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Electronic Confinement Effects on the Reaction Field Type Calculations of Solvent Effects

Victor García, David Zorrilla* and Manuel Fernández

We analyze some procedures to introduce the effect of confining the electrons of the hydrogen atoms in cavitation spheres like those used in the self-consistent reaction field models for studying the solvent influence on molecular properties [as polarizable continuum model (PCM), or conductor screening model (COSMO)]. We have found that the boundary conditions to be applied have an important effect on the system energy that by no means should be neglected in this type of calculations. We have found as well that “-nG” expansion technique could be applicable in this kind of calculations (even at the

very simple “-3G” level) and lead us to a relatively simple form of applying the theory. Moreover, we have found a way to define the cavitation radius of PCM calculations, by minimizing the system energy with respect to this parameter, which could be a more satisfactory procedure—at least from a theoretical point of view—than the use of empirical values characteristic of most of the PCM or COSMO standard calculations. © 2013 Wiley Periodicals, Inc.

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Introduction

The theoretical study of the properties of molecules in solution is a subject on which there has been significant progress in recent years.^[1–4] Some of the more widely used models to calculate the solvent effects are the polarizable continuum model (PCM), which supports many different versions,^[5–27] or the conductor screening model (COSMO).^[28–32] All these procedures consider the solute molecule contained in a cavity formed by intersecting spheres: The main assumption of this work is that the inclusion of a molecule in a cavity should change the boundary conditions applicable to the determination of the electronic wavefunction, which in turn affects significantly to the energy levels achieved.^[33–53] This is an effect that is not explicitly taken into account when PCM, COSMO, or similar models are applied. In this article, we propose a way of introducing the electronic confinement in the calculation of solvent effects different from those appeared in Hsu et al.^[28] Borgoo et al.,^[54] or Cammi et al.^[55] Hsu et al. use even tempered basis functions with radial part:

$$R_{nl}(r) = N_l(\zeta_{kl}) e^{-\zeta_{kl} r^2} \quad (1)$$

$$\zeta_{kl} = \alpha_l \beta_l^k \quad k = 1, 2, 3 \dots N_l \quad (2)$$

multiplied by a factor:

$$s(r) = \begin{cases} \left[1 - \left(\frac{r}{r_0} \right)^n \right] & \text{for } 0 < r < r_0 \\ 0 & \text{for } r \geq r_0 \end{cases} \quad (3)$$

which ensures the cancellation of the wavefunction in the space occupied by the solvent.

Instead of using this procedure, we propose to use nG-expansions of more standard basis functions multiplied by a

polynomial trimming function defined in a short interval $r_0 - \delta < r < r_0$:

$$f(r, r_0, \delta) = \begin{cases} 1 & \text{for } 0 \leq r \leq r_0 - \delta \\ -\frac{3}{\delta}(r - r_0) - \frac{3}{\delta^2}(r - r_0)^2 & \\ -\frac{1}{\delta^3}(r - r_0)^3 & \text{for } r_0 - \delta \leq r \leq r_0 \\ 0 & \text{for } r \geq r_0 \end{cases} \quad (4)$$

This choice has two main advantages, one of practical order and another one of more theoretical nature: First of all, by using nG expansions, we avoid the need of using any special software to obtain the “in solvent” wavefunctions: any of the standard software permitting the use of combinations of Gaussians as basis set would be valid. We have used the well-known GAUSSIAN package.^[56]

From a more theoretical point of view, the use of functions such as Eq. (4) instead of Eq. (3) has the advantage of modifying the original *in vacuo* wavefunctions only near to the solvent, maintaining the wavefunction in the neighborhoods of the nuclei as similar as possible to the isolated molecule case.

In the following sections, first we present the foundations of the method, then we point out some of the difficulties encountered in its application, and finally we apply the explained methodologies to the case of hydrogen molecules dissolved in some solvents: water, benzene, and n-octane. The results achieved supply a way to obtain *ab initio* cavitation radii similar to the one proposed by Hsu et al.^[28] (the

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minimization of the total energy of the confined molecule with regard to the size of the cavity), but more easy to apply. The radius obtained by us for hydrogen (2.7 Å) is too high but results of the same order of magnitude than the commonly accepted empirical value (1.22 Å).^[9] This seems to indicate that the functions and expansions proposed can be qualitatively correct, but points out the need of searching for functions still more suitable for the determination of this radius.

