Quasi-Random Integration in Quantum Chemistry: Efficiency, Stability, and Application to the Study of Small Atoms and Molecules Constrained in Spherical Boxes

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Received 13 March 2006; accepted 16 August 2006

DOI 10.1002/qua.21221

ABSTRACT: This project consists of two parts. In the first part, a series of test calculations is performed to verify that the integrals involved in the determination of atomic and molecular properties by standard self-consistent field (SCF) methods can be obtained through Halton, Korobov, or Hammersley quasi-random integration procedures. Through these calculations, we confirm that all three methods lead to results that meet the levels of precision required for their use in the calculation of properties of small atoms or molecules at least at a Hartree–Fock level. Moreover, we have ensured that the efficiency of quasi-random integration methods that we have tested is Halton=Korobov>Hammersley≫pseudo-random. We also find that these results are comparable to those yielded by ordinary Monte Carlo (pseudo-random) integration, with a calculation effort of two orders of smaller magnitude. The second part, which would not have been possible without the integration method previously analyzed, contains a first study of atoms constrained in spherical boxes through SCF calculations with basis functions adapted to the features of the problem: Slater-type orbitals (STOs) trimmed by multiplying them by a function that yields 1 for $0 < r < (R\text{-}\delta)$, polynomial values for $(R\text{-}\delta) < r < R$ and null for $r > R$, R being the radius of the box and δ a variationally determined interval. As a result, we obtain a equation of state for electrons of small systems, valid just in the limit of low temperatures, but fairly simple. Int J Quantum Chem 107: 879–893, 2007

Key words: Monte Carlo integration; pseudo-random integration; quasi-random integration; atomic integrals; atom in a box; molecular integrals

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International Journal of Quantum Chemistry, Vol 107, 879–893 (2007)

1. Introduction

In principle, numerical integration methods can be used to calculate the expectation value of any wave function applied to any quantum mechanical operator. In practice, however, the convergence of these calculations is often slow [1–6]. Recently, Rodriguez et al. [7] showed that quasi-random integration methods could be used to compute efficiently the one- and two-electron integrals needed by many quantum chemistry calculations. In the present work, we use this integration method to calculate the properties of several small atoms and molecules.

We have developed a software able to carry out restricted or unrestricted Hartree–Fock (RHF or UHF) or second-order Møller–Plesset (MP2) calculations for small atoms or molecules with several types of nonstandard basis functions, as well as the ordinary Slater-type orbital (STO) or Gaussian-type orbital (GTO) basis functions, through pseudo-random and quasi-random numerical integrations [8]. By using this software, we have verified the usefulness of quasi-random integration methods by calculating the atomic and molecular properties of a variety of small systems. The atoms and molecules that we have used for this verification (H, He, Li, H_2, LiH) are very simple; however, the properties to be calculated (atomic energy, R_e, D_e, ϖ_e, $\varpi_e X_e$, dipole moment and Mulliken atomic charges) depend on such a high number of independent integrals, where the results are a very appropriate test framework in which to evaluate the reliability of different numerical integration procedures in the field of quantum chemistry, particularly in relation to the study of systems within enclosures whose volume is somewhat smaller than the volume occupied by the systems under the usual conditions.

After ascertaining that quasi-random methods allow for the calculation of properties of free hydrogen, helium, and lithium atoms and H_2 and LiH molecules within an acceptable precision level, we have applied them to analyze the expected behavior of hydrogen, helium, and lithium atoms, and the H_2 molecule, constrained in spherical boxes of diverse radii by using the Hartree–Fock–Roothaan method with a new type of basis function, and we have obtained an approach to an "equation of state" for the electrons of these atoms.

Finally, we want to emphasize that quasi-random integration has been essential for the managing of the nonstandard basis functions used to carry out the confined atoms and molecules Hartree–Fock calculations presented in Tables IV and VIII.

2. Integration Procedures

2.1. GENERATION OF INTEGRATION POINTS

Quasi-random integration methods [9] differ from the pseudo-random method in the way integration points are chosen. Integration points are no longer selected following a completely pseudo-random method; instead, there is a purpose behind their choice, which is to minimize the error in multiple dimension integrals. We compare the results obtained when integration points are generated by (i) Halton sequences [10], (ii) Korobov sequences [11, 12], (iii) Hammersley sets of points [13], and (iv) pseudo-random numbers (i.e., "traditional" Monte Carlo). The inclusion of the last one allows us to corroborate how substantially quasi-random methods improve the pseudo-random method.

The Halton sequences have been obtained using the subroutine proposed by Berblinger and Schlier [14], which is substantially faster than the direct programming of the Halton algorithm employed at the beginning of our research [7, 15–17]. The Korobov sequences have been chosen according to the following criteria: If α is an irrational number, and its decimal part $\alpha - \ln t(\alpha)$ is called (α), and $\alpha_1 \quad \alpha_2 \ldots \alpha_s$ is linearly independent in the field of rational numbers, the coordinates of the *n*th point of the Korobov sequence are

$$q_i(n) = (n\alpha_i) \qquad i = 1, 2, \ldots, S, \tag{1}$$

where S is the dimension of the integral to be computed. In [9] or [18], it has been proposed to use

$$(\alpha_1, \alpha_2, \alpha_3, \ldots, \alpha_S) = 2^{(1/s+1)}, 2^{(2/s+1)}, 2^{(3/s+1)}, \ldots, 2^{(s/s+1)}. \tag{2}$$

After some preliminary tests, we have chosen the square roots of the S first prime numbers as generators α_i. The coordinates $q_i(n)$ can be subsequently obtained in FORTRAN writing the command:

$$\text{RAN} = \text{DN*BAS} - \text{DINT(DN*BAS)}, \tag{3}$$

where RAN = $q_i(n)$ if BAS = α_i ($=\sqrt{2}, \sqrt{3}, \sqrt{5}, \sqrt{7}, \ldots$) and "DN" is the number **n** matching every point generated expressed in double precision. It is important to emphasize that the use of double precision has proved be essential to obtain a valid generator for high values of **n**. This is because the products $\mathbf{n} \cdot \alpha_i$ are irrational numbers and its truncation error is negligible only when the number of significant figures we are using is higher than the number of digits in $\mathbf{n}^2$.

Hammersley integrations have been made choosing the radial coordinate as

$$R = -\mathrm{DLOG}(GR)/P, \tag{4}$$

with GR the points obtained by uniformly dividing the [0, 1] interval. This allows us to extend the integration interval to [0, ∞]. Parameter P is the exponent of the density function described in the next section, and the remaining coordinates are generated through the Halton method. Finally, the pseudo-random numbers used in the pseudo-random integration have been obtained in the standard fashion, by means of the subroutine proposed in Numerical Recipes, page 199 [19].

