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# Approximate calculation of physical properties of enclosed central field quantum systems

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It is shown that certain formulas satisfied by exact eigenfunctions are very useful to obtain good approximations for the values of physical properties of enclosed central field quantum systems, even though one uses rather poor trial functions. The properties studied in this work (under the assumption of the validity of a very simple model) are the hyperfine splitting and the pressure of the system.

## I. INTRODUCTION

It is possible to obtain excellent approximations for the eigenvalues of a wide variety of quantum mechanical models by means of variational procedures and a suitable choice of trial functions. Besides, when one applies the Rayleigh-Ritz variational method, the approximate eigenvalues are upper bounds with respect to the exact values. Notwithstanding, it is a well-known fact that variational functions which give very good eigenenergies produce in many cases poor results for calculating other properties of the system. This behavior makes it necessary to develop new methods which would allow us to compute with enough accuracy, physical properties other than energy.

Lately there has been a renewed interest with regard to quantum mechanical models that are subjected to Dirichlet boundary conditions. This kind of models constitutes a first approximation in the study of pressurized systems. Within this area, several physical properties have a marked interest, in addition to the energy, among which hyperfine splitting,<sup>1-6</sup> polarizability,<sup>4,7,9</sup> nuclear magnetic shielding,<sup>4,8,9</sup> and pressure<sup>1,4,7</sup> deserve particular mention.

The hyperfine splitting is given by the Fermi contact term, whose calculation requires the knowledge of the value corresponding to the wave function in the origin, i.e.,  $\Psi(0)$ . Then, it is clear that we need a good enough method to compute accurately local properties, such as  $\Psi(0)$ . In this connection, the works presented by Trivedi<sup>10</sup> and Killingbeck and Galicia<sup>11</sup> are of special interest. The former gives an expression to calculate  $\Psi(0)$ , which is based upon the relationship  $\Delta(1/r) = -4\pi\delta(\vec{r})$ .

The second work presents several alternative formulas to determine the Fermi contact term. However, the results obtained in both cases are related to models under usual boundary conditions, and consequently, they cannot be applied in a direct fashion to the analysis of pressurized systems.

In this work we show which are the modifications that must be introduced in the expressions deduced by Trivedi<sup>10</sup> and Killingbeck and Galicia,<sup>11</sup> in order to be applied in those cases where the wave function is constrained to fulfill the Dirichlet boundary conditions. The presence of these boundary conditions allows one to deduce several alterna-

tive formulas to calculate  $\Psi(0)$ , which are not admissible when the wave function makes null, in an asymptotic way, at infinite.

In order to perform the necessary comparisons with respect to the exactness of these formulas, we employ a simple model which has been widely studied: the hydrogen atom enclosed within a container with spherical impenetrable walls. This particular choice is due to the fact that all the quantities of physical interest have been computed for this model.

Although, as stated previously, the aim of this work is to study the properties of pressurized systems, our results may possess a deep interest in other closely related fields, where it is necessary for the calculation of  $\Psi(0)$ , too.<sup>12-16</sup>

The paper is organized as follows: in Sec. II we develop various alternative mathematical formulas for  $\Psi(0)$  as well as for the pressure exerted on the system (according to the model under consideration). In addition, we show several properties associated with the solutions of the Schrödinger equation, which were not considered before.<sup>1-8</sup> These properties permit one to determine the quality of the trial wave functions. In Secs. III and IV we calculated  $\Psi(0)$  with the help of the relations deduced in Sec. II, using two very simple approximate functions. In this manner, we can test their degree of goodness with respect to the calculation of  $\Psi(0)$ . In Sec. V we make a comparison of the various mathematical expressions to calculate the pressure using three different trial functions. Finally, in Sec. VI we offer a brief commentary about the general conclusions derived from the previous sections.

## II. SOME MATHEMATICAL PROPERTIES OF BOUNDED CENTRAL FIELD MODELS

The stationary Schrödinger equation for a particle with mass  $m$ , that is moving under the influence of a central field potential  $V(r)$ , within a spherical volume of radius  $r_0$ , has the form

$$-\frac{\hbar^2}{2m}\Delta\Psi(\vec{r}) + V(r)\Psi(\vec{r}) = E\Psi(\vec{r}), \quad (1a)$$

$$\Psi|_{r=r_0} = 0. \quad (1b)$$

Owing to the spherical symmetry of the potential function and the boundary conditions, the wave function  $\Psi_{nlm}(\vec{r})$  can

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be written as a product of a radial function  $R_{nl}(r)$  and the spherical harmonic  $Y_l^m(\theta, \varphi)$ .