Atoms Constrained in Spherical Boxes: The Boundary Conditions

The idea of studying atoms confined in spherical boxes dates back to the early ages of quantum mechanics^[34–53,57] and has been applied in a wide variety of fields of physics and chemical physics, such as the simulation of the effects of pressure on atomic properties,^[35–51] the liquid state cell model,^[52,53] semiconductor quantum dots,^[57] or the influence of solvents on molecular properties.^[3] 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 the electrons become more restricted, as well as it occurs for the energy levels of the particle in a box model.

There are a variety of methods for the quantitative study of the energy of atoms in boxes. They span from the exact resolution of the Schrödinger equation in some favorable cases to perturbative theories, also including the variational method, which has become a very useful tool for researching systems constrained in boxes with different symmetries.^[58–63] 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.^[64–66] In our work of 2007,^[33] we carry out this kind of calculations by using the Roothaan method with basis functions adapted to the boundary conditions of the problem. There we introduced the trimmed Slater-type orbitals^[33] (TSTO) as basis functions. This kind of functions was defined as the product of an standard STO function $N_{n,\alpha} r^n e^{-\alpha r} Y_l^m(\theta, \varphi)$ by a trimming function $f(r, r_0, \delta)$ whose value is zero for " r " greater than the trimming radius r_0 , it is unity for $0 < r < r_0 - \delta$, and it is a polynomial between $r = r_0 - \delta$ and $r = r_0$, which is the function Eq. (4) previously defined.

The size δ of the transition interval where the function passes from being a STO to become exactly null is variationally calculated for each r_0 value. The polynomial $f(r, r_0, \delta)$ is selected by taking into account the continuity conditions required for the wavefunctions, namely:

1. (a) Continuity of the function, first derivative and second derivative in $r = r_0 - \delta$ (because the potential should be considered continuous in $r = r_0 - \delta$).
2. (b) Continuity exclusively of the function in the frontier point $r = r_0$ (because the potential is considered infinite for $r \geq r_0$).

These conditions are related to the situation in which electrons suddenly meet a totally rigid barrier on arriving to $r = r_0$. We suppose it is the most appropriate choice to calculate the

solvent effects in a first attempt that could be improved further on. A four parameter polynomial has been chosen as trimming function (Fig. 1), because the number of continuity conditions to be applied are four (one at $r = r_0$ and three at $r = r_0 - \delta$):

$$f(r, r_0, \delta) = \begin{cases} 1 & \text{for } 0 \leq r \leq r_0 - \delta \\ a_0 + a_1(r - r_0) + a_2(r - r_0)^2 + a_3(r - r_0)^3 & \text{for } r_0 - \delta \leq r \leq r_0 \\ 0 & \text{for } r \geq r_0 \end{cases} \quad (5)$$

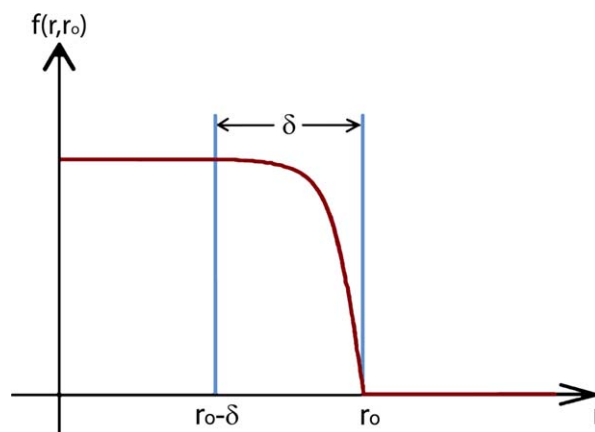


Figure 1. Trimming function for a rigid box. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The value of the a_i coefficients can be calculated in terms of the parameter δ , applying the continuity conditions. The results are:

$$a_0 = 0 \quad a_1 = -\frac{3}{\delta} \quad a_2 = -\frac{3}{\delta^2} \quad a_3 = -\frac{1}{\delta^3} \quad (6)$$

The computation of the integrals required to apply the Roothaan's method with this kind of basis functions is not possible by exact procedures. In our article of 2007,^[33] we use quasi-Monte Carlo methods (QMC)^[67–71] to calculate the integrals and minimal basis sets of trimmed STO, to study the behavior of some atoms and small molecules constrained in spherical boxes. First columns of Table 1, obtained with the same procedure used in Ref. [33], shows the energies of a hydrogen atom confined in a sphere of radius r_0 for several values of this radius, and the corresponding variationally optimized values for the δ parameter.