2.2. CHOICE OF DENSITY FUNCTIONS

In quasi-random integration methods, as in pseudo-random integration, the use of an appropriate density function in sampling is very important to accelerate the convergence ratio [15, 16]. To be useful for random or quasi-random integrations, density functions $w(\vec{r})$ must accomplish two conditions: (i) sampling of $w(\vec{r})$ should be sufficiently effective, and (ii) function $w(\vec{r})$ should be as similar to the integrand as possible.

In our context, integrands have the form

$$r^{n_\mu+n_\nu+2}e^{-\alpha r}F_{\mu\nu}(\theta, \varphi)\sin\theta,$$

where $F_{\mu\nu}(\theta, \varphi)$ is not a very complicated function of polar coordinates θ, φ. For example, when all the orbitals implicated in the integral are of type "s", $F_{\mu\nu}(\theta, \varphi) = \text{constant}$.

Density functions $w(r) = C_r \exp(-pr)$ for r coordinate, $w(\theta) = C_\theta \sin\theta$, and $w(\varphi) = C_\varphi$ fulfill the first condition, and their product is reasonably similar to the integrand $r^n e^{-\alpha r}\sin\theta$. Consequently, when the integral calculated is a one-electron and monocentric one, and the basis functions are STO or quite similar to these, we use the density function [7, 17]:

$$w(r, \theta, \varphi) = \frac{p}{4\pi}\exp(-pr)\sin\theta. \tag{5}$$

The value of the parameter p, optimized for overlap integrals with STOs of type "s", is

$$p = \frac{\alpha_\mu + \alpha_\nu}{n_\mu + n_\nu + 3}, \tag{6}$$

where α_μ, α_ν, n_μ, n_ν are the parameters of the Slater basis functions involved in the integral. For integrals of a type other than overlap integrals, this value is not the best choice, but it has proved sufficiently good in previous calculations [7, 17].

When the integral has two centers M and N as in molecular calculations, the weight function $w(r, \theta, \varphi)$ can be centered at a point C determined by the expression:

$$\vec{C} = \frac{\alpha_\mu^2\vec{M} + \alpha_\nu^2\vec{N}}{\alpha_\mu^2 + \alpha_\nu^2}. \tag{7}$$

Even though this choice is not optimized, we have found that it yields very good results. It is based in a well-known property of Gaussian functions: the product of two Gaussians centered at different points is another Gaussian centered on a particular point by a formula similar to [7]. In addition to this property, we have the possibility to represent approximately ("STO-1G"), each Slater orbital, by a Gaussian $\exp(-\beta r^2)$ with exponent β proportional to the square of the exponent "a" of the STO $r^n\exp(-ar)$ considered [20, 21].

For two electron integrals (pq|rs), the density function used has been

$$W(r_1, \theta_1, \varphi_1, r_2, \theta_2, \varphi_2) = \frac{p_1}{4\pi}\frac{p_2}{4\pi}\exp(-p_1r_1 - p_2r_2)\sin\theta_1\sin\theta_2 \tag{8}$$

with

$$p_1 = \frac{\alpha_p + \alpha_q}{n_p + n_q + 3} \qquad p_2 = \frac{\alpha_r + \alpha_s}{n_r + n_s + 3}. \tag{9}$$

That means that the position of the first electron is generated with the help of a weight function, while another weight function is used to generate the position of the second electron. The center of the first one is located in

$$\vec{O}(1) = \frac{\vec{P}\cdot\alpha_p^2 + \vec{Q}\cdot\alpha_q^2}{\alpha_p^2 + \alpha_q^2}, \tag{10}$$

while the center of the second one is in

TABLE I

Hartree–Fock energies obtained for H, He, and Li atoms by using quasi-random (Halton, Korobov, Hammersley) and standard MC integration (RND).*

		10^4	10^5	10^6	10^7
H (−0.5000000)	HAL	−0.4999189	−0.4999911	−0.4999993	**−0.4999999**
	KOR	−0.5000342	−0.5000020	−0.5000000	**−0.5000001**
	HAM	−0.4999862	−0.4999994	−0.5000000	**−0.5000000**
	RND	−0.5004050	−0.4991489	−0.5000228	**−0.5001**086
He (−2.8476563)	HAL	−2.8568489	−2.8492684	−2.8483132	**−2.8476**721
	KOR	−2.8504421	−2.8489009	−2.8478704	**−2.8476**252
	HAM	−2.8414565	−2.8473245	−2.8476986	**−2.847**5394
	RND	−2.8335285	−2.8438863	−2.8459965	**−2.847**9495
Li (−7.4184820)	HAL	−7.4324696	−7.4210610	−7.4195383	**−7.4185**012
	KOR	−7.4235902	−7.4204091	−7.4188369	**−7.4184**330
	HAM	−7.4094606	−7.4179209	−7.4186157	**−7.418**3001
	RND	−7.3949305	−7.4086246	−7.4150542	**−7.41**93901

* STO-18G values (in parentheses) is used as exact value to calculate errors. Correct numbers corresponding to 10^7 integration points are underlined.

$$\vec{O}(2) = \frac{\vec{R}\cdot\alpha_r^2 + \vec{S}\cdot\alpha_s^2}{\alpha_r^2 + \alpha_s^2}. \tag{11}$$

(For a detailed explanation of these functions and centers, see Refs. [15], [17], and [21].)

3. Study of the Feasibility of Quasi-Random Integration Methods Through Some Standard Calculations

The sets of integration points described in Section 2.1 have been used to compute all the integrals S_{pq}, T_{pq}, V_{pq}, X_{pq}, and $(pq|rs)$ necessary to evaluate the energy, electronic distribution, and dipole moment of the atoms and molecules mentioned below. Minimal basis sets with variationally optimised exponents have been used for the calculation of this properties; the exponents are the same as those given in [22] (atoms) and [23] (molecules):

H $a_{1s}(H) = 1.0000$
He $a_{1s}(He) = 1.6875$
Li $a_{1s}(Li) = 2.6906$
$a_{2s}(Li) = 0.6396$
H_2 $a_{1s}(H) = 1.1892$
LiH $a_{1s}(H) = 0.9766$
$a_{1s}(Li) = 2.6909$
$a_{2s}(Li) = 0.7075$
$a_{2p}(Li) = 0.8449$

The results of evaluating the energy of atoms with the help of numeric integration using 10^4, 10^5, 10^6, and 10^7 points are shown in Table I. Each of the three quasi-random methods lead to similar results, all of them significantly better than in the case of the pseudo-random integration. For the particular case of 10^7 points, the Halton method seems to be slightly more precise than the other two, even if the difference cannot be regarded as very significant. The results are much worse for multielectronic systems than they are for hydrogen, as it should be expected considering that the level of precision obtained for integrals is much lower for two-electron (six-dimension) integrals than for one-electron (three-dimensional) ones [7, 17]. As we can see in Table I, the quasi-random Halton integration method leads to an accuracy of $\sim 10^{-4}$ a.u. in He or Li energies. This can be enough for the study of some problems and not for some other. We will see at the end of this work that to build up a equation of state for the atomic electrons, it is enough to reach a precision of $\sim 10^{-4}$ a.u. in energies. So we will carry out calculations for confined atoms using 10^7–10^8 integrations points. The STO-18G results have been taken as "exact," as its error is smaller than the rounding error of the data presented.

