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REGULAR ARTICLE

Ground-state energy for confined H_2: a variational approach

Hugo de Oliveira Batael[1] · **Elso Drigo Filho**[1]

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Abstract

Ground-state energies for confined H_2 molecule are computed using the variational method. The approach proposed here uses a molecular wave function of the valence bond type, written as the sum of the covalent term and the ionic term. The molecule is confined in an impenetrable prolate spheroidal box. The atomic orbitals are built from a previous suggestion inspired by the factorization of the Schrödinger equation. The aim of this work is to propose a new wave function to be used for the confined hydrogen molecule. The polarizability and quadrupole moment are also calculated. The results obtained are in agreement with other results present in the literature, and they lead to a discussion about the relevance of the ionic term in the wave function.

Keywords Molecular confinement · Hydrogen molecule · Variational method · Ground-state energy · Polarizability · Quadrupole moment

1 Introduction

Confined systems attracted the attention of the scientific community for their behavior different to free ones [1, 2]. The spatial confinement affects the physical and chemical properties of atoms and molecules, such as energy levels, polarizability and the quadrupole moment [3–6]. The results of this confinement are applied in a variety of situations such as high-pressure systems [7], zeolites [8], carbon nanotubes [9].

In the study of confined molecules, special attention has been devoted to the ionic hydrogen molecule (H_2^+) [10–15] and the neutral hydrogen molecule (H_2) [16–19]. Small polyatomic molecules have also been analyzed [20–23]. In particular, the eigenvalues of energy for hydrogen molecule inside an impenetrable prolate spheroidal box, with the Born–Oppenheimer approximation, have been discussed in the literature [16, 17, 19], where the eigenvalues are obtained using the variational method and Quantum Monte Carlo technique.

The main objective of this study is to obtain the eigenvalues of energy for a confined hydrogen molecule from the variational method by using a molecular wave function. This function is simpler than others present in the literature [16, 19] and permits results with good numerical accuracy. The suggested trial eigenfunction is also used to compute the polarizability and the quadrupole moment for the H_2 molecule.

Recently, the eigenvalues of energy for a confined hydrogen ion molecule [15] have been obtained by the variational method using a molecular function described as a linear combination of atomic orbitals of 1 s state with just one variational parameter. In this work, the methodology adopted by da Silva et al. [15] is extended for the hydrogen molecule, as previously suggested [24]. In this way, a molecular function of the valence bond type [25] is proposed for a confined hydrogen molecule. This function is the sum of the covalent term and the ionic term, the relevance of this last term being discussed in the present case. The atomic wave functions used to describe the ground state of the molecule have the same shape as the ground state (1s) for a confined hydrogen atom [26].

The ground-state energy eigenvalues are determined for the hydrogen molecule inside a prolate spheroidal box, adopting that the nuclei are fixed at the foci. The numerical values are obtained from the variational method [27] by using a molecular function with one or two variational

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✉ Hugo de Oliveira Batael
hugobatelll@gmail.com

[1] Physics Department, Institute of Biosciences, Humanities and Exact Sciences, São Paulo State University (UNESP), São José do Rio Preto, São Paulo 15054-000, Brazil

parameters. For a better understanding of the system and a test for numerical precision, the relevance of the ionic term in trial wave function was analyzed. In this way, the results obtained by using the wave function in three situations: (1) when the weight of the ionic term is used as a variational parameter (2) with this term is discarded and (3) for the parameter that describes the ionic term fixed equal to one are all discussed.

In order to complete the analysis, the polarizability and the quadrupole moment for the hydrogen molecule are calculated following those made by LeSar and Herschbach [6].

The organization of this work is as follows. In Sect. 2, the mathematical approach used to obtain the ground-state energy for H_2 molecule is introduced. The results are presented in Sect. 3. Section 4 is devoted to some remarks and conclusions.