Trimmed and Truncated STO Gaussian Expansions

We have investigated the possibility of obtaining Gaussian expansions for the TSTO introduced in the previous section and we have obtained suitable combinations "TSTO-nG" to use in a parallel way to the usual STO-nG expansions. TSTO-nG expansions can be combined with standard programs that, such as GAUSSIAN,^[56] admit basis sets defined by the user. However, if we substitute the exact TSTO functions by the

Table 1. Energies of the H atom in rigid spherical box obtained with TSTO and 10^8 Hammersley integration⁷¹ QMC³³ points for different radii.

r_0 (a.u.)	δ (opt)	E (Hammersley)	E (TSTO-3G)	E (TtSTO-3G)
25.0	–	–0.5000000	–0.4949071	–0.4949071
10.0	2.108	–0.4999992	–0.4949087	–0.4949073
8.0	2.249	–0.4999734	–0.4950593	–0.4949388
6.0	2.388	–0.4992258	–0.4965316	–0.4958294
5.0	2.457	–0.4961865	–0.4961089	–0.4967494
4.0	2.525	–0.4825319	–0.4871069	–0.4949969
3.5	2.559	–0.4633344	–0.4723751	–0.4900616
3.0	2.593	–0.4228466	–0.4400642	–0.4776812

The same energies obtained with trimmed STO expanded with three Gaussians (TSTO-3G), and with truncated STO (TtSTO-3G). For a graphical comparison, see Figure 3.

TSTO-nG expansions, the continuity conditions, which required to define the transition interval δ , lose much of its importance, and the expansion of STO simply “truncated,” or what is the same, the expansion of the function $f(r, r_c) \cdot r^n \exp(-\alpha r)$ with:

$$f(r, r_c) \begin{cases} = 1 & \text{for } 0 < r < r_c \\ = 0 & \text{for } r \geq r_c \end{cases} \quad (7)$$

leads to a function similar to a TSTO-nG having a r_0 radius slightly greater than r_c radius (Fig. 2). Here, we will call TtSTO to the truncated Slater functions and TtSTO-nG to their Gaussian expansions, which can be obtained by the same procedures than TSTO-nG expansions, using our program UCA-GSS.^[72] We only need to introduce the data $r_0 = r_c$ and $\delta = 0$ into the program. However, TtSTO-nG expansions do not require the variational optimization of a δ parameter, and we will see later on this article, that they are able to lead to results not very different from those obtained with TSTO-nG expansions. In Figure 3, the confinement energy of the hydrogen atom calculated without Gaussian expansions is compared with the one obtained with the expansion of the trimmed STO (TSTO-3G). Also, a similar comparison with the expansion of

the truncated STO (TtSTO-3G) is carried out. The curves TSTO-3G and TtSTO-3G are qualitatively similar to the “exact” curve, obtained by using quasi-Montecarlo integration. The quantitative difference is by no means negligible, but it can be reduced by using an “effective radius” longer than the actual radius. From our point of view, the truncated orbitals TtSTO-3G seems to be a slightly better option, just because they are easier to obtain. Nevertheless, the truncation radius r_c could result in a worse estimation of the zone in which the orbital becomes unappreciable than the radius r_0 of the trimmed orbitals.

In Table 2, we can see the confinement energies for a hydrogen molecule with its electrons confined inside two intersecting spheres like those used in PCM models. Figure 4 displays graphically the results obtained by using TSTO, TSTO-3G, and TtSTO-3G. We can notice that the confinement energy quickly increase for radii under 5.00 a.u. Also we can see that the energies can be approximately estimated using Gaussian expansions TSTO-3G, at least from a qualitative point of view.

Achieving the TSTO or TtSTO Gaussian Expansions

At the beginning of this study, we intended to obtain the exponents b_μ and coefficients a_μ of the Gaussian expansion of our trimmed Slater functions:

$$F = f(r, r_0, \delta) r^n \exp(-\alpha r) \cong \sum_{\mu=1}^n a_\mu \exp(-b_\mu r^2) = G \quad (8)$$

by using the standard method proposed by Stewart^[73–75] to find the well-known STO-nG functions. That is, we minimize the function:

$$\varepsilon = \int (F - G)^2 d\tau \quad (9)$$

respect to the exponents and coefficients of the expansion. This minimization leads to a system of $2n$ linear and nonlinear