In the case of H_2 and LiH molecules, values were found for a set of properties that depend on

TABLE II
Properties of the H_2 molecule by using quasi-random and random integration.*

		10^4	10^5	10^6	10^7
R_e (a.u.) (1.383)	HAL	1.402	1.383	1.382	**1.383**
	KOR	1.373	1.384	1.384	**1.383**
	HAM	1.413	1.403	1.383	**1.38**2
	RND	1.369	1.390	1.393	**1.38**4
E_e (a.u.) (−1.12821)	HAL	−1.13483	−1.12840	−1.12865	**−1.128**43
	KOR	−1.13491	−1.13166	−1.12866	**−1.128**30
	HAM	−1.12749	−1.12825	−1.12834	**−1.1282**5
	RND	−1.15182	−1.12962	−1.12533	**−1.1282**4
ω_e(cm^{-1}) (5214.2)	HAL	5446.4	5140.9	5232.9	**52**22.6
	KOR	5666.5	5478.9	5223.4	**52**21.3
	HAM	5281.6	5087.8	5226.4	**52**27.8
	RND	6095.1	5253.5	5183.4	**52**54.5
$\omega_e\chi_e$(cm^{-1}) (172.3)	HAL	74.5	160.5	171.0	**171**.6
	KOR	196.1	166.5	166.4	**171**.8
	HAM	57.9	110.0	169.6	**171**.8
	RND	187.6	187.3	131.6	**1**61.4
P_H (1.000)	HAL	1.009	1.001	1.000	**1.000**
	KOR	0.997	1.000	1.000	**1.000**
	HAM	1.001	1.000	1.000	**1.000**
	RND	0.984	0.998	0.997	**0.99**9
μ_e(D) (0.00000)	HAL	0.0303	0.0025	0.0009	**0.0000**
	KOR	0.0070	0.0013	0.0016	**0.00**07
	HAM	0.0037	0.0007	0.0000	**0.000**1
	RND	0.0245	0.0009	0.0062	**0.00**31

* Values used as reference (in parentheses) are obtained by STO-18G basis functions. Correct numbers corresponding to 10^7 integration points are underlined.

one-electron and two-electron integrals: (i) the bond distance R_e, (ii) the total energy E_e, (iii) the harmonic vibration frequency ω_e, (iv) the anharmonicity constant $\omega_e\chi_e$, and some other properties depending only on one-electron integrals: (v) the electronic population of the H and Li atoms: P_H and P_{Li}, and (vi) the dipole moment μ_e.

Tables II and III show the results of the evaluation of all these parameters integrating with 10^4, 10^5, 10^6, and 10^7 points. One can note that, like in the case of atoms, the results of all three quasi-random integration methods are similar (a bit better Halton or Korobov, than Hammersley) and much better in general than those of the pseudo-random method.

4. Study of Some Atoms Constrained in Spherical Boxes by Using Quasi-Random Integration Methods

4.1. INTRODUCTION

The idea of studying atoms confined in spherical boxes dates back to the early ages of quantum mechanics [24] and has been applied in a wide variety of fields of physics and chemical physics, like the simulation of the effects of pressure on atomic properties [24–40], the liquid state cell model [41, 42], semiconductor quantum dots [43], or the influence of solvents on molecular properties [44]. For more references in this field, the reader

TABLE III
Properties of the LiH molecule by using quasi-random and random integration.*

		10^4	10^5	10^6	10^7
R_e (a.u.) (3.051)	HAL	3.156	3.076	3.052	**3.051**
	KOR	3.317	3.109	3.052	**3.05**3
	HAM	3.147	3.004	3.056	**3.051**
	RND	2.993	3.045	3.055	**3.0**49
E_e (a.u.) (−7.96997)	HAL	−7.98833	−7.97255	−7.97086	**−7.9700**5
	KOR	−7.97886	−7.97332	−7.97069	**−7.9699**0
	HAM	−7.96302	−7.96923	−7.97001	**−7.969**78
	RND	−7.84120	−7.90048	−7.97901	**−7.969**76
ω_e(cm^{-1}) (1501.0)	HAL	2183.8	1610.5	1492.9	**15**12.6
	KOR	2321.5	1339.1	1540.5	**14**92.8
	HAM	1880.5	1614.2	1524.9	**150**7.8
	RND	1489.9	1782.9	1470.2	**15**21.8
$\omega_e\chi_e$(cm^{-1}) (18.6)	HAL	178.8	44.0	21.7	**2**0.6
	KOR	163.6	−126.3	24.3	**1**2.2
	HAM	113.0	68.9	24.4	**1**9.8
	RND	263.1	151.3	13.2	22.5
P_H (1.352)	HAL	1.329	1.355	1.356	**1.35**5
	KOR	1.375	1.354	1.355	**1.35**5
	HAM	1.337	1.360	1.355	**1.35**5
	RND	1.370	1.320	1.346	**1.35**2
P_{Li} (2.648)	HAL	2.671	2.645	2.644	**2.64**5
	KOR	2.625	2.646	2.645	**2.64**5
	HAM	2.663	2.640	2.645	**2.64**5
	RND	2.630	2.680	2.654	**2.648**
μ_e(D) (5.946)	HAL	5.868	5.893	5.918	**5.9**14
	KOR	5.934	5.933	5.915	**5.9**14
	HAM	5.842	5.934	5.914	**5.9**14
	RND	5.847	5.860	5.895	**5.9**10

* Values used as reference (in parentheses) are obtained by STO-18G basis functions. Correct numbers corresponding to 10^7 integration points are underlined.

may consult Fröman et al. [34], who present a list of 64 publications appearing up to 1984, or Varshni [45].

