 1 shows the electronic energy eigenvalues for each volume and the comparison of these results with those shown in Refs. [7] and [10].

The results in Table 1 show that the wave function proposed in this paper presents electronic energy eigenvalues close to those values given in Refs. [7] and [10]. The value obtained practically coincides with that shown in the literature for $V = 749\ a_0^3$. Another result to be noted is that related to $V = 24.8\ a_0^3$. In this case, the results from the literature point to

an energy eigenvalue of zero, while our results show a slightly negative eigenvalue.

However, it is worth remembering that the variational principle states that the results found by the variational method are always greater than or equal to the actual values. As the results obtained here are lower than the previous results, it can be concluded that these results are quantitatively better than the previous ones.

Other findings in the literature for the energy eigenvalues are given in Ref. [8]. These results are particularly interesting since they include the average polarizability calculations for the confined H_2^+ molecule. These calculations are also reproduced here. To determine the average polarizability, first the electronic energy must be calculated to fix the variational parameter β in the suggested wave function. Using this parameter in the wave function (10), $\langle z^2 \rangle$, and $\langle x^2 \rangle$ can be calculated and, hence, the average polarizability (α). The electron energy eigenvalues found for each volume (V) of the cavity shown in Ref. [8] are shown in Table 2. Each cavity has a different-sized major axis ($R\xi_c$).

The data in Table 2 suggest that the wave function used is appropriate, since the results of the energy eigenvalues are smaller than the results from the literature, except for the first result ($R\xi_c = 12$), where the results practically coincide. In this case, the difference is in the fourth decimal place corresponding to a very small error of about 0.13%. In Ref. [8], the

Table 3. Values of $\langle x^2 \rangle$ and $\langle z^2 \rangle$ calculated for different volumes (V) obtained using the suggested wave function (10) and the results from the literature.[8]

V	β	$\langle z^2 \rangle$	$\langle x^2 \rangle$	$\langle z^2 \rangle_{[8]}$	$\langle x^2 \rangle_{[8]}$	$\mid \langle z^2 \rangle_{[8]} - \langle z^2 \rangle \mid$	$\mid \langle x^2 \rangle_{[8]} - \langle x^2 \rangle \mid$
879	1.086	1.325	0.788	1.134	0.632	0.191	0.156
502	1.154	1.219	0.743	1.103	0.613	0.116	0.130
252	1.261	1.029	0.648	1.010	0.556	0.019	0.092
167	1.326	0.886	0.571	0.912	0.500	0.026	0.071
104	1.389	0.714	0.475	0.770	0.420	0.056	0.055
59.4	1.440	0.530	0.366	0.596	0.326	0.066	0.040
30.2	1.470	0.356	0.256	0.415	0.229	0.059	0.027
12.8	1.462	0.207	0.156	0.249	0.140	0.042	0.016
3.81	1.385	0.094	0.075	0.116	0.067	0.022	0.008

Table 4. Parallel ($\alpha_\parallel$), perpendicular ($\alpha_\perp$), and average (α) polarizability values obtained from the trial wave function (10) and the results found in the literature[8] ($\alpha_{\parallel [8]}$, $\alpha_{\perp [8]}$, and $\alpha_{[8]}$) for different volumes.

V	β	$\alpha_\parallel$	$\alpha_\perp$	α	$\alpha_{\parallel [8]}$	$\alpha_{\perp [8]}$	$\alpha_{[8]}$	$|\alpha_{\parallel [8]}-\alpha_\parallel|$	$|\alpha_{\perp [8]}-\alpha_\perp|$	$|\alpha_{[8]}-\alpha|$
879	1.086	7.026	2.485	3.999	5.140	1.600	2.780	1.886	0.885	1.2188
502	1.154	5.947	2.206	3.453	4.864	1.501	2.622	1.083	0.705	0.8308
252	1.261	4.235	1.681	2.532	4.083	1.238	2.186	0.152	0.443	0.3464
167	1.326	3.138	1.306	1.917	3.328	0.998	1.775	0.190	0.308	0.1415
104	1.389	2.037	0.901	1.280	2.372	0.707	1.262	0.335	0.194	0.0176
59.4	1.440	1.123	0.535	0.731	1.421	0.425	0.757	0.298	0.110	0.0261
30.2	1.470	0.507	0.262	0.344	0.688	0.209	0.369	0.181	0.053	0.0254
12.8	1.462	0.172	0.097	0.122	0.247	0.078	0.134	0.075	0.019	0.0119
3.81	1.385	0.036	0.022	0.027	0.054	0.018	0.030	0.018	0.004	0.0032