2 Methods

The Hamiltonian for a confined H_2 molecule in the Born–Oppenheimer approximation [25], in atomic units, is:

$$\hat{\mathrm{H}}_{\mathrm{H}_2} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{A(1)}} - \frac{1}{r_{B(1)}} - \frac{1}{r_{A(2)}} - \frac{1}{r_{B(2)}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}} + V_{\mathrm{c}}, \tag{1}$$

where the Laplacian operators are related to the kinetic energies, the indices 1 and 2 refer to electrons, the indices A and B refer to nuclei, r_{12} is the distance between the electrons, and R_{AB} is the distance between the nuclei. V_{c} is the confining potential, which is adopted as zero inside the cavity and infinity outside.

The molecular wave function used is a valence bond type with the wave atom function inspired by a confined atom system. In this way, for the hydrogen molecule, the wave molecular function used is given by:

$$\psi_{\mathrm{H}_2} \propto \psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2) + \lambda[\psi_A(1)\psi_A(2) + \psi_B(1)\psi_B(2)], \tag{2}$$

where ψ_A and ψ_B are the atomic orbitals A and B for each electron 1 and 2, and λ is a parameter that represents the contribution of the ionic term in the molecular function. The atomic function used here is based on the ground state of the spherically confined hydrogen atom.

From Eq. 2, it is possible identify the covalent term (ψ_{C}) and the ionic term (ψ_{I}) as:

$$\psi_C \propto \psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2) \text{ and } \psi_I \propto \psi_A(1)\psi_A(2) + \psi_B(1)\psi_B(2). \tag{3}$$

The supersymmetric quantum mechanics formalism has been used in order to introduce wave functions for confined systems [26, 28], in particular for the hydrogen atom. The wave functions used by Drigo Filho and Ricotta [26] to describe the spherically confined atomic orbital are given by:

$$\psi_{A(B)} \propto (R_{\mathrm{c}} - r_{A(B)})e^{-\mu r_{A(B)}}, \tag{4}$$

where A and B represent different atomic systems, $(R_{\mathrm{c}} - r_{A(B)})$ is the confined term, R_{c} is the radius of the confining sphere, and μ is the variational parameter. In order to build the molecular wave function, it is convenient to express the atomic function in an appropriate coordinate system, which, in the present case, is the confocal elliptic coordinates (ξ, η, φ), given by:

$$\xi_i = \frac{r_{A(i)} + r_{B(i)}}{R_{AB}}; \quad \eta_i = \frac{r_{A(i)} - r_{B(i)}}{R_{AB}}, \tag{5}$$

φ is the same as the spherical coordinates and in this expression the index i represents the electrons 1 and 2. An ellipsoid of revolution is described for ξ fixed. Then, the confinement can be obtained by the restriction of this coordinate. In this way, the range of variation of the coordinates is $1<\xi<\xi_{\mathrm{c}}$; $-1<\eta<1$; $0<\varphi<2\pi$. This range defines the size of the cavity ($1/\xi_{\mathrm{c}}$ is the eccentricity). The prolate spheroid, defined by $\xi=\xi_{\mathrm{c}}$ and the interfocal distance equal to R_{AB}, has a major axis equal to $R_{AB}\xi_{\mathrm{c}}$, and the two other axes have the same size, i.e., $R_{AB}(\xi_{\mathrm{c}}^2-1)^{1/2}$. Figure 1 is a pictorial representation of the confined H_2 molecule.

The Laplacian, in prolate spheroidal coordinates, considering an azimuthal symmetry, is given by:

$$\nabla_i^2 = \frac{4}{R_{AB}\left(\xi_i^2 - \eta_i^2\right)}\left[\frac{\partial\left(\xi_i^2 - 1\right)}{\partial\xi_i}\frac{\partial}{\partial\xi_i} + \frac{\partial\left(1 - \eta_i^2\right)}{\partial\eta_i}\frac{\partial}{\partial\eta_i}\right], \tag{6}$$

and the barrier of potential, V_{c}, is:

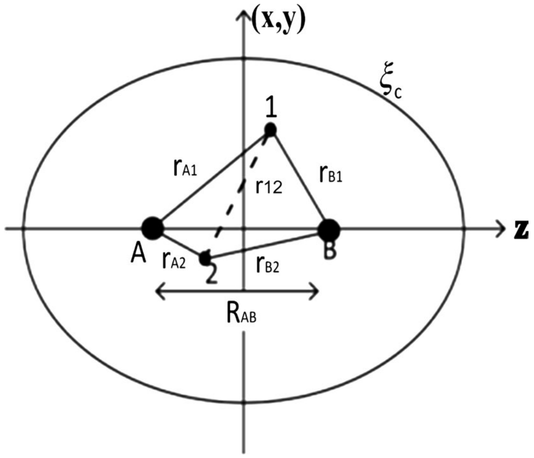

Fig. 1 H_2 molecule inside an ellipsoidal cavity ξ_{c} is related to the eccentricity of the bounding cavity, A and B are the atomic nuclei, r_{A_i} is the distance between the atomic nucleus A and the electrons (1 and 2), r_{B_i} is the distance between the atomic nucleus B and the electrons (1 and 2), and R_{AB} is the internuclear distance

$$V_c = \begin{cases} 0, & 1 < \xi_i < \xi_c \\ \infty, & \xi_i > \xi_c \end{cases} \tag{7}$$

From the conditions of the problem under analysis, the ansatz wave functions proposed for the atomic function, in complete analogy to Eq. 4, are written following those suggested by da Silva et al. [15]:

$$\psi_A(i) \propto \left(\xi_c - \xi_i\right) e^{-\mu(\xi_i+\eta_i)} \text{ and } \psi_B(i) \propto \left(\xi_c - \xi_i\right) e^{-\mu(\xi_i-\eta_i)} \tag{8}$$

The term that describes electron repulsion can be given by the multipolar expansion in prolate spheroidal coordinates [29]. In the present case, there is no explicit dependence on the coordinate φ, and so this expansion is written as:

$$\frac{1}{r_{12}} = \frac{2}{R_{AB}} \sum_{k=0}^{\infty} (2k+1) P_{\mathrm{k}}(\xi_<) Q_{\mathrm{k}}(\xi_>) P_{\mathrm{k}}(\eta_1) P_{\mathrm{k}}(\eta_2), \tag{9}$$

where $P_{\mathrm{k}}(\xi)$ represents the Legendre functions of the first kind and the $Q_{\mathrm{k}}(\xi)$ are the Legendre functions of second kind, as defined by Slater [29].

The mean value of $\hat{\mathrm{H}}_{\mathrm{H}_2}$ is given by:

$$\hat{\mathrm{H}}_{\mathrm{H}_2} = \frac{\int \psi^*_{\mu,\lambda} \hat{\mathrm{H}}_{\mathrm{H}_2} \psi_{\mu,\lambda} \mathrm{d}V}{\int \psi^*_{\mu,\lambda} \psi_{\mu,\lambda} \mathrm{d}V}, \tag{10}$$

where the trial function is given by Eq. 2, $\psi_{\mu,\lambda}$, with the atomic orbitals indicated in Eq. 8.

Following the variational method [27], the eigenvalue obtained in Eq. 10 is an upper limit of eigenvalue of energy. To improve the numerical accuracy of the results, the eigenvalue of energy for the confined molecule is found by minimizing the mean value of the Hamiltonian $\langle \hat{\mathrm{H}}_{\mathrm{H}_2} \rangle$, Eq. 10, in terms of the two variational parameters, μ and λ, for each value of ξ_{c}.

The calculations of polarizability and the quadrupole moment are made following the LeSar and Herschbach [6] approach. Thus, the polarizability is given by:

$$\alpha = \left(\alpha_{\parallel} + 2\alpha_{\perp}\right)/3, \tag{11}$$

where

$$\alpha_{\parallel} = 8\left(\langle z^2 \rangle - \langle z_1 z_2 \rangle\right)^2 \text{ and } \alpha_{\perp} = 8\left(\langle x^2 \rangle - \langle x_1 x_2 \rangle\right)^2. \tag{12}$$

z and x are the Cartesian coordinates, where $\langle z^2 \rangle = \langle z_1^2 \rangle = \langle z_2^2 \rangle$, $\langle x^2 \rangle = \langle x_1^2 \rangle = \langle x_2^2 \rangle$ and indices 1 and 2 represent the electrons, as symmetry is respected $\langle x^2 \rangle = \langle y^2 \rangle$ and $\langle x_1 x_2 \rangle = \langle y_1 y_2 \rangle$.