From a qualitative point of view, the effect of placing an atom inside a box should be an elevation in its energy levels, which rise as the movement of electrons becomes more restricted. That brings about a relation of the atomic energy to the volume of the box which, by analogy to the case of the molecules of a gas constrained in the same volume, suggests the idea of finding out the corresponding equation of state.

The variety of existing methods for a quantitative study of the energy of atoms in boxes spans from the exact resolution of the Schrödinger equation in favorable cases [46] to perturbative theories, also including the variational method, which has become a very useful tool for researching systems constrained in boxes with different symmetries [47–52]. For example, research has been carried out in the helium atom within a spherical box, with the intention of modeling the effect of pressure in atoms with more than one electron [53–55]; this atom has also been studied within a box with paraboloidal limits [56], and inside a half-infinite space with paraboloidal bounds [57], as well as in a spheroidal box [58].

An interesting way to carry out this kind of calculation is to use the Roothaan method with basis functions adapted to the boundary conditions of the problem. The main difficulty in this method is focused on the evaluation of the atomic and molecular integrals with nonstandard basis functions. For example, an integral:

$$(\mathrm{pq}|\mathrm{rs}) = \iint \chi_p(1)\chi_q(1)\frac{1}{r_{12}}\chi_r(2)\chi_s(2)d\tau_1 d\tau_2$$

with four basis functions with radial part $r^n e^{-\alpha r}$ (STO), all of them within the interval $0 < r < \infty$ and referred to the same center, it is easy to solve. When the centers of the basis functions are different, the problem is more difficult, but it can be treated through STO-nG expansions. Nevertheless, these procedures are not valid for our case: we want to test the usefulness, to study constrained systems, of basis functions that look like standard basis functions in the permitted areas and change softly when approaching the limits of the forbidden areas. Specifically, we will propose later to study atoms in spheres with radii R, by using basis functions that are an STO within the interval $0 < r < R\text{-}\delta$, and are the product of the STO and an adequate polynomial function within $R\text{-}\delta < r < R$, with the value of δ parameter variationally calculated.

Integrals as (pq|rs) are not analitically solvable with the type of basis functions that we have described in the precedent paragraph (nor with the corresponding integration limits). Not even when they are only one-centered. Nevertheless, quasi-random integration methods allow for carrying out these calculations in a very simple and extendible way, as they facilitate the use of Hartree–Fock–Roothaan methods with basis functions adapted to the contour conditions of the box containing the atom. In the following pages we present calculations made for hydrogen, helium and lithium atoms with the help of the software **UCA–CMC**, which also gives the possibility to easily study other atoms or molecules. This software has been entirely developed by us and is available for free at our website [8].

4.2. BASIS FUNCTIONS FOR THE STUDY OF ATOMS CONSTRAINED IN SPHERICAL BOXES

Standard basis functions are obviously not valid to study atoms constrained in boxes, since they fail to comply with the boundary condition $\psi(r \geq r_0) = 0$. Given that the first eigenfunctions of the atom in the box should be similar to those of the free atoms when the intersection radius r_0 of the box is not too small, a sound alternative can be based on "trimming" the standard functions multiplying them by a function that equals to zero for $r > r_0$. Using the most immediate choice, the simple step:

$$f(r;\, r_0) = \begin{cases} \text{constant} & \text{for} \quad r < r_0 \\ 0 & \text{for} \quad r > r_0 \end{cases} \tag{12}$$

as the trimming function will not be valid, since the radial functions $R(r) = R_0(r) \cdot F(r)$ obtained after trimming would not fulfil the continuity conditions needed for R(r) to belong to the same Hilbert space as the exact functions.

In Ref. [23], focused on the case of the hydrogen atom, hydrogenoid functions multiplied by a trimming function of the type:

$$f(r;\, r_0) = \begin{cases} (1-r/r_0)^k & \text{for} \quad r \leq r_0 \\ 0 & \text{for} \quad r > r_0 \end{cases} \tag{13}$$

are used as a basis functions. In this work, we have defined our trimming functions having three parts: $0 < r < r_0 - \delta$ constant, $r_0 - \delta < r < r_0$ polynomial, $r > r_0$ null. In addition, we have used the Clementi and Raimondi basis functions for atomic calculations [22] as a starting point. To make them fit calculations within spherical boxes, we have multiplied them by two types of trimming functions $f(r, r_0; \delta)$:

1. *Corresponding to a rigid box $f_R(r, r_0; \delta)$:* Continuity of the first- and second-order derivatives of basis functions in $r = r_0 - \delta$ is required. But only the basis functions—not its derivatives—have to be continuous in $r = r_0$.
2. *Corresponding to a not completely rigid box $f_R(r, r_0; \delta)$:* Continuity of the basis functions and their first- and second-order derivatives both in $r = r_0 - \delta$ and in $r = r_0$ is required. We have called this kind of no-rigid box "soft," whose energy levels are, as we will see, rather differ-

ent from its equivalents in a "traditional" rigid box. The parameter r_0 will be called the "trimming radius," while the parameter δ, which determines where the basis function is no longer a pure STO, will be called the "transition width" (Figs. 1 and 2).

The first case is related to the situation in which electrons suddenly meet a totally rigid barrier upon arriving to $r = r_0$. It is the most appropriate choice to calculate the pressure exerted by the electrons on the box containing the atom. A four-parameter polynomial has been chosen as trimming function (Fig. 1), since the number of continuity conditions to be applied is four (one in $r = r_0$ and three in $r = r_0 - \delta$):

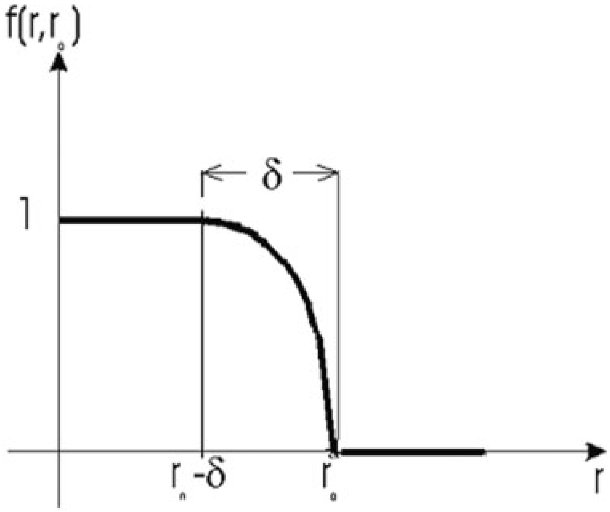

FIGURE 1. Trimming function for a rigid box.