The absolute differences of the polarizabilities ($|\alpha_{\parallel [8]}-\alpha_\parallel|$, $|\alpha_{\perp [8]}-\alpha_\perp|$, and $|\alpha_{[8]}-\alpha|$) are indicated in the last three columns.

variational method is also used based on the calculation performed but, however, with a different trial wave function from that proposed here and with two variational parameters.

With variational parameters of Table 2 and eqs. (15a) and (15c) which relate the Cartesian coordinates to the prolate spheroidal coordinates, the mean values of x^2 and z^2 can be calculated. These mean values of x^2 and z^2 relate, respectively, to the parallel polarizability eq. (14a) and perpendicular polarizabilities eq. (14b). Finally, these two results give the average polarizability given in eq. (13). The mean values of x^2 and z^2 used to determine the perpendicular and parallel polarizabilities are calculated using the molecular wave functions (10) with their respective normalization for different eccentricities and internuclear distances. The results obtained are show in Table 3.

In Table 3, we find that, for volumes greater than or equal to 252 a_0^3, the $\langle z^2 \rangle$ values are lower than those indicated in the literature and, for volumes below 252 a_0^3, the values of $\langle z^2 \rangle$ are higher. The values of $\langle x^2 \rangle$ obtained in this work are all lower than those in the literature. However, it can be seen that the values of $\langle x^2 \rangle$ and $\langle z^2 \rangle$ are calculated from a wave function which, according to the variational principle, best describes the system being studied, since it leads to a lower energy value. The exception is the case where the volume is equal to 879 a_0^3 where the results practically coincide (Table 2). From the results for the values of $\langle x^2 \rangle$ and $\langle z^2 \rangle$, the values of the parallel, the perpendicular and the mean polarizability are calculated. These values are presented in Table 4.

The values of the parallel ($\alpha_\parallel$) and perpendicular ($\alpha_\perp$) polarizabilities are calculated from eqs. (14a) and (14b), respectively.

Similarly to that observed for the values of $\langle z^2 \rangle$, for volumes greater than or equal to 252 $a_0^{[3]}$ the parallel polarizabilities obtained are lower than those found in the literature and for smaller volumes, higher parallel polarizability values result than those indicated in the literature. The perpendicular polarizability values obtained in this study, similar to the values of $\langle x^2 \rangle$, are all lower than those in the literature. In general, the average polarizability (α), calculated from equation (13), is close to those values obtained in Ref. [8] using a wave function with two variational parameters. The best agreement between the results can be observed for the confinement volume equal to 104 a_0^3.

The confined H_2^+ molecule in the excited state $1\sigma_u$

No studies were found in the literature for the excited state $1\sigma_u$, which prevents a comparison of results. However, the success of the proposed treatment for the ground state condition $1\sigma_g$ indicates that the same methodology can be applied to other states, in particular, to state $1\sigma_u$. The symmetry of the problem and the different parity between these states permit a direct extension of the trial function from the ground state to the first excited state. However, in principle, the methodology can be adapted for other excited states as it was successfully carried out for central force potentials (see, for instance, Ref. [22]). The electronic energy eigenvalues $E_{\beta_{1\sigma u}}$ are calculated from the trial wave function (11) and the Hamiltonian (5). The calculation of the average polarizability depends on the variational parameter ($\beta_{1\sigma u}$), which is obtained by using the variational method, the wave function (11) and the Hamiltonian (5).