The radial function  $R(r)$  (for the sake of simplicity we will omit unnecessary subindices) satisfies the differential equation

$$-\frac{1}{2}u''(r) + U_l(r)u(r) = Eu(r), \quad (2a)$$

$$u(r) = rR(r); \quad u(0) = u(r_0) = 0, \quad (2b)$$

$$U_l(r) = V(r) + \frac{l(l+1)}{2r^2}. \quad (2c)$$

In what follows, we will use atomic units. The boundary conditions (1b) and (2b) were introduced with the purpose to be able to define the pressure  $P(r_0)$  for the quantum system<sup>7</sup>:

$$P(r_0) = -\partial E / \partial \Omega = -1/(4\pi r_0^2) \frac{\partial E}{\partial r_0};$$

$$\Omega = \frac{4}{3}\pi r_0^3. \quad (3)$$

The pressure is related to the kinetic energy and the virial of the force due to the potential  $V(r)$ , through the quantum mechanical virial theorem<sup>17,18</sup>:

$$-r_0 \frac{\partial E}{\partial r_0} = 2\langle T \rangle - \langle rV' \rangle = 2E - \langle 2V + rV' \rangle. \quad (4)$$

The change of the energy with the radius  $r_0$  is proportional to the square of the slope of  $u(r)$  on the surface<sup>19,20</sup>:

$$\frac{\partial E}{\partial r_0} = -\frac{1}{2}u'(r_0)^2 = -\frac{1}{2}r_0^2 R'(r_0)^2, \quad (5)$$

whenever  $u(r)$  is normalized

$$\int_0^{r_0} u^2(r) dr = 1. \quad (6)$$

If Eq. (2a) is multiplied by an integrable function  $F(r)$ , and then is integrated between 0 and  $r_0$ , we obtain the following expression for the  $s$  states ( $l=0$ ):

$$F(r_0)u'(r_0) - F(0)u'(0) = \int_0^{r_0} \{2F(V-E) - F''\}u dr. \quad (7)$$

This last equation is equivalent to that deduced by Killingbeck and Galicia<sup>11</sup> when  $r_0 = \infty$  and  $F(r_0)u'(r_0) = 0$ . For  $F(r) = 1$  and  $F(r) = r$ , Eq. (7) gives

$$u'(0) = u'(r_0) + 2 \int_0^{r_0} (E - V)u dr, \quad (8)$$

$$r_0 u'(r_0) = 2 \int_0^{r_0} r(V - E)u dr. \quad (9)$$

The substitution of Eqs. (5) and (9) in Eq. (8), allows us to arrive at two relations for  $u'(0)$ :

$$u'(0) = u'(r_0)(|u'(r_0)|)^{-1} \left( -2 \frac{\partial E}{\partial r_0} \right)^{1/2} + 2 \int_0^{r_0} (E - V)u dr, \quad (10)$$

$$u'(0) = 2 \int_0^{r_0} (E - V) \left( 1 - \frac{r}{r_0} \right) u dr. \quad (11)$$

As a general rule, we can deduce any number of formulas for  $u'(0) = R(0)$  as desired. However, here we will restrict our-

selves to the three given before, plus an additional one to be presented in the next section.

Equation (5) assures us that the energy is a decreasing monotonous function of the sphere radius. Naturally, an acceptable trial function within a certain range of  $r_0$  values must reproduce this behavior in such a range. Furthermore, it should be of great interest to be able to determine the change of  $R(0)$  with  $r_0$ , in order to have a way of testing the quality of the trial function. Such dependence has not been reported in a rigorous manner in those previous works related with the subject at hand [Refs. 1-9, 19 and 20 (and references cited therein)].

In the following, we will show that for certain potential functions and for the ground state,  $R(0)$  is a monotonous decreasing function of  $r_0$ .

**Lemma I.** Let  $g(r)$  be an integrable function within  $(0, r_0)$  such that  $g(r) > 0$  if  $0 < r < r_1$ , and  $g(r) < 0$  if  $r_1 < r < r_0$ . Let  $f(r)$  be an increasing monotonous function in  $(0, r_0)$  such that  $f(r)g(r)$  is integrable in the interval. Then

$$\int_0^{r_0} f(r)g(r)dr < f(r_1) \int_0^{r_0} g(r)dr. \quad (12)$$

The demonstration is immediate, if one takes into account that

$$\int_0^{r_1} \{f(r) - f(r_1)\}g(r)dr < 0$$

and

$$\int_{r_1}^{r_0} \{f(r) - f(r_1)\}g(r)dr < 0.$$

**Lemma II.** There is one and only one zero of  $\partial u / \partial E$  between two consecutive zeros of  $u(r)$ .

**Demonstration.** The differentiation of Eq. (2a) with respect to  $E$ , the multiplication of the result by  $u(r)$ , and the final integration between 0 and  $r$  allows us to obtain the relationship

$$u'(r) \frac{\partial u(r)}{\partial E} - u(r) \frac{\partial u'(r)}{\partial E} = 2 \int_0^r u^2 dr. \quad (13)$$