$$f_R\left(r, r_0; \delta\right) = \begin{cases} 1 & \text{for} \quad 0 < r < r_0 - \delta \\ a_0 + a_1(r - r_0)a_2(r - r_0)^2 + a_3(r - r_0)^3 & \text{for} \quad r_0 - \delta < r < r_0 \\ 0 & \text{for} \quad r > r_0. \end{cases} \tag{14}$$

The value of the a_i coefficients can be calculated in terms of the width δ of the transition area, applying the continuity conditions. The results are

$$a_0 = 0 \qquad a_1 = -3/\delta \qquad a_2 = -3/\delta^2 \qquad a_3 = -1/\delta^3.$$

The second case is related to a situation in which the electrons arrive to the forbidden region not as abruptly as in the first case. We consider this case useful for modeling atoms for which, despite not being actually confined, the probability of finding the electrons beyond a given distance to the nucleus is intended to be negligible (as when applying the ZDO approach of semi-empirical methods). For the trimming function of the soft box (Figs. 2 and 3), a fifth-grade polynomial function has been chosen, since it is the simplest function among those giving a chance to apply the six continuity conditions required (three in $r = r_0$ and three in $r = r_0 - \delta$):

$$f_B(r, r_0; \delta) = \begin{cases} 1 & \text{for} \quad 0 < r < r_0 - \delta \\ a_0 + a_1(r - r_0) + a_2(r - r_0)^2 + a_3(r - r_0)^3 + a_4(r - r_0)^4 + a_5(r - r_0)^5 & \text{for} \quad r_0 - \delta < r < r_0 \\ 0 & \text{for} \quad r > r_0. \end{cases} \tag{15}$$

The values obtained for the a_i coefficients of (15) are

$$a_0 = a_1 = a_2 = 0 \qquad a_3 = -10/\delta^3 \qquad a_4 = -15/\delta^4 \qquad a_5 = -6/\delta^5$$

The energies calculated for the atoms depend on the value chosen for δ, especially when the intersection radius is small. For the calculations shown onward, the value of this parameter has been variationally determined.

4.3. ENERGY OF ATOMS CONFINED IN SPHERICAL BOXES

To compute the integrals required to apply the Roothaan's method, the Halton procedure with 10^6, 10^7, and 10^8 points has been used. As the first part of this work places on record, it has proved to be precise enough to study the three systems discussed below.

Tables IV and V show the energies of H, He, and Li atoms confined in "rigid" and "soft" spherical boxes for a variety of intersection radii, obtained

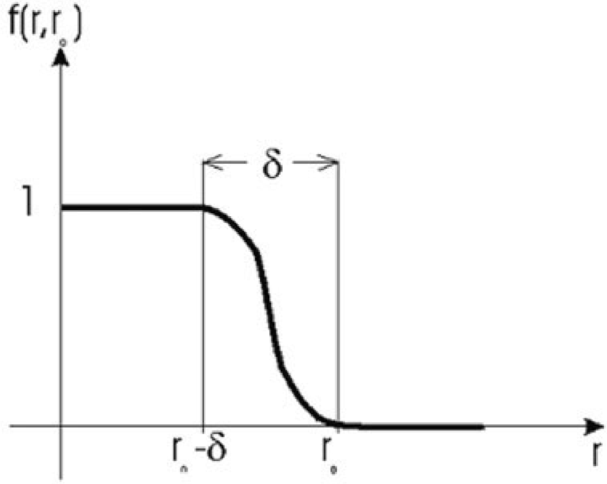

FIGURE 2. Trimming function for a "soft" (i.e., no-rigid) box. Continuity of derivatives of basis functions is required in $r = r_0 - \delta$ and in $r = r_0$.

using our UCA–CMC software [8].[1] In Table IV, the transition width (δ) has been variationally optimized for each radius. In Table V, the δ transition width values have been calculated by means of a parabolic relation $\delta = a + bR + cR^2$ determined by least-square fitting of the (R_i; δ_i^{opt}) data of Table IV, leading to the small differences between comparable results in Tables IV and V.

The first conclusion to be drawn from Table IV is that, as can be expected, the results become similar to those of an untrimmed basis as the intersection radius grows. It is also remarkable that the results change significantly depending on whether the box is rigid or soft, given that the values obtained for energy are lower in the case of rigid boxes. This result may be somewhat unpredictable, since from some standpoints it might seem plausible that placing a system inside a rigid box should elevate the eigenvalues of the energy more than in the case of the box being soft. That does not happen in the case analyzed, for the sizes of the rigid and soft boxes compared are identical, and more restrictions are actually applied in the soft box than in the rigid one.

4.4. EQUATION OF STATE OF THE ELECTRONS OF ATOMS CONFINED IN SPHERICAL BOXES

The results of the preceding section, obtained employing continuous basis functions whose first- and second-order derivatives are continuous in $0 \leq r < R_0$, with the additional condition of being continuous in $r = R_0$ (i.e., those corresponding to a "rigid" box), can also be used to easily obtain an equation of state for the electrons of H, He, and Li atoms in spherical boxes. Taking the fundamental equation of thermodynamics dU = TdS-PdV and the Maxwell relations, one can easily establish the relation [59]:

$$P = T\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial U}{\partial V}\right)_T. \qquad (16)$$

Assuming that the atom is in its ground state (T = 0), and identifying the internal energy U to the lowest eigenvalue of the Schrödinger equation, we can estimate the value of pressure P calculating the derivative of the energy with respect to the volume of the box containing the atom:

$$P = -\left(\frac{\partial E}{\partial v}\right)_T, \qquad (17)$$

where v is the volume occupied by electrons of the confined atom, and E is the energy in this volume. To assign a functional relation between the atom

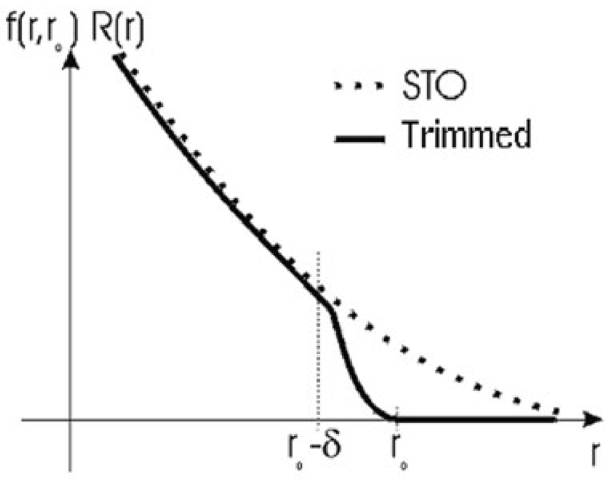

FIGURE 3. 1s original and trimmed radial functions of the type "soft box."