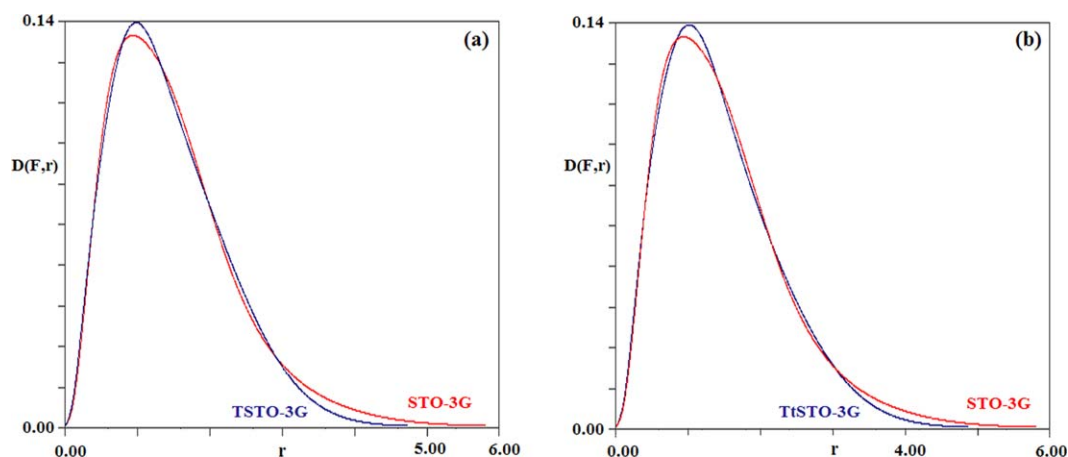


Figure 2. a) Radial distribution function comparison between a TSTO-3G expansion within $\alpha = 1$, $r_0 = 5.00$ a.u., and $\delta = 2.525$; and a STO-3G expansion within $\alpha = 1$. b) Radial distribution function comparison between a TtSTO-3G expansion within $\alpha = 1$ and $r_c = 4.00$ a.u.; and a STO-3G expansion within $\alpha = 1$. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

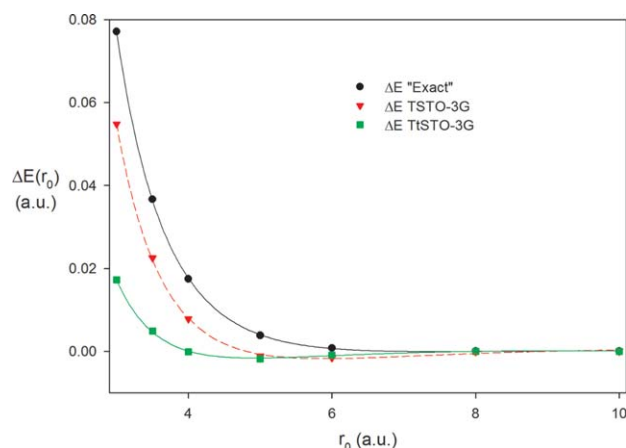


Figure 3. Confinement energy $E(r_0) - E(\infty)$ of the H atom calculated with TSTO-3G and TtSTO-3G functions. Both of them are compared with the exact curve obtained with Hammersley,⁷¹ 108 points QMC³³ numerical integrations. The results obtained with TtSTO-3G basis functions can be improved by using an adequate truncation radius. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

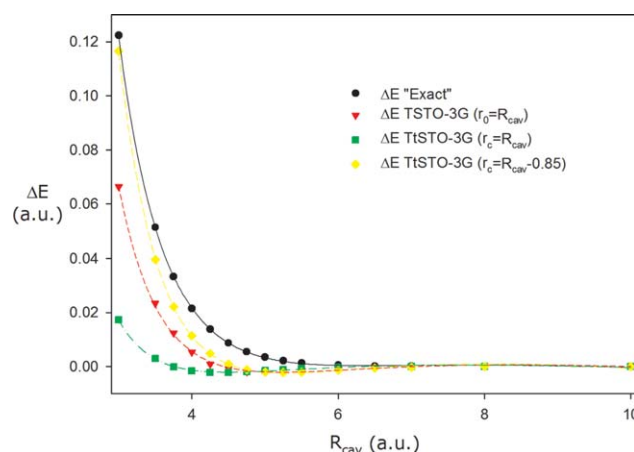


Figure 4. Confinement energy $E(r_0) - E(\infty)$, calculated with TSTO-3G ($r_0 = R_{cav}$), TtSTO-3G ($r_c = R_{cav}$), and TtSTO-3G ($r_c = R_{cav} - 0.85$) for a H_2 molecule with its electrons confined in intersecting spheres of radius r_0 centered in the nuclei. Comparison with the "exact" curve obtained with TSTO and Hammersley,⁷¹ 108 points QMC³³ numerical integration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

equations, which determine the coefficients a_μ and exponents b_μ . Linearizing the system by the usual methods allow achieving, iteratively, the exponents b_μ and the coefficients a_μ , from an initial set of exponents b_μ^0 , that must be chosen *a priori*. In 2009, we developed a program (an initial version of the current UCA-GSS)^[72] that allowed to reproduce the Stewart^[73,74] or Fernández Rico^[75] calculations in an easy way, and also allowed to obtain Gaussian expansions of the Slater orbitals with noninteger powers of r .