The quadrupole moment is given by:

$$\Theta = \frac{1}{2} R_{AB}^2 - 2(\langle z^2 \rangle - \langle x^2 \rangle). \tag{13}$$

The Cartesian coordinates x and z can be written in (ξ, η, φ) coordinates as :

$$x_i = \frac{1}{2} R_{AB} \cos \varphi_i \left[\left(\xi_i^2 - 1\right)\left(1 - \eta_i^2\right)\right]^{1/2} \text{ and } z_i = \frac{1}{2} R_{AB} \xi_i \eta_i. \tag{14}$$

3 Results and discussions

The method discussed in the previous section is used to compute the ground-state energy of the confined hydrogen molecule as a function of the confining parameter $R_{AB}\ \xi_{\mathrm{c}}$ (major axis of the ellipsoid).

The eigenvalues of energy are found by the variational method [27] with the molecular function proposed in Eq. 2, and the atomic orbitals are described by Eq. 8. The results obtained for the energies are compared with others present in the literature [17, 19].

The integrals from Eq. 10 are solved numerically, and the repulsion integrals are solved by using the expansion given in Eq. 9 with nine terms of the sum. The criterion used for fixing the number of terms is when the eigenvalue energy does not change to fourth decimal place, on the introduction of a new term to the sum. Thus, the expected numerical error in the eigenvalue of energy is ~ 10^{-4}. Wolfram Mathematica software was used to make the numerical calculations (license from the Universidad de Valladolid, Spain).

Table 1 shows the results obtained by the proposed method and the results found in the literature [17, 19]. It can be seen that the numerical results obtained in this study are similar to previously published results. Comparing the values obtained here with results obtained using Quantum Monte Carlo shown in Pang [17], the largest error is about 5%. Similarly, the results obtained here agree with results found in a paper by Colín-Rodríguez and Cruz [19]. In this cited study, the eigenvalues are obtained using a molecular function composed of atomic orbitals 1*s* and 2*p*-like for a hydrogen atom. The results in this case are close to those results found here, and the largest error is 4%. For the last line in Table 1, the value used for R_{AB} is long enough to admit that the system represents a free molecule [30]. In general, the results obtained indicate that the function proposed here is appropriate for describing the confined hydrogen molecule. Also, the function proposed is simple and it is generated at a low computational cost.

Another indication that the trial function is appropriate to apply in the present problem is that, for a large value of $R_{AB}\xi_{\mathrm{c}}$, the eigenvalues of energy become close to the value obtained for the free molecule. This value is found, for example, using a 40 term James-Coolidge-type expansion [30], and it is 1.17444 hartrees. The difference between this value and the one computed here for $R_{AB}\xi_{\mathrm{c}} = 13$ is $< 3\%$.

Table 1 shows that the value of the variational parameter λ, which quantifies the weight of the ionic term, Eq. 2, decreases and changes the signal for ξ_{c} between 8 and 10. This variation in the value of λ could indicate changes in

Table 1 Numerical results for H_2 ground-state energy obtained by the proposed approach, $E_{(H_2)}$, and the results presented in Pang [17], Colín-Rodriguez and Cruz [19]