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[1] The UCA–CMC software has been thoroughly tested with basis functions "s" and "p." This software also supports "d" and "f" basis functions; however, only simple cases are covered so far by the tests performed with these types of functions.

TABLE IV

Comparison of the energies of H, He, and Li atoms in rigid and soft boxes.*

	R (a.u.)	δ_{opt} (rigid)	$E_{(rigid\ box)}$	δ_{opt} (soft)	$E_{(soft\ box)}$
H	3	2.568	−0.4228661	1.285	−0.3017934
	4	2.581	−0.4825323	1.258	−0.4533223
	6	2.331	−0.4992263	1.135	−0.4978895
	8	2.284	−0.4999733	0.860	−0.4999231
	10	2.099	−0.4999992	0.450	−0.4999978
	∞	—	−0.4999999	—	−0.4999999
He	3	1.115	−2.8221568	0.630	−2.7955391
	4	1.014	−2.8459982	0.579	−2.8442944
	6	0.717	−2.847667	0.633	−2.8476639
	8	0.485	−2.8476722	0.383	−2.8476721
	10	0.292	−2.8476719	0.317	−2.8476719
	∞	—	−2.8476721	—	−2.8476721
Li	3	3.4235	−6.7816557	1.496	−6.1126862
	4	3.611	−7.1894324	1.956	−6.9616245
	6	4.752	−7.3788369	2.645	−7.3226969
	8	5.773	−7.4107702	2.688	−7.3937648
	10	7.350	−7.4170283	2.326	−7.3226969
	∞	—	−7.4185012	—	−7.4185012

* Data are obtained through quasi-random Halton integration and 10^7 points. Transition width δ has been variationally optimized for each case. Calculations for He and Li are Hartree–Fock–Roothaan with Clementi–Raimondi best-atom basis functions [45].

energy and the box volume, we can test a van der Waals type equation as an initial approach:

$$P = \frac{RT}{v - b} - \frac{a}{v^2} \tag{18}$$

replacing (17) in (18) and considering that the atom is in its ground state (T = 0), we find that:

$$\left(\frac{\partial E}{\partial v}\right)_T = \frac{a}{v^2} \tag{19}$$

and integrating this relation:

$$E - E_\infty = -\frac{a}{v} \tag{20}$$

where E_∞ represents the internal energy for an atom in a box of infinite volume.

Table V shows the values of the energies. In Table VI we can see that the value of $a = -v(E - E_\infty)$ depends on the value of the volume used to compute it. A better relation between the energy of the atom in the rigid box and the box volume can be easily obtained from a virial-like expansion:

$$E - E_\infty = \frac{c_1}{v} + \frac{c_2}{v^2} + \frac{c_3}{v^3} + \ldots, \tag{21}$$

from which pressure can be deduced as the derivative with respect to the volume. In Figure 4 we can see the result of a least square fitting the energies of Li, calculated for $R_0 \geq 3$ Bohr, to a three-term series like (21) and to a van der Waals-like equation (20). Table VII summarizes the results and predicts the errors obtained by these fittings. In Figure 4 we can see that a 3-term Virial type formulae is a reasonable choice for the equation of state of the electrons of the H, He, or Li atoms, for which using atomic units for all variables, we can write:

$$P_H = \frac{-1.2}{V^2} + \frac{3.7 \cdot 10^3}{V^3} + \frac{-2.5 \cdot 10^5}{V^4} \tag{22}$$

$$P_{He} = \frac{-0.2}{V^2} + \frac{1.7 \cdot 10^2}{V^3} + \frac{9.1 \cdot 10^4}{V^4} \tag{23}$$

TABLE V

Energies of H, He, and Li atoms, in rigid spherical boxes, obtained through 10^6, 10^7, and 10^8 Halton integration points.*

	R (a.u.)	δ	$E_{(10^6)}$	$E_{(10^7)}$	$E_{(10^8)}$
H	3	2.593	−0.4228466	−0.4228466	−0.4228466
	3.5	2.559	−0.4633344	−0.4633344	−0.4633344
	4	2.525	−0.4825319	−0.4825319	−0.4825319
	5	2.457	−0.4961865	−0.4961865	−0.4961865
	6	2.388	−0.4992258	−0.4992258	−0.4992258
	8	2.249	−0.4999733	−0.4999734	−0.4999734
	10	2.108	−0.4999992	−0.4999992	−0.4999992
	∞	—	−0.5	−0.5	−0.5
He	3	1.131	−2.8226068	−2.8221312	−2.8221258
	3.5	1.059	−2.8413795	−2.8409415	−2.840938
	4	0.988	−2.8463857	−2.8459717	−2.8459697
	5	0.853	−2.8479357	−2.8475489	−2.8475488
	6	0.725	−2.8480117	−2.8476369	−2.8476377
	8	0.491	−2.848008	−2.847641	−2.8476423
	10	0.288	−2.8480065	−2.8476408	−2.8476423
	∞	—	−2.8480061	−2.8476721	−2.8476423
Li	3	3.373	−6.7816573	−6.7813978	−6.7814797
	3.5	3.539	−7.0438785	−7.0437767	−7.0438586
	4	3.723	−7.189192	−7.1892507	−7.1893071
	5	4.145	−7.3257736	−7.3258756	−7.3259227
	6	4.639	−7.3785338	−7.3786623	−7.3787311
	8	5.842	−7.4105839	−7.4106424	−7.4106943
	10	7.333	−7.4168517	−7.4169133	−7.4169595
	∞	—	−7.4183079	−7.4185012	−7.4184331

* Details of calculations are the same as in Table IV except δ values, that has been improved by a least-square fitting of the data $\{R_i; \delta_i^{opt}\}$ obtained with 10^7 integration points. This improvement of δ values is responsible for the slight differences between equivalent results in this table and in Table IV.

$$P_{Li} = \frac{2.9 \cdot 10^1}{V^2} + \frac{2.2 \cdot 10^4}{V^3} + \frac{-2.0 \cdot 10^6}{V^4}. \qquad (24)$$

5. H_2^+ and H_2 Confined Molecules

The quasi-random integration methods that we have presented and the UCA–CMC software [8] can be used directly to study molecules whose electrons are confined inside intersecting spheres centred on nuclei. We have done some preliminary calculations of this kind, on H_2^+ and H_2 molecules at their experimental internuclear distances. In Table VIII we can see the results for H_2^+ and H_2 by using Halton integration with 10^7 and 10^8 points and a minimal basis set of two 1s atomic orbitals. Exponents has been optimized for the unconfined molecule, $\alpha(H_2^+) = 1.238$ a.u. and $\alpha(H_2) = 1.189$ a.u. The transition widths δ have been variationally optimized for each trimming radius R_i of the basis functions.