Table 5. Numerical results of total electronic energy eigenvalues in the excited state $1\sigma_u$ ($E_{\beta_{1\sigma u}}$) for cavities of different volumes.

$R\xi_c$	V	$E_{\beta_{1\sigma u}}$	$\beta_{1\sigma u}$	$\langle z^2 \rangle_{1\sigma u}$	$\langle x^2 \rangle_{1\sigma u}$	$\alpha_{\parallel 1\sigma u}$	$\alpha_{\perp 1\sigma u}$	$\alpha_{1\sigma u}$
12	879	−0.1509	0.8323	1.8026	0.3905	12.9978	0.6098	4.7391
10	502	−0.1215	0.8387	1.6876	0.3599	11.3919	0.5180	4.1426
8.0	252	−0.0472	0.8389	1.4771	0.3082	8.7273	0.3799	3.1624
7.0	167	0.0383	0.8297	1.3064	0.2705	6.8266	0.2926	2.4706
6.0	104	0.1983	0.8077	1.0841	0.2246	4.7011	0.2018	1.7016
5.0	59.4	0.5029	0.7679	0.8266	0.1737	2.7333	0.1207	0.9916
4.0	30.2	1.1092	0.7068	0.5670	0.1224	1.2858	0.0600	0.4686
3.0	12.8	2.4772	0.6197	0.3345	0.0754	0.4476	0.0227	0.1643
2.0	3.81	6.4414	0.4989	0.1530	0.0367	0.0937	0.0054	0.0348

The minimized variational parameter $\beta_{1\sigma u}$ is shown in the third column. Also shown are the average values x^2 and z^2 and the perpendicular ($\alpha_{\perp 1\sigma u}$), parallel ($\alpha_{\parallel 1\sigma u}$) and average ($\alpha_{1\sigma u}$) polarizabilities
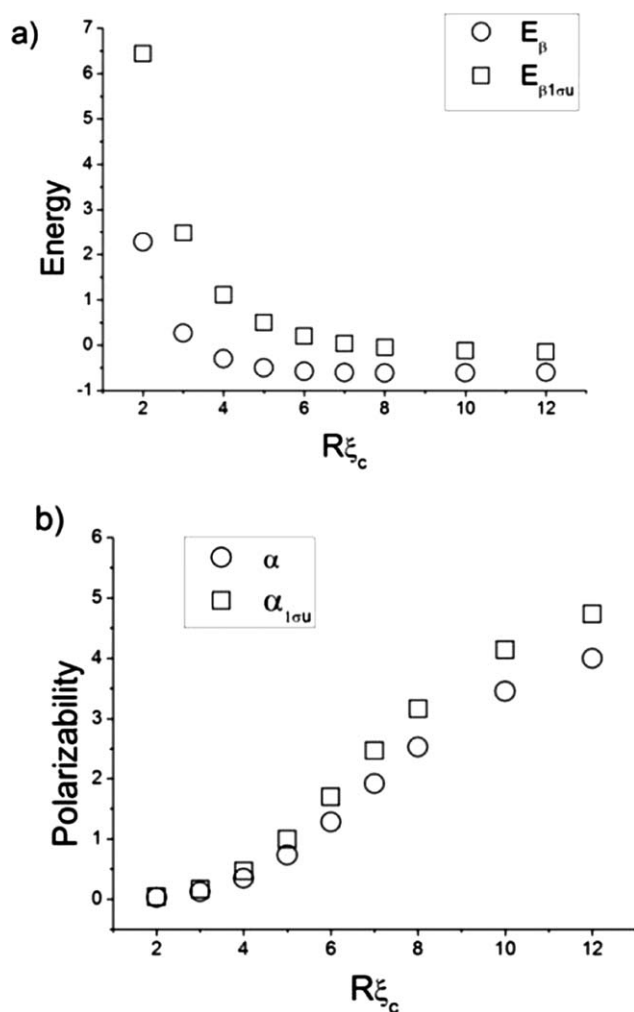
Figure 2. a) Energies eigenvalues computed from ground state (E_β) and first excited state ($E_{\beta 1\sigma u}$), and b) polarizabilities average computed from ground state (α) and first excited state ($\alpha_{1\sigma u}$).