If  $r_i$  and  $r_j$  are two consecutive zeros of  $u(r)$ , from Eq. (13) we deduce the inequalities

$$u'(r_i) \partial u(r_i) / \partial E > 0;$$

$$u'(r_j) \partial u(r_j) / \partial E > 0. \quad (14)$$

Since  $\text{sgn } u'(r_i) \neq \text{sgn } u'(r_j)$ , then we can assert that  $\partial u(r) / \partial E$  has at least one zero  $r'$  within the interval  $(r_i, r_j)$ . But because of

$$\left( \frac{\partial u}{\partial E} \right)'(r') = \frac{\partial u'(r')}{\partial E} = -\frac{2}{u(r')} \int_0^{r'} u^2 dr, \quad (15)$$

we conclude that  $r'$  is the only zero of  $\partial u / \partial E$  within the interval  $(r_i, r_j)$ .

**Lemma III.** If  $f(r)$  is a monotonous increasing and integrable function in  $(0, r_0)$ , and

$$\langle f \rangle = \int_0^{r_0} f(r)u^2(r)dr \quad (16)$$

then, the inequality

$$\frac{\partial \langle f \rangle}{\partial r_0} > 0 \quad (17)$$

is satisfied for the ground state.

*Demonstration.*

$$\frac{\partial \langle f \rangle}{\partial r_0} = 2 \frac{\partial E}{\partial r_0} \int_0^{r_0} f(r) u \frac{\partial u}{\partial E} dr. \quad (18)$$

If  $u(r)$  represents the ground state, by Lemma II  $g(r) = u(r) \partial u(r) / \partial E$  possesses one and only one zero within  $(0, r_0)$ . From Eq. (13) it follows that  $\text{sgn } \partial u(r_0) / \partial E = \text{sgn } u'(r_0)$ , which assures us that  $g(r) > 0$  for  $0 < r < r_1$  and  $g(r) < 0$  for  $r_1 < r < r_0$ . Then, from Lemma I and the normalization condition (6), we arrive at Eq. (17).

*Theorem.* If  $-V'(r)$  and  $2V(r) + rV'(r)$  are monotonously increasing functions in the interval  $(0, r_0)$ , then

$$\partial R^2(0) / \partial r_0 < 0 \quad (19)$$

is verified for the ground state.

*Demonstration.* Replacing  $F(r)$  by  $u'(r)$  in Eq. (7), we obtain

$$u'(r_0)^2 - u'(0)^2 = -2 \langle V' \rangle, \quad (20)$$

$$\partial u'(0)^2 / \partial r_0 = 2 \partial \langle V' \rangle / \partial r_0 - 2 \partial^2 E / \partial r_0^2. \quad (21)$$

From the virial theorem (4), it follows that

$$-r_0 \partial^2 E / \partial r_0^2 = 3 \partial E / \partial r_0 - \partial \langle 2V + rV' \rangle / \partial r_0. \quad (22)$$

According to Lemma III and the hypothesis of this theorem, it is deduced that  $\partial^2 E / \partial r_0^2 > 0$  and  $\partial \langle V' \rangle / \partial r_0 < 0$ , so that it concludes the demonstration of Eq. (19).

*Corollary.* For any potential with the general form  $V(r) = \lambda r^\alpha$ ,  $R_{1s}(0)^2$  is a decreasing function of  $r_0$ , whenever  $\lambda > 0$  and  $0 < \alpha < 1$  or  $\lambda < 0$  and  $-2 < \alpha < 0$ .

The conditions imposed on  $V$  and  $u$  to prove Eq. (19) are, surely, too restrictive. However, the result afforded by the previous theorem is sufficient for our present purposes, because it includes the bounded hydrogen atom as a particular case:

$$\lambda = -1 < 0 \text{ and } \alpha = -1.$$

### III. HYPERFINE SPLITTING: 2s HYDROGEN-LIKE TRIAL FUNCTION

The hyperfine splitting is given by the Fermi contact term  $A$ ,

$$A = \frac{2}{3} \mu_0 \mu_N g_s g_I |R(0)|^2 \quad (23)$$

and its determination requires the previous knowledge of  $R(0)$ . All the symbols in Eq. (23) have their usual meaning.<sup>1-6</sup>

The purpose of this section is to perform the calculation of  $A$  for the hydrogen ground state [ $V(r) = -1/r$ ] using the trial wave function

$$R(r) = N(\alpha, r_0)(r_0 - r) \exp(-\alpha r/2), \quad (24)$$

where  $N(\alpha, r_0)$  is the normalization factor.