For the neutral molecule the expected behavior is observed: the energy raise as the volume diminishes ($E_\infty < E_{6.0} < E_{5.0} < \ldots$). In contrast, for the ionized molecule the energy presents a small minimum in R = 4.5 a.u. for the rigid box, and in R = 6.0 a.u. for the "soft" box. By comparing the results obtained with 10^7 and with 10^8 points, we realize that the origin of the anomaly is not in the numerical errors of the energies. We think that the minimum is due to an inconvenient effect of having

TABLE VI

Variation of the parameter a = $-v(E - E_\infty)$ of the van der Waals type equation upon variation of the volume used to compute it and least-square fitting of the parameter.*

	Points	V = 113.1	V = 179.6	V = 268.1	V = 523.6	V = 904.8	V = 2144	V = 4189	Fitted "a"
H	10^6	−8.725864	−6.584951	−4.682904	−1.996749	−0.700481	−0.057263	−0.003351	7.48 ± 0.75
	10^7	−8.725864	−6.584951	−4.682904	−1.996749	−0.700481	−0.057263	−0.003351	7.48 ± 0.75
	10^8	−8.725864	−6.584951	−4.682904	−1.996749	−0.700481	−0.057263	−0.003351	7.48 ± 0.75
He	10^6	−2.872600	−1.190103	−0.434402	−0.036861	0.005067	0.004075	0.001676	2.09 ± 0.42
	10^7	−2.888615	−1.208781	−0.455849	−0.064508	−0.031848	−0.066699	−0.131109	2.11 ± 0.41
	10^8	−2.885855	−1.204057	−0.448396	−0.048957	−0.004162	0.000000	0.000000	2.10 ± 0.42
Li	10^6	−72.003655	−67.245573	−61.422124	−48.450960	−35.986842	−16.565397	−6.099731	68.57 ± 2.62
	10^7	−72.054866	−67.298572	−61.458208	−48.498764	−36.045472	−16.854498	−6.651396	68.62 ± 2.62
	10^8	−72.037901	−67.271632	−61.424831	−48.438445	−35.921607	−16.597138	−6.172616	68.60 ± 2.62

* These values correspond to spheres whose radii are 3, 3.5, 4, 5, 6, 8, and 10 Bohr. Calculations have been done with 10^6, 10^7, and 10^8 Halton integration points. Volumes in Bohr^3.

optimized the transition width δ in an independent way for each value of the radius of the interlocking spheres: the variational optimization of the parameter δ is more effective for some values of R than for others, and it mask the confinement effects if these are small. To confirm this hypothesis, we have repeated the calculation of E(R_i) maintaining a fixed value of the transition width δ. In this new calculation the minimum disappears, as we can see in Figure 5.

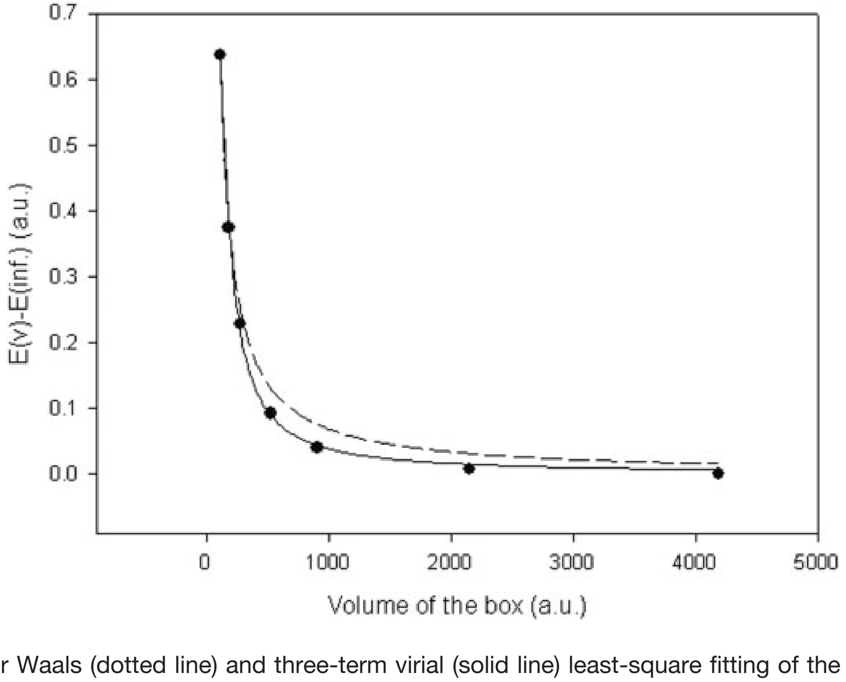

FIGURE 4. van der Waals (dotted line) and three-term virial (solid line) least-square fitting of the energy of Li in a rigid spherical box as a function of volume. The points are the data {E_i; V_i} used to obtain the parameters shown in Table V with 10^8 points. The dotted line is built using the parameter a = 68.60 a.u. in Table VI, and the solid line is built through the Table VII parameters $c_1 = 28.5$, $c_2 = 1.09 \cdot 10^4$, $c_3 = -6.73 \cdot 10^5$ (a.u.). The representations obtained for He and H atoms are very similar.

TABLE VII

Three-term virial type fitting $\sum_{k=1}^{3} (c_k/v_k)$ of the energy E(v)-E(∞) of H, He, and Li in a rigid spherical box as a function of volume for $3 \leq R \leq 10$ Bohr.*

Atom	N points	c_1	c_2	c_3
H	10^6	-1.16 ± 0.15	$(1.86 \pm 0.05) \cdot 10^3$	$(-8.44 \pm 0.43) \cdot 10^4$
	10^7	-1.16 ± 0.15	$(1.86 \pm 0.05) \cdot 10^3$	$(-8.44 \pm 0.43) \cdot 10^4$
	10^8	-1.16 ± 0.15	$(1.86 \pm 0.05) \cdot 10^3$	$(-8.44 \pm 0.43) \cdot 10^4$
He	10^6	$(-2.41 \pm 1.11) \cdot 10^{-1}$	$(8.30 \pm 3.92) \cdot 10^1$	$(3.05 \pm 0.31) \cdot 10^4$
	10^7	$(-1.97 \pm 1.17) \cdot 10^{-1}$	$(7.58 \pm 4.13) \cdot 10^1$	$(3.09 \pm 0.33) \cdot 10^4$
	10^8	$(-2.32 \pm 1.09) \cdot 10^{-1}$	$(8.49 \pm 3.87) \cdot 10^1$	$(3.03 \pm 0.31) \cdot 10^4$
Li	10^6	$(2.86 \pm 0.51) \cdot 10^1$	$(1.08 \pm 0.18) \cdot 10^4$	$(-6.71 \pm 1.44) \cdot 10^5$
	10^7	$(2.86 \pm 0.50) \cdot 10^1$	$(1.08 \pm 0.18) \cdot 10^4$	$(-6.70 \pm 1.43) \cdot 10^5$
	10^8	$(2.85 \pm 0.51) \cdot 10^1$	$(1.09 \pm 0.18) \cdot 10^4$	$(-6.73 \pm 1.44) \cdot 10^5$

* van der Waals and virial fittings for Li are shown in Figure 4. Data from 10^6, 10^7, and 10^8 Halton integration points.