In the first phase of the research presented now, UCA-GSS program was just modified so that the function F could be a trimmed Slater orbital with parameters r_0 and δ chosen by the user. But the results were not satisfactory at all, due to

numerical problems, which are more acute for the expansion of TSTO orbitals than for the standard STO case. To achieve a fully satisfactory result from the viewpoint of numerical errors, it has been necessary to develop a method to improve the exponents b_μ of the Gaussian expansions based on the following considerations:

The condition to be met by the G expansion of the function F is:

$$\int (F-G)^2 d\tau = \text{MINIMUM} \quad (10)$$

so applying the definition:

R (a.u.)	δ (opt)	Hammersley	TSTO-3G ($r_0 = R_{cav}$)		TtSTO-3G ($r_c = R_{cav}$)		TtSTO-3G ($r_c = R_{cav} - 0.85$)	
			Confined	In H_2O	Confined	In H_2O	Confined	In H_2O
∞	—	−1.12820	−1.119224	−1.119224	−1.119224	−1.119224	−1.119224	−1.119224
10.00	(1.7)	−1.12820	−1.119224	−1.119225	−1.119224	−1.119225	−1.119224	−1.119225
8.00	(1.7)	−1.12819	−1.119232	−1.119234	−1.119226	−1.119226	−1.119240	−1.119243
7.00	(1.7)	−1.12813	−1.119336	−1.119339	−1.119249	−1.119249	−1.119437	−1.119441
6.50	(1.7)	−1.12802	−1.119556	−1.119559	−1.119317	−1.119519	−1.119807	−1.119814
6.00	1.76	−1.12770	−1.120053	−1.120057	−1.119519	−1.119979	−1.120478	−1.120487
5.50	1.79	−1.12687	−1.120781	−1.120788	−1.119978	−1.120323	−1.121242	−1.121258
5.25	1.83	−1.12605	−1.121135	−1.121144	−1.120323	−1.120720	−1.121432	−1.121453
5.00	1.87	−1.12475	−1.121320	−1.121331	−1.120720	−1.121110	−1.121242	−1.121269
4.75	1.92	1.12270	−1.121120	−1.121134	−1.121110	−1.121389	−1.120349	−1.120386
4.50	1.98	−1.11946	−1.120186	−1.120205	−1.121388	−1.121382	−1.118283	−1.118335
4.25	2.04	−1.11443	−1.118303	−1.118328	−1.121381	−1.120818	−1.114402	−1.114475
4.00	2.11	−1.10671	−1.113952	−1.113987	−1.120817	−1.119289	−1.107814	−1.107919
3.75	2.20	−1.09488	−1.106811	−1.106859	−1.119287	−1.116225	−1.097078	−1.097234
3.50	2.24	−1.07683	−1.095847	−1.095914	−1.116222	−1.102009	−1.079619	−1.079858
3.00	2.24	−1.00578	−1.052834	−1.052967	−1.102002	−1.119225	−1.002651	−1.003215

Calculations are carried out with minimal basis set with exponent $\alpha = 1.19$, at internuclear distance $R = 0.74$ Å. The column "Hammersley" correspond to calculations with QMC integration³³ and 10^8 integration points. Subsequent columns contain the results obtained with -3G gaussian expansions. The value of the δ parameter becomes irrelevant for radius $R_{cav} > 6$ a.u. Therefore a constant value $\delta = 1.7$ a.u. has been used for these cases.

$$G = \sum_{i=1}^m C_i \exp(-b_i r^2) = \sum_{i=1}^m C_i g_i \quad (11)$$

and differentiating with respect to the coefficients C_i and exponents b_i we obtain the equations:

$$\sum_{i=1}^m S_{ki}^{(2)} C_k = F_i^{(2)} \quad (12)$$

$$\sum_{i=1}^m S_{ki}^{(4)} C_k = F_i^{(4)} \quad (13)$$

where $S_{ki}^{(m)}$ and $F_i^{(m)}$ are the integrals:

$$S_{ki}^{(m)} = \int g_k g_i r^m dr \quad (14)$$

$$F_i^{(m)} = \int F g_i r^m dr \quad (15)$$

If we have a good enough approximation $\{\tilde{b}_i\}$ to the optimal exponents $\{b_i\}$ and we use a second-order Taylor expansion of the function $\exp(-br^2)$:

$$e^{-br^2} \approx e^{\tilde{b}r^2} (1 - \gamma r^2) = \tilde{g} (1 - \gamma r^2) \quad (16)$$

where $\gamma = b - \tilde{b}$ and $\tilde{g} = \exp(-\tilde{b}r^2)$, and we define:

$$g = e^{-br^2} = e^{-\tilde{b}r^2} e^{-\gamma r^2} \approx \tilde{g} - \gamma r^2 \tilde{g} \quad (17)$$

nonlinear Eqs. (12) and (13) give rise, by substituting Eq. (17) in Eqs. (14) and (15) to a system of $2m$ equations with m unknowns C_i and m unknowns γ_i :

$$\sum_{k=1}^m \tilde{S}_{ki}^{(2)} C_k + \tilde{F}_i^{(4)} \gamma_i = \tilde{F}_i^{(2)} \quad i=1, \dots, m \quad (18)$$

$$\sum_{k=1}^m \tilde{S}_{ki}^{(4)} C_k + \tilde{F}_i^{(6)} \gamma_i = \tilde{F}_i^{(4)} \quad i=1, \dots, m \quad (19)$$

from which we determine iteratively the optimal exponents:

$$b_i = \tilde{b}_i + \gamma_i \quad (20)$$

by solving a linear approximation to Eqs. (18) and (19) nonlinear system

$$\sum_{k=1}^m \tilde{S}_{ki}^{(2)} C_k + \tilde{F}_i^{(4)} \gamma_i = \tilde{F}_i^{(2)} \quad i=1, \dots, m \quad (21)$$

$$\sum_{k=1}^m \tilde{S}_{ki}^{(4)} C_k + \tilde{F}_i^{(6)} \gamma_i = \tilde{F}_i^{(4)} \quad i=1, \dots, m \quad (22)$$

where the $\tilde{S}_{ki}^{(m)}$ integrals are the $S_{ki}^{(m)}$ ones, calculated with the approximate \tilde{b}_i exponents. In Eqs. (18) and (19) and Eqs. (21) and (22), the symbols $\tilde{F}_i^{(m)}$ and $\tilde{S}_{ki}^{(m)}$ represent the integrals Eqs. (14) and (15) calculated with approximate exponents \tilde{b}_i .

Linear Eqs. (21) and (22) have the advantage, over the nonlinear system Eqs. (12) and (13), that it determines simultaneously the exponents b_i and the coefficients C_i , and do it from a system of linear equations. In return, they have the disadvantage that it only "works" properly when the approximate exponents \tilde{b}_i are very close to the optimal exponents b_i . Most of the values of the approximate exponents \tilde{b}_i in this article has been obtained by first using the standard method, and then get them improved by the use of the above described procedure.

In the current version of the UCA-GSS program, it has been introduced the minimization of the error function (10) by using Eqs. (18) and (19) as an option, which is convenient to use when the function to expand is a TSTO or a TtSTO. Nevertheless, it does not seem necessary to use this improvement when developing an usual STO (with integer or noninteger power of r).

PCM/TSTO-3G Calculation of the Energy of the Dissolved Hydrogen Molecule

As can be seen in Table 2 (or in Fig. 4), the confinement energy induced by the change of boundary conditions of the electrons of the H_2 molecule in the spheres of the PCM models can be important, even for radii rather bigger than the usually used in those models. Note (in Fig. 4) that the use of a reduced truncation radius ($r_c = R_{cav} - 0.85$ a.u.) for the TtSTO-3G basis functions approaches the energy results to the "exact" TSTO ones. Figure 5 shows the dependence of the energy of the H_2 dissolved in H_2O with the PCM cavitation radius used (R_{cav}), calculated with the standard PCM model of Gaussian 09 and the STO-3G basis functions ($r_c = \infty$) quoted in Table 3. When the PCM cavitation radius become lower than the empirical value habitually used in the model ($R_{cav} = 1.22$ Angstrom = 2.68 Bohr), the energy decreases in an unacceptable way. In Figure 6, we can see the result of adding to the PCM energies of Figure 5 and the electronic confinement energies calculated via TSTO and QMC-Hammersley^[33,71] integrations: the curve in Figure 5 shows an increasing behaviour