This function satisfies the virial theorem for every  $r_0$  value considered, if the scaling factor is adjusted variationally [ $\alpha = \alpha(r_0)$ ].<sup>21</sup> Then, the trial function (24) coincides with the exact eigenfunction when  $r_0 = 2$  a.u. ( $\alpha = 1$ ) and  $r_0 \rightarrow \infty$  ( $\alpha \rightarrow 2$ ). In the second column of Table I we show the  $A$  values calculated with great exactness by Ley-Koo and Rubinstein<sup>4</sup> ( $A_1$ ) for different  $r_0$  values. The third column ( $A_2$ ) shows the  $A$  values computed directly with the function (24) [ $R(0) = N(\alpha, r_0)r_0$ ].<sup>21</sup>

The results show that  $A_2$  decreases monotonically up to a certain minimum value, from which it increases to reach asymptotically the free atom value. This behavior is not acceptable, according to the preceding theorem. Since the function (24) does not possess adjustable parameters other than  $\alpha$ , the pathological behavior can only be corrected by means of the employment of other alternative expressions to calculate  $R(0)$ . The columns in Table I with the headings  $A_3$ ,  $A_4$ , and  $A_6$  correspond to the computation of the Fermi contact term with the equations (8), (10), and (11), respectively.

TABLE I. Fermi contact term  $A$  from the trial function (24) (in mT).

$r_0$ (a.u.)	$A_1^a$	$A_2^b$	$A_3^c$	$A_4^d$	$A_5^e$	$A_6^f$
0.536 22	2317.03	3071.64	1877.60	2496.89	2176.23	2447.52
0.913 33	604.00	733.94	532.52	638.72	584.41	632.02
1.054 86	431.40	508.50	389.89	452.72	420.72	449.16
1.221 95	310.81	254.07	288.11	323.21	305.41	321.51
1.412 79	288.98	251.50	217.48	235.65	226.47	234.95
1.513 01	199.60	215.31	191.68	204.33	197.96	203.91
1.712 08	157.81	164.63	154.45	159.91	157.16	159.79
1.901 92	131.05	132.85	130.18	131.61	130.90	131.60
2.000 00	120.51	120.51	120.51	120.51	120.51	120.51
2.445 58	89.30	84.88	91.39	87.92	89.65	87.83
3.041 87	69.34	63.34	72.31	67.62	69.95	67.28
4.086 71	56.07	50.78	59.34	55.15	57.23	54.46
4.933 58	52.58	48.52	55.63	52.41	54.01	51.63
5.370 65	51.78	48.29	54.60	51.85	53.22	51.11
5.801 19	51.32	48.31	53.87	51.55	52.70	50.86

<sup>a</sup> Exact (Ref. 4).

<sup>b</sup> Direct calculation of  $R(0)$ .

<sup>c</sup> Equation (8).

<sup>d</sup> Equation (10).

<sup>e</sup> Equation (25),  $a = b = 0.5$ .

<sup>f</sup> Equation (11).

Formulas (8) and (10) represent the two extreme cases of

$$u'(0) = u'(r_0) \left\{ a + \frac{b}{u'(r_0)} \left( -2 \frac{\partial E}{\partial r_0} \right)^{1/2} \right\} + 2 \int_0^{r_0} (E - V) u \, dr, \quad (25)$$

where  $a + b = 1$ . The parameters  $a$  and  $b$  can be chosen in such a way that  $R(0)$  has an acceptable behavior.

In this work we have chosen arbitrarily  $a = b = 0.5$ , and the results are displayed in the sixth column of Table I ( $A_5$ ).

The numerical values allow us to arrive at some interesting conclusions: (a) According to preceding expectations, all the formulas for  $R(0)$  yield the correct result when  $r_0 = 2$  and  $r_0 \rightarrow \infty$ . (b) The quantities  $A_i$  ( $i = 3, 4, 5, 6$ ) decrease monotonically, in agreement with Eq. (19). It is self-evident that using Eqs. (8), (10), (11), and (25) corrects the incorrect behavior of the trial function (24). (c) The most exact results are obtained from Eqs. (11) and (25). It is wholly natural that with a proper choice of  $a$  and  $b$  in Eq. (25), we could get even better results. (d) Equations (8) and (10) give upper and lower bounds to  $A$ , in a wide range of  $r_0$  values:  $A_3 < A_1 < A_4$  if  $0 < r_0 < 2$ ;  $A_4 < A_1 < A_3$  if  $2 < r_0 \leq 5$ . This behavior explains why the linear combination of both expressions produces better results than each one alone. It should be of marked usefulness to be able to set up in an *ab initio* manner which are the trial functions and the expressions that yield rigorous upper and lower bounds to  $R(0)^2$ .

#### IV. HYPERFINE SPLITTING: PARABOLIC-LIKE TRIAL FUNCTION

The trial function (24) used in the preceding section, allows us to calculate with a great accuracy any property of the system around the point  $r_0 = 2$  a.u. and when  $r_0$  is large enough. This property is due to the fact that in both situations the approximate function coincides with the exact one. This condition may be satisfied only for the most simple models: hydrogen atom, harmonic oscillator, etc. But for more complex systems (pressurized atoms and molecules with more than one electron) the eigenfunctions associated to the free system are not known, so that it is mandatory to resort to trial functions which give approximate results in the whole range of  $r_0$  values. Consequently, it should be of extreme usefulness to know if the formulas (8), (10), (11), and (25) produce better results than the direct calculation of  $R(0)$

when the trial function deviates from the exact one within the whole range of  $r_0$  values.