Using the constraint given by eq. (9), the energy is minimized and the value of the parameter $\beta_{1\sigma u}$ is determined with the values of variational parameters $\beta_{1\sigma u}$, the average x^2 and z^2 values are calculated.

Then the values of the average, parallel, and perpendicular polarizabilities from eqs. (13), (14a), and (14b), respectively, are calculated. Table 5 shows the electron energy eigenvalues, average values of x^2 and z^2 (calculated as already normalized functions of molecular waves (11)) and perpendicular ($\alpha_{\perp 1\sigma u}$), parallel ($\alpha_{\parallel 1\sigma u}$), and average ($\alpha_{1\sigma u}$) polarizabilities for the excited state, $1\sigma_u$ of the hydrogen molecular ion and these values are calculated for different cavity volumes. The internuclear distance is determined by the relationship $R\xi_c$.

As expected, comparing the data in Tables 2 and 5, it can be seen that the energies eigenvalues of the excited state are higher than those of the ground state. Analyzing Tables 5 and 4, one can find that the polarizability of the H_2^+ molecule is greater when the molecule is in the excited state $1\sigma_u$. These relations can be observed in the plots in Figure 2.

In terms of the energies eigenvalues (Fig. 2a), it is noted that the largest distortion of these eigenvalues occur in strong
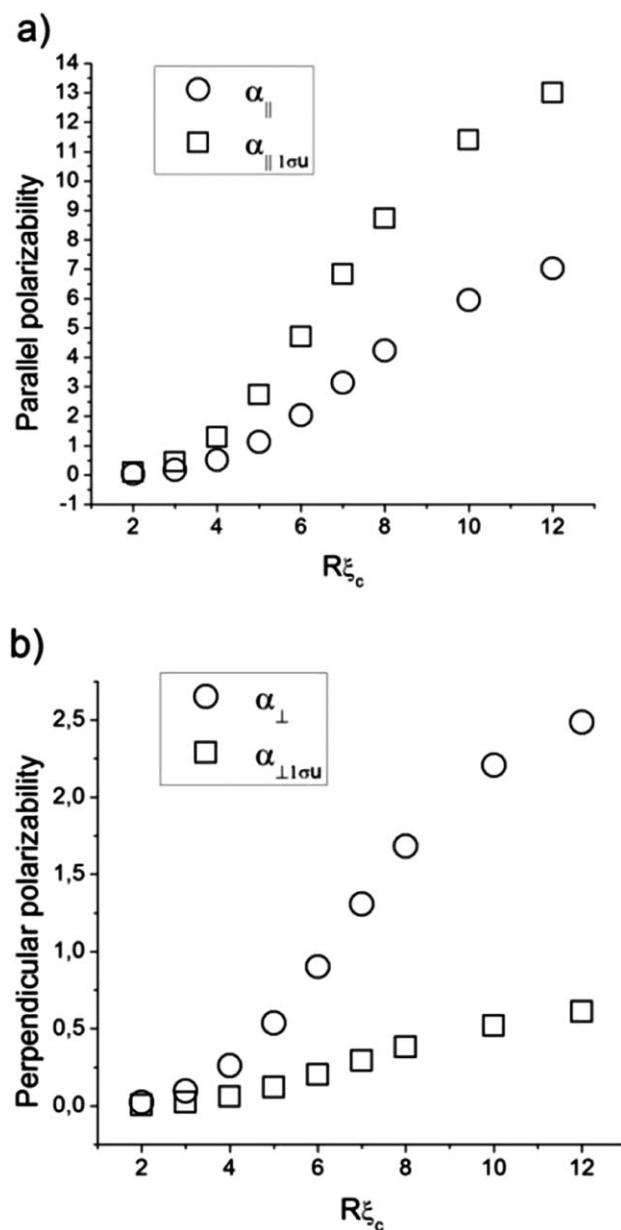