$R_{AB}\xi_c$	R_{AB}	ξ_c	μ	λ	$E_{(H_2)}$	E^a	E^b	$\frac{E_{H_2}-E^{a,b}}{E_{(H_2)}}$
2	0.454	4.405	0.160	− 0.68	4.6217	–	4.6433	0.5%
	0.4493	4.52	0.160	− 0.68	4.6212	4.5944	–	0.6%
3	0.683	4.392	0.234	− 0.56	0.6711	–	0.6934	3.2%
4	0.885	4.519	0.311	− 0.48	− 0.4503	–	− 0.4321	4%
	0.8949	4.4697	0.315	− 0.46	− 0.4510	−0.4749	–	5%
6	1.177	5.097	0.455	− 0.27	− 1.0209	–	− 1.0079	1.27%
	1.1771	5.0972	0.430	− 0.28	− 1.0210	−1.0523	–	3%
8	1.321	6.0560	0.528	− 0.1	− 1.1219	–	− 1.1102	1.04%
	1.3503	5.9246	0.577	− 0.11	− 1.1237	−1.1533	–	2.7%
10	1.372	7.288	0.637	0.02	− 1.1431	–	− 1.1292	1.2%
	1.3985	7.150	0.648	0.03	− 1.1436	−1.1702	–	2.3%
12	1.386	8.6580	0.686	0.11	− 1.1465	–	− 1.1322	1.1%
13	1.4	9.2658	0.760	0.14	− 1.1466	–	–	–

The geometric parameters R_{AB} and ξ_c are given as the variational parameters μ and λ. The relative difference between the results obtained here and others [17, 19] is presented in the last column. The energies are in hartree units, and the distances are in bohr

[a] Results presented in Pang [17]

[b] Results presented in Colín-Rodriguez and Cruz [19]

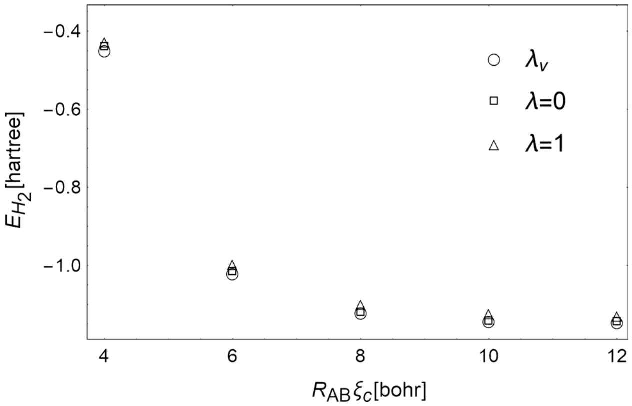

Fig. 2 Eigenvalues of energy for hydrogen molecule $E_{(H_2)}$ versus the major axis of the confinement ellipsoid. The eigenvalues are obtain by using λ as a variational parameter, λ_V, for $\lambda = 0$ and $\lambda = 1$

the physical propriety of the H_2 under certain conditions of confinement. However, the eigenvalue of energy obtained by using $\lambda=0$ is not changed in a significant way from the results obtained using λ as a variational parameter (Fig. 2). The largest difference, in this case $((E_{(H_2)\lambda_{\min}} - E_{(H_2)\lambda=0})/E_{(H_2)\lambda_{\min}})$, was 1.8% for $R_{AB}\xi_c = 3$. The advantage in using the molecular function with $\lambda=0$ is the simplification of the calculations.

Figure 2 shows the behavior of the eigenvalue of energy as a function of the confinement parameter $R_{AB}\xi_c$. The values are obtained by using λ as a variational parameter, for $\lambda = 0$ and $\lambda = 1$. The values of the ground-state energy eigenvalue for the system were seen to decrease as the major axis of the ellipsoid ($R_{AB}\xi_c$) increased.

In a complementary manner, the eigenvalues of energy for $\lambda=0$, which corresponds to discarding the ionic term, are compared with the parameter fixed at $\lambda=1$, which is equivalent to giving the ionic term the same weight as the covalent term in the molecular function. For the values of the major axis shown in Table 1, the molecular function Eq. 2 with $\lambda=0$ leads to an eigenvalue of energy smaller than that obtained with $\lambda=1$ (Fig. 2). The variational principle establishes that a lower eigenvalue is closer to the exact result for the analyzed system. This result reinforced the conclusion that the ionic term only makes a small contribution to the final results.