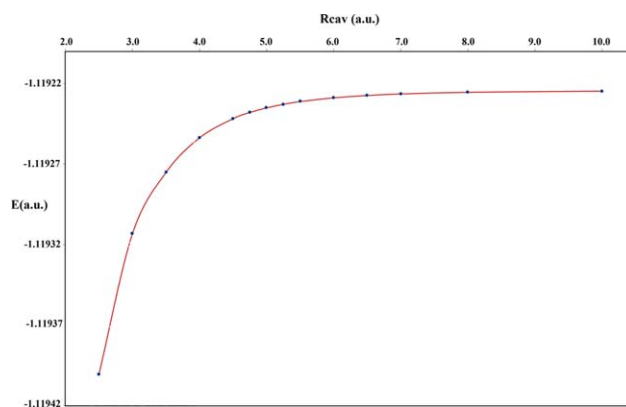


Figure 5. Standard PCM energy (STO-3G) of H_2 in water as a function of the cavitation radius assigned to the H atom. The cavitation radius R_{cav} and the energy E are expressed in a.u. The energy decreases spuriously as R_{cav} goes to zero. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 3. Exponents and coefficients achieved with the Gaussian expansion of a 1s STO-3G and 1s TtSTO-3G with truncation radius $r_c = 4.37$ a.u.

STO-3G ($r_c = \infty$)		TtSTO-3G ($r_c = 4.37$ a.u.)	
Exponents	Coefficients	Exponents	Coefficients
3.1545901535	0.1543289673	4.7350786784	0.0971732767
0.5746125343	0.5353281423	0.8334881844	0.4267412805
0.1555125765	0.4446345422	0.2033037093	0.6037163739
Both of the functions correspond to a STO exponent $\alpha = 1.19$.			

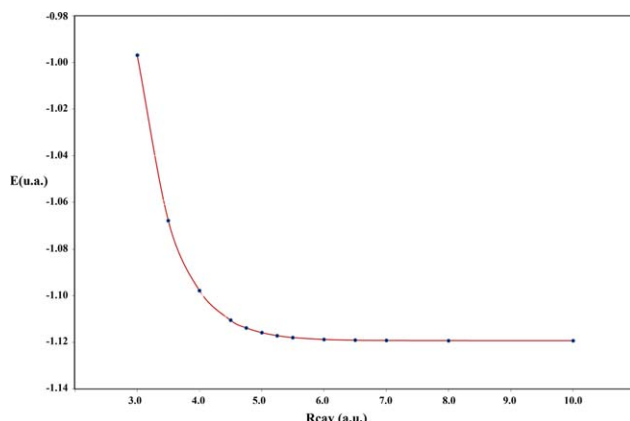


Figure 6. PCM energy of H_2 in water, adding the confinement energy calculated with TSTO basis functions and cuasimontecarlo integration. The behavior of the energy curve is more satisfactory than in Figure 8 but there are not a minimum. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

while the curve in Figure 6 shows a decreasing one. This shows that the effect of the confinement is higher than the effects taken into account by the standard PCM method.

Moreover, confinement alters the energies because it changes the wavefunction. So taking into account the confinement should change the solute–solvent interaction energy, which should be calculated using basis functions corresponding to atoms in spherical cavities, instead of using a “molecule *in vacuo*” basis set. Therefore, the combination of both effects (confinement and polarization) should be taken into account to calculate the molecular properties in solution.

In Figure 7, plotted with a different scale than Figures 5 and 6 to show the minimum, the result of applying the PCM method to H_2 molecules dissolved in H_2O , with TSTO-3G basis functions with radii equal to the cavitation ones are represented. We found a minimum energy at $R_{cav} = r_0 = 5.25$ a.u. with a depth $E(r_0) - E(\infty) = 1.98 \cdot 10^{-3}$ a.u. (1.24 Kcal/mol). From a qualitative point of view, this result seems quite satisfactory, because it explains the existence of a preferred cavitation radius (even though the result is quite larger than the empirical value usually used in PCM or COSMO models), and lies in the order of magnitude of the experimental solvation enthalpy of H_2 in water (0.97 Kcal/mol).^[76]

It is interesting to underline that the confinement effect could be even more important than the polarization effect. In

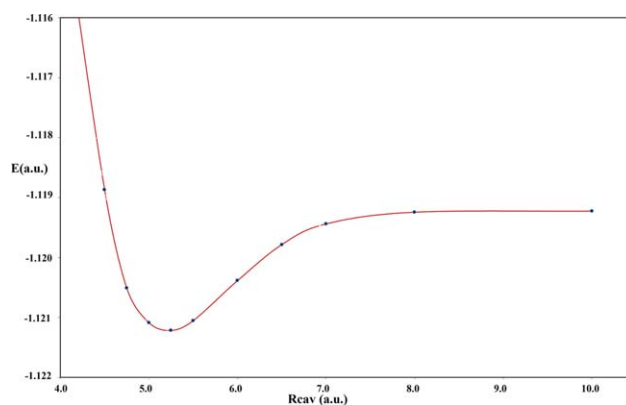


Figure 7. PCM energy of H_2 in water, calculated with TSTO-3G basis functions with $r_0 = R_{cav}$. Vertical scale has been selected to appreciate the minimum. The position and the depth of the minimum are in the same order of magnitude than the experimental values (see the text). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fact, the comparison of the energies calculated with the confined basis functions (without solvent), and including the solvent show results quite similar (see Table 2).