As an illustrative example, let us consider the following simple function, which is normalized in  $(0, r_0)$ :

$$R(c, r) = (15r_0^{-5})^{1/2} \left[ \frac{1}{2}(c^2 + cr_0) + \frac{1}{4}r_0^2 \right]^{-1/2} \times (r - r_0)(r + c). \quad (26)$$

In order that the energy  $E(c) = \langle H \rangle$  calculated with the function (26) can attain its minimum value, the parameter  $c$  must satisfy the condition

$$c^2 + \frac{8}{3}(2 + \frac{3}{4}r_0)c + \frac{8}{3}r_0(1 + \frac{1}{8}r_0) = 0. \quad (27)$$

The two roots  $c_-$  and  $c_+$  of this second order equation are negative and they fulfill the inequality  $|c_+| < r_0 < |c_-|$ .

Since the function  $R(c_+, r)$  presents a zero within  $(0, r_0)$ , it may be considered as an approximation to the  $2s$  state. The trial function (26) is interesting enough, because it permits us to approach simultaneously the first two  $s$  states of any central field problem. In Table II we present the approximate energies  $E(c_-)$  and  $E(c_+)$ , together with the  $c_-$  and  $c_+$  values for different sizes of the sphere. From the comparison of these quantities with the eigenvalues  $E_{1s}$  and  $E_{2s}$ , calculated with a greater accuracy,<sup>9,22</sup> it follows that the function (26) approaches in a better manner the  $1s$  state than the  $2s$  state. Besides, the approximate energy corresponding to the ground state takes a null value when  $c_- = -3$  and  $r_{00} = 1.8377$ , which is in excellent agreement with the exact value  $r_{00} = 1.835\,246\,4$ .

Table III offers the results of the Fermi contact term, computed with the function (26) and the formulas (8), (10), (11), and (25). The data permit us to derive several interesting conclusions, which are in accordance with those obtained in the preceding section: (a) Equations (8), (10), (11), and (25) give better results than the direct calculation of  $R(0)$  in the whole range of  $r_0$  values. Particularly, the results calculated from Eq. (25) (choosing arbitrarily  $a = b$ ) are very good.

As previously noted, the accuracy of this equation may be increased performing an appropriate adjustment of the parameters  $a$  and  $b$ . Owing to the polynomial form of the trial function (26), it is not possible to use it for large  $r_0$  values, because it gives quite wrong results. (b) In large portions of the interval considered, Eqs. (8) and (10) supply upper and lower bounds to  $R(0)$ , which explains clearly the success of Eq. (25). (c) An especially interesting fact is that for a certain  $r_0$  value, say  $r_0^*$ , the approximate energy  $E(c_-)$  presents a

TABLE II. Energies of the first two  $s$  states calculated with the trial function (26).

$r_0$	$ c_- $	$E(c_-)$	$E_{1s}^a$	$ c_+ $	$E(c_+)$	$E_{2s}^b$
1.760	2.297 29	0.073 93	0.072 50	0.827 00	4.9106	4.6213
1.920	3.034 88	-0.066 23	-0.069 38	0.896 55	3.9942	3.7289
2.030	3.081 92	-0.132 50	-0.143 73	0.943 79	3.4928	3.2416
2.265	3.183 96	-0.251 00	-0.259 18	1.043 19	2.6700	2.4432
2.670	3.364 72	-0.358 1	-0.373 7	1.209 56	1.7581	1.5620
3.609	3.806 95	-0.409 2	-0.470 7	1.572 20	0.7673	0.6130

<sup>a</sup> Reference 22.

<sup>b</sup> Reference 9.

TABLE III. Fermi contact term  $A$  from the trial function (26) (in mT).

$r_0$	$A_1^a$	$A_2^b$	$A_3^c$	$A_4^d$	$A_5^e$	$A_6^f$	$E(c_-)$	$E^g$
0.536 22	2317.03	3097.13	1942.94	2494.87	2210.29	2455.58	12.6143	12.5000
0.913 33	604.00	727.67	559.50	635.42	596.86	631.97	3.1415	3.1250
1.054 86	431.96	498.42	410.98	449.01	429.78	447.69	2.0074	2.0000
1.221 95	310.81	341.11	304.27	319.01	311.60	318.70	1.1854	1.1834
1.412 79	228.98	236.35	229.56	230.88	230.88	230.88	0.6174	0.6173
1.513 01	199.60	199.29	202.03	199.25	200.64	199.23	0.4133	0.4132
1.712 08	157.81	147.16	161.88	154.20	158.02	153.97	0.1260	0.1250
1.901 92	131.05	114.22	135.29	125.28	130.24	124.74	-0.0526	-0.0555
2.000 00	120.51	101.33	124.53	113.84	119.13	113.11	-0.1208	-0.1250