By using the rigid box data quoted in Table VIII and operating as in the atomic case, it is possible to deduce relations between the electronic energy or the pressure, and the volume of the pair of interlocking spheres:

$$V = \frac{2\pi}{3}(4r^3 + h^3 - 3h^2 r), \qquad (25)$$

where $h = r - (R/2)$, r being the radius of spheres and R the internuclear distance (R = 1.988 a.u. for H_2^+ and R = 1.401 a.u. for H_2). In this way, two expressions comparable to (22)–(24) can be deduced:

$$P_{H_2^+} = \frac{-3.6}{V^2} + \frac{3.2 \cdot 10^3}{V^3} + \frac{1.4 \cdot 10^4}{V^4} \qquad (26)$$

TABLE VIII

Comparison of the energies of H_2^+ and H_2 in rigid and soft boxes defined by two intersecting spheres of radius r.*

	R (a.u.)	V (a.u.^{3})	δ_{opt} (rigid box)	$E_{(rigid\ box)}$		δ_{opt} (soft box)	$E_{(soft\ box)}$	
				10^7	10^8		10^7	10^8
H_2^+	3.0	167.25	2.313	−0.5397491	−0.5397722	1.184	−0.5369819	−0.5369587
	3.5	254.04	2.713	−0.5723702	−0.5723897	1.187	−0.5692627	−0.5692815
	4.0	365.95	3.187	−0.5834451	−0.5834466	1.424	−0.5805630	−0.5805674
	4.5	506.12	3.734	−0.5870255	−0.5870073	1.896	−0.5845602	−0.5845494
	5.0	677.68	4.354	−0.5880652	−0.5880435	2.601	−0.5861594	−0.5861335
	6.0	1127.56	5.813	−0.5881777	−0.5881595	4.715	−0.5879638	−0.5879454
	∞	—	—	−0.5865159	−0.5864977	—	−0.5865159	−0.5864977
H_2	3.0	151.99	2.235	−1.0054862	−1.0055110	0.826	−0.9904087	−0.9904269
	3.5	232.79	2.235	−1.0766593	−1.0766888	0.805	−1.0705654	−1.0705962
	4.0	337.78	2.105	−1.1065389	−1.1066094	0.777	−1.1045815	−1.1046466
	4.5	470.11	1.975	−1.1193212	−1.1194022	0.763	−1.1187619	−1.1188432
	5.0	632.91	1.871	−1.1246355	−1.1247148	0.735	−1.1244872	−1.1245667
	6.0	1062.51	1.760	−1.1276392	−1.1276704	0.702	−1.1276317	−1.1276630
	∞	—	—	−1.1281937	−1.1281835	—	−1.1281937	−1.1281835

* Internuclear distances $R(H_2^+) = 1.988$ a.u. and $R(H_2) = 1.401$ a.u. are the experimental values for the unconfined molecules. Calculations with minimal basis sets with exponents optimized for the unconfined molecules $\alpha(H_2^+) = 1.238$ a.u., $\alpha(H_2) = 1.189$ a.u. and quasi-random integration (Halton) with 10^7 and 10^8 points.

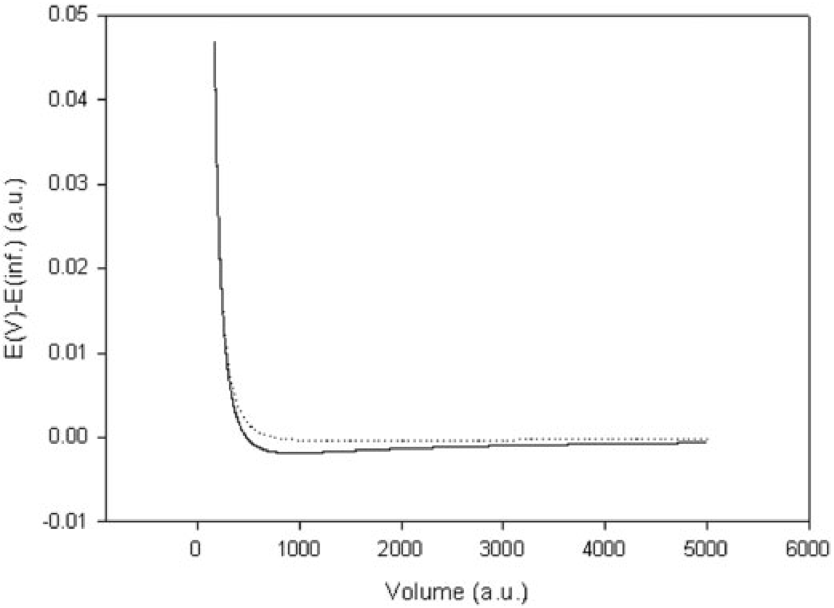

FIGURE 5. Comparison of the energies of the H_2^+ molecule ion with their electron confined inside two overlapped spheres. The curve with a minimum (solid line) corresponds to a variational optimization of the transition width δ for each volume of the interlocking spheres. The upper curve, without minimum (dotted line), has been calculated with a fixed value of the transition width δ (=2.313 a.u.).

$$P_{H_2} = \frac{-4.2}{V^2} + \frac{8.5 \cdot 10^3}{V^3} + \frac{-3.6 \cdot 10^5}{V^4} \qquad (27)$$

It is interesting to point out that the pressure exerted by the electrons of H_2 is much more similar to the pressure exerted by the electron of the hydrogen atom than to the corresponding to the helium atom. These preliminary results are merely tentative, as a minimal basis set with STO exponents optimized for free molecule is far from the best choice. Nevertheless, it seems to us that is enough to prove the usefulness of the quasi-random integration in a molecular context.

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