Following LeSar and Herschbach [6], the polarizability, Eq. 11, and the quadrupole moment, Eq. 13, are calculated. The results are shown in Table 2. The mean values are obtained by using the same eigenfunction that was used to compute the energy eigenvalue, including the variational parameters, shown in Table 1.

Table 2 shows that the results are in agreement with those given in LeSar and Herschbach [6]; the biggest error obtained for the polarizability is 6.4% for $R_{AB}\xi_c=4$ and for the quadrupole moment is 11.4% when $R_{AB}\xi_c=6$. In order to analyze the relevance of variation of the ionic term for system propriety, the results obtained with λ as a variational

Table 2 Polarizability α and quadrupole moment Θ for H_2 as a function of major axis, $R_{AB}\xi_c$, obtained by using the proposed wave function Eq. 2, and the results shown in LeSar and Herschbach [6]

$R_{AB}\xi_c$	R_{AB}	α	α^a	$(\alpha - \alpha^a)/\alpha$	Θ	Θ^a	$\Theta - \Theta^a/\Theta$
2	0.455	0.0494	0.047	0.049	0.0807	0.082	0.016
3	0.686	0.2094	0.197	0.056	0.1786	0.174	0.026
4	0.893	0.5439	0.509	0.064	0.2919	0.272	0.068
6	1.208	1.6993	1.606	0.055	0.4819	0.427	0.114
8	1.355	2.8766	2.769	0.038	0.5314	0.490	0.077
10	1.395	3.6153	3.406	0.058	0.5023	0.493	0.019

The quantities are in atomic units

[a] Results shown in LeSar and Herschbach [6]

parameter were compared with results with fixed $\lambda = 0$. There is no significant difference between the results, which indicates that this term is not relevant for the calculation developed here. From this condition ($\lambda = 0$), the biggest error, when compared to λ as a variational parameter, for the polarizability is 4.7% for $R_{AB}\xi_c = 4$ and, for the quadrupole moment, the largest difference was 1.2% for $R_{AB}\xi_c = 6$.

It is important to emphasize that the proposed molecular function is a compact function that introduced just two variational parameters, Eq. 2, and the results obtained in this work are in agreement with others previously published in the literature [17, 19]. The results obtained using λ as a variational parameter and results to $\lambda = 0$ are better than the results obtained by Colín-Rodriguez and Cruz [19], which indicates that the cited work overestimates the value of the ionic term weight. For $\lambda = 1$, the results found here are worse than those found by Colín-Rodriguez and Cruz since the atom function used here is missing the *p*-like orbital, in the case where the two molecular functions are compared. In this way, for molecules that are more complex, the ionic term can be discarded, as a first approach, and the results are not affected in a significant way. The difference found for the confined hydrogen molecule is $< 2\%$. Thus, the mathematical calculation is simplified to a molecular wave function dependent on just one variational parameter.

4 Conclusions

The ground-state energies for confined H_2 molecule were calculated by the variational method, the molecular orbitals used as a trial function in a combination modified atomic orbitals. The wave functions for confined hydrogen atom, suggested by supersymmetric quantum mechanics formalism [26], are used as an input in this approach. The results shown in Table 1 indicate the accuracy of the treatment. The approach used to describe the H_2 molecule shows a good numerical agreement between the results of energy eigenvalues obtained here and other results presented in the literature [17, 19].

The results showed that it is possible to obtain the eigenvalues of energy using a simple molecular wave function, compared with others proposed [16, 19]. This results in a low computational cost and allows an analysis with more detail of the system in terms of the parameters involved. The results obtained in this study showed that the weight of the ionic term (λ) goes from a positive value to a negative value as a function of the confinement parameter, ξ_c. However, the contribution of this term in energy minimization is small and, for the polarizability and quadrupole moment, this term does not change the results in any significative way, compared white $\lambda = 0$. However, for $\lambda = 1$, the values of energy increase, which indicates, by the variational principle, a worsening in the quality of the results.

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