<sup>a</sup> Exact result (Ref. 4).<sup>b</sup> Direct calculation of  $R(0)$ .<sup>c</sup> Equation (8).<sup>d</sup> Equation (10).<sup>e</sup> Equation (25),  $a = b = 0.5$ .<sup>f</sup> Equation (11).<sup>g</sup> Reference 4.

maximum approach to the exact value. Under these conditions, all the approximate quantities  $A_i$  give excellent results too. In order to calculate  $r_0^*$ , it is not necessary to know the exact solutions, because this particular value is fixed with a great exactness by the condition  $A_2(r_0^*) = A_4(r_0^*)$ . A simple computation produces at once the results:

$$r_0^* = 1.513\,78, c_-^* = -2.865\,17, R^*(0) = 3.960\,30, \\ A^* = 199.04\,\text{mT}, E^* = 0.411\,88. \quad (28)$$

Using the perturbational polynomial given in Ref. 22, we obtain an energy value  $E = 0.411\,83$ . This value is nearly coincident with our approximate value. This great success of the trial function (26) is due to the fact that when  $r_0 = r_0^*$ , the exact eigenfunction behaves like a second order polynomial. This assertion is corroborated in Table IV where  $R(c_-^*, r)$  is shown together with the exact eigenfunction (obtained by numerical integration of the Schrödinger equation).

According to appearances, for those  $r_0$  values where the trial function obeys the quantum mechanical virial theorem and some of the equations [(8), (10), or (11)], we can expect good results.

In Table V we display the value of the Fermi contact term, calculated with Eq. (10) and the function  $R(c_-^*, r)$ . Since  $c$  is fixed, the trial function does not satisfy the virial theorem (except, of course, for  $r_0 = r_0^*$ ). In spite of this, the  $A$

value is appreciably improved, and between  $r_0 = 1.2$  and  $r_0 = 2$ , the error is less than 2%.

The trial functions used in these last two sections have been optimized in such a way to obtain the best possible energy value, i.e., in order that  $\langle H \rangle$  reaches its minimum value. It is a well known fact that the variational principles enhance the trial functions in an average sense, so that we cannot expect that such functions furnish acceptable values for local properties. As a special case, we must expect that the direct calculation of  $R(0)$  using variationally optimized trial functions will not produce good enough results. On the other hand, formulas (8), (10), (11), and (25) contain some integrals, which compensate, up to a certain extent, the local errors of  $R(r)$ . This property explains the better accuracy of the  $R(0)$  calculation, as one can appreciate in Tables I, II, and V.

In order to judge this fact more clearly, in Fig. 1 we have plotted the exact function  $R_{1s}(r)$  together with the approximate function (26) for  $r_0 = 2$ . It is seen that  $R(c, r)$  approaches to a great extent the exact wave function in the complete range of  $r$  values with the exception of the zone  $r < 0.4$  a.u. The larger error occurs in the neighborhood of  $r = 0$ , which is precisely the zone of interest to compute the Fermi contact term. This large local deviation of the trial function is much more important in the direct calculation of  $R(0)$  than in the employment of the alternative formulas (8), (10), (11), and (25). The trial function (26) is an excellent example in support of these expressions.

TABLE IV. Ground state wave function for the hydrogen atom when  $r_0 = r_0^* = 1.513\,78$ .

$r$	$R(c_-^*, r)$	$R_{1s}(r)^a$
0.00	3.96	3.96
0.20	3.20	3.20
0.40	2.51	2.51
0.60	1.89	1.89
0.80	1.34	1.35
1.00	0.87	0.88
1.20	0.48	0.48
1.40	0.15	0.15
1.50	0.02	0.02

<sup>a</sup> From numerical integration of the Schrödinger equation.TABLE V. Fermi contact term  $A$  from the trial function (26) and Eq. (10) with  $c_- = c_-^* = -2.865\,17$  (in mT).

$r_0$	$A$	% Error <sup>a</sup>
0.536 22	2482.59	7.1
0.913 33	629.73	4.3
1.054 86	444.86	3.0
1.221 95	316.45	1.8
1.412 79	230.01	0.4
1.513 01	199.24	0.2
1.712 08	155.98	1.2
1.901 92	128.91	1.6
2.000 00	118.52	1.7

<sup>a</sup> % Error =  $100|A - A_{\text{exact}}|/A_{\text{exact}}$ .