Figure 3. a) Parallel polarizability obtained from ground state ($\alpha_\parallel$) and first excited state ($\alpha_{\parallel 1\sigma u}$), and b) perpendicular polarizabilities obtained from ground state ($\alpha_\perp$) and first excited state ($\alpha_{\perp 1\sigma u}$).

confinement regime. The gap on the ground state energy and the first excited state energy also decreases when the confinement parameter increases. For weak confinement, i.e. large values of the parameter $R\xi_c$, the energies eigenvalues tend to the eigenvalues of the molecule without confinement. This tendency is observed in Figure 2a.

The polarizability behavior shown in Figure 2b indicates that for stronger confinement regime the polarizability tends to zero for both analyzed states. On the other extreme, for a large value of $R\xi_c$, one observes that the difference between the polarizability increases.

The parallel and perpendicular components of the polarizability shown in Table 4 (ground state) and Table 5 (excited state) are plotted in Figure 3. It can be noted in both cases that the values tend to zero for small values of the

confinement parameter. The remarkable result is the behavior of the curves in these cases. The parallel polarizability (Figure 3a) for the ground state ($\alpha_\parallel$) is greater than in the excited state ($\alpha_{\parallel 1\sigma u}$). For the perpendicular polarizability, the situation is reversed. These results are probably related to the geometry adopted, particularly with the different sizes of the axis.

Conclusions

In this paper we introduce a new trial wave function to describe confined molecular systems starting from atomic wave functions and study the hydrogen molecular ion, H_2^+, using the variational method using these functions, eqs. (10) and (11).

Regarding the ground state electronic energies (Tables 1 and 2), the trial wave function proved satisfactory. The results are close to the values indicated by other authors. It can be seen that the energy values obtained are the same as or lower than those shown in other studies,[7,8,10] i.e. the results obtained, according to the variational principle, are numerically better or equivalent to those reported in the literature. These results are obtained despite using only one variational parameter in the present work. It is important to stress that even though the problem has been attacked by different approaches; the methodology introduced here is very simple and provides accurate results.

In some cases, particularly for large confinement volumes, the average polarizability of the molecule in the ground state (Table 4) obtained in this work show results with a significant difference when compared to previous results.[8] However, the polarizabilities calculated here are obtained from a wave function that better describes the confined H_2^+ molecule, indicating that the results presented in this paper are quantitatively better than those presented in previous works.

The electronic properties for the H_2^+ molecule in the excited state $1\sigma_u$ were also calculated. As expected, the resulting energy eigenvalues for the excited state $1\sigma_u$ are greater than the eigenvalues of the ground state. The molecular polarizability increases when the molecule is excited to state $1\sigma_u$. As far as can be seen by the authors, these results are unpublished. However, the successful application of the treatment to the ground state $1\sigma_g$ is an indication that the same approach can be applied to the state $1\sigma_u$.

In addition, it was noted that the results obtained for energies in both states are in qualitative agreement with recent results obtained for spherically cavities from diffusion Monte Carlo method.[23] In particular, the behavior of energy as a function of the confinement parameter is similar. Complementary, admitting that for large values of the confinement volume the system tends to the free one, the results for the H_2^+ without confinement (for instance, Refs. [24,25]) can be compared with the results obtained here for the larger value of the volume. The ground state energy obtained for the system without confinement by Flolov is $-0.602\,633\,511\,30$[24] and by Pilón and Baye is $-0.597\,139\,063\,123\,4$[25] while the result obtained here for $V = 879\ a_0^{[3]}$ is -0.6031 (Table 2). It is worth noting that the cited results[24,25] were achieved without the Born-Oppenheimer approximation.

One can conclude that the approach proposed here leads to a good quantitative description of the confined H_2^+ molecule. It is important to note that the trial wave functions introduced for use in the variational method are based on atomic wave functions and require only one variational parameter, which simplifies the mathematical treatment of the problem.

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