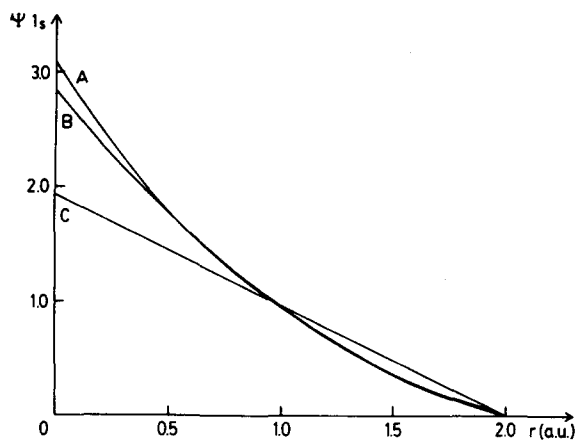


FIG. 1. Ground state for pressurized hydrogen atom ( $r_0 = 2$ ). A: Exact wave function. B: Equation (26). C: Equation (32).

## V. PRESSURE CALCULATION

Equations (3)–(5) allow us to calculate the pressure in several ways:

$$P = -(4\pi r_0^2)^{-1} \frac{\partial E}{\partial r_0}, \quad (29)$$

$$P = (4\pi r_0^3)^{-1} (2E - \langle V \rangle), \quad (30)$$

$$P = \frac{1}{8\pi} R'(r_0)^2. \quad (31)$$

The expressions (29) and (31) are of a general nature, while Eq. (30) is only valid for Coulombic potentials. If the pressure is calculated with a trial wave function which satisfies the virial theorem, then Eqs. (29) and (30) will produce identical results,<sup>17</sup> which in turn, will be different from that obtained with Eq. (31). According to the conclusions derived in the previous sections, we can affirm that the pressure calculated via Eqs. (29) or (30) will be nearer to the exact value than that derived from Eq. (31), because the latter expression depends on the local values of the trial wave function.

For the purpose of corroborating these statements, we present in Table VI the values corresponding to  $-\partial E/\partial r_0$  and  $r_0^2 R'(r_0)^2/2$ , calculated with the functions (24) and (26). We have included the value of  $-\partial E/\partial r_0$  computed with the perturbative polynomial of Ref. 22 as the exact result for the range considered of  $r_0$  values.

It is very suggestive that functions as different as (24) and (26) provide similar and quite good results for the change of the energy with  $r_0$  (see third and fifth column in Table VI). However, it is necessary to point out that this agreement does not hold for large enough  $r_0$  values, because while function (24) leads to the exact result when  $r_0 \rightarrow \infty$ , the parabolic function (26) (which does not present an appropriate exponential decrease) gives unacceptable results.

It is a relatively easy matter to determine when a given trial function ceases to be acceptable, by resorting to the general properties of the solutions deduced in Sec. II.

In Table VII we present the exact pressure values ( $P_{1s}$ )<sup>4</sup> and those calculated by substituting Eqs. (24) and (26) into Eq. (29) or (30). We have added the computations performed with the trial function

$$R(r) = (30r_0^{-5})^{1/2}(r_0 - r), \quad (32)$$

in order to obtain additional information about the influence of the trial function on the estimated value of the pressure.

Although the function (32) deviates to a great extent from the exact one (see Fig. 1), it satisfies the virial theorem and gives a satisfactory approximation for the pressure of the system (see  $P_1$  in Table VII). The results reported in Table VII show plainly that the pressure is a property that may be calculated with a great accuracy, even with very poor quality functions, such as (26) and (32). A remarkable fact is that for small  $r_0$  values, the pressures calculated via the trial functions (32), (26), and (24) ( $P_1$ ,  $P_2$ , and  $P_3$ , respectively) deviate in a similar way from the exact value ( $P_{1s}$ ). This behavior makes us suppose that for large pressures the aforesaid approximate functions must be quite alike among themselves but their respective forms do not coincide with the exact one.

Much more important is the fact that in the neighborhood of  $r_0^*$  [see Eq. (28)],  $P_2$  approaches appreciably  $P_{1s}$ . This is a new confirmation of the assertion made in the preceding

TABLE VI. Numerical comparison between  $-\partial E/\partial r_0$  and  $\frac{1}{2} r_0^2 R'(r_0)^2$  calculated with the trial functions (24) and (26).

$r_0$	$-\frac{\partial E^a}{\partial r_0}$	$-\frac{\partial E^b}{\partial r_0}$	$\frac{1}{2} r_0^2 R'(r_0)^2^b$	$-\frac{\partial E^c}{\partial r_0}$	$\frac{1}{2} r_0^2 R'(r_0)^2^c$
0.536 22	55.5492	56.1708	74.9930	56.1767	77.6625
0.913 33	10.0470	10.1345	12.1933	10.1420	13.1090
1.054 86	6.2330	5.9482	7.2241	6.2867	7.9038
1.221 95	3.7925	3.8120	4.1424	3.8210	4.6401
1.412 79	2.2951	2.2989	2.3254	2.3089	2.6876
1.513 01	1.8014	1.8002	1.7483	1.8107	2.0587
1.712 08	1.1524	1.1445	1.0184	1.1561	1.2510
1.901 92	0.7787	0.7668	0.6218	0.7796	0.8016
2.000 00	0.6426	0.6292	0.4844	0.6426	0.6426

<sup>a</sup> Perturbational results (Ref. 22).

<sup>b</sup> Trial function (26).

<sup>c</sup> Trial function (24).

TABLE VII. Pressure calculation ( $P \times 10^{-6}$  atm).

$r_0$	$P_{1s}^a$	$P_1^b$	$P_2^c$	$P_3^d$
0.536 22	4463.277	4512.919	4513.432	4513.903
0.913 33	278.268	280.526	280.691	280.899
1.054 86	129.418	130.243	130.363	130.532
1.221 95	58.681	58.897	58.983	59.122
1.412 79	26.567	26.550	26.611	26.726
1.513 01	18.181	18.117	18.168	18.274
1.712 08	9.083	8.983	9.021	9.113
1.901 92	4.973	4.869	4.897	4.979
2.000 00	3.712	3.610	3.634	3.712
2.445 58	1.108	1.026	1.039	1.102
3.041 87	0.271	0.212	0.217	0.268
4.086 71	...	...	0.031	0.031

<sup>a</sup> Exact result (Ref. 4).<sup>c</sup> Trial function (26).<sup>b</sup> Trial function (32).<sup>d</sup> Trial function (24).

section: when a trial wave function satisfies simultaneously the virial theorem and another theoretical relationship [such as Eq. (8), (10), or (11)] for some  $r_0$  value, we can expect very good results from it for the determination of the properties of the system around that particular point.

From Eq. (30) it is deduced at once the relation

$$\Delta P = P - P_{1s} = \frac{1}{4\pi r_0^3} \left\{ 2(E - E_{1s}) + \int_0^{r_0} (u_{1s}^2 - u^2) dr \right\} \\ \geq \frac{1}{4\pi r_0^3} \int_0^{r_0} (u_{1s}^2 - u^2) V(r) dr, \quad (33)$$

where  $P_{1s}$ ,  $E_{1s}$ , and  $u_{1s}$  represent the exact quantities, and  $P$ ,  $E$ , and  $u$  are the approximate ones. Equation (33) assures us that when  $\Delta P < 0$ , the trial function overestimates the average value of the potential.

## VI. CONCLUSIONS

We deem that results presented in this work may prove to be valuable, because they show in a clear manner, that when appropriate exact expressions are used, it is possible to calculate certain physical properties with an acceptable accuracy, even if very simple trial functions are chosen. The most remarkable example is the determination of the Fermi contact term. In this case, the direct computation of  $R(0)$  produces very poor results because the trial wave functions, which are optimized in a variational way, do not reproduce locally the exact eigenfunction. Especially, the approximate functions studied in this work deviate to a greater extent from the exact function in the neighborhood of  $r = 0$ .

In Sec. III we applied a trial function which is coincident with the exact function for just two  $r_0$  values. Even with this function, the values of  $R(0)$  calculated in a direct fashion, have a pathological behavior in the large  $r_0$  regime. However, such abnormal behavior of this function is corrected up to a great degree, when  $R(0)$  is determined with Eqs. (8), (10),

(11), and (25). As commented formerly, the success of these expressions is due basically to the fact that in them no local value of the trial function is decisive [especially in Eqs. (10) and (11)].

The behavior of many physical properties, defined in terms of the simple model considered in this work, may be known beforehand from the properties of the Schrödinger equation solutions. Some of these properties were shown in Sec. II and then they were used along the subsequent sections to determine the confidence range attributable to a given trial function. It is worth noting, however, that theoretical results presented in Sec. II are far from being of a general character, and a better exposition of them would be desirable to treat the bounded systems.

A relevant fact found in Sec. IV is the existence of crossings among the Fermi contact term values calculated with different formulas. At first sight, all the properties of the system can be computed with an appreciable exactness in these crossings. In order to be completely sure of the theoretical and practical value of these crossings, it would be convenient and necessary to use more complex trial functions with a larger number of variational parameters. In turn, these parameters could be optimized in such a manner to obtain the best possible energy value or, alternatively, that the trial function should fulfill simultaneously several theoretical relationships chosen in a proper way.

In closing, we wish to point out that if the variational parameters  $\alpha$  and  $c$  in the trial functions (24) and (26), respectively, are optimized in such a way that Eqs. (8), (10), or (11) are satisfied, the results are even worse than those reported in this work. This fact makes us conjecture that the virial theorem possesses a remarkable importance to optimize trial functions, even though these functions are applied to calculate properties other than energy.

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