PCM/TtSTO-3G Calculations

As previously said, the use of trimmed basis functions has the disadvantage of requiring a variational optimization of the transition interval δ , which is different for each type of atom and for an atom isolated or belonging to a molecule. To check if it could be possible to elude this problem, we have tried to replace the expansions of TSTO trimmed functions with expansions of TtSTO truncated functions which do not require the definition of any transition interval. In the first place, we have used a truncation radius equal to the cavitation one, $r_c = R_{cav}$. After, we have used a truncation radius slightly lower than the cavitation one, $r_c = R_{cav} - 0.85$ a.u., to compensate that the expansions of the truncated functions keep a value higher than zero a little beyond the truncation radius used. The 0.85 a.u. value has been selected by comparing the radial distribution function of a TSTO-3G with several r.d.f. of TtSTO-3G functions corresponding to different values of the distance between r_c and R_{cav} (see Figs. 2a and 2b).

In the first case, we obtain the results given in the penultimate columns of Table 2 or 4. The minimum energy appears at $r_c = 5.30$ Bohr and correspond to $E(R) - E(\infty) = 2.17$ mH.

In the second case, using a truncation radius 0.85 a.u. smaller than the cavitation one, $r_c = R_{cav} - 0.85$ a.u., we find the results given in the last columns of the Table 2 or 4. The minimum energy is produced at $R_{cav} = 5.22$ Bohr ($r_c = 4.37$ Bohr), and correspond to $E(R) - E(\infty) = 2.22$ mH.

Last, we have studied the effect of changing the solvent by repeating the calculations carried out for the H_2O with C_6H_6 , and with n-octane. As it can be seen in Table 5, the position of the minimum energy with respect to the cavitation radius depends insignificantly on the solvent used. This is in good agreement with the use of constant cavitation radii of the standard PCM or COSMO calculations. The depth of the

Table 4. Confinement energies $E(R)-E(\infty)$ in hartrees, of the H_2 molecule with its electrons confined in intersecting spheres centered in the nuclei.

R (a.u.)	Hammersley	TSTO-3G ($r_0 = R_{cav}$)	TtSTO-3G ($r_c = R_{cav}$)	TtSTO-3G ($r_c = R_{cav}-0.85$)
10.00	0.00000	0.000000	0.000000	0.000000
8.00	0.00001	-0.000008	-0.000001	-0.000016
7.00	0.00007	-0.000112	-0.000025	-0.000212
6.50	0.00018	-0.000332	-0.000294	-0.000583
6.00	0.00050	-0.000828	-0.000754	-0.001254
5.50	0.00133	-0.001557	-0.001099	-0.002018
5.25	0.00215	-0.001911	-0.001495	-0.002208
5.00	0.00345	-0.002096	-0.001885	-0.002017
4.75	0.00550	-0.001896	-0.002164	-0.001124
4.50	0.00874	-0.000962	-0.002157	0.000941
4.25	0.01377	0.000921	-0.001592	0.004822
4.00	0.02149	0.005272	-0.000063	0.011410
3.75	0.03332	0.012413	0.003002	0.022146
3.50	0.05137	0.023377	0.017222	0.039606
3.00	0.12242	0.066390	0.055055	0.116574

The column "Hammersley" correspond to calculations with QMC integration³³ and 10^8 integration points.

Table 5. Cavitation radius for minimum energy and depth of the minimum for H_2 dissolved in H_2O , C_6H_6 , and $n-C_8H_{18}$.

	H_2O	C_6H_6	$n-C_8H_{18}$
R_{cav} (a.u.)	5.2209	5.2217	5.2218
ΔE (a.u.)	-0.002219	-0.002142	-0.002135

minimum obtained scarcely depends on the solvent, and is practically equal for benzene and n-octane.

In Table 3, the values of the exponents and coefficients of the truncated TtSTO-3G expansion in $r_c = 4.37$ Bohr (that lead us to a minimum energy when is associated to a cavitation radius of 5.22 Bohr), are compared with the ones of an untruncated STO-3G. To obtain exponents and coefficients for other truncation radii (bigger than 2.5 Bohr), it can be used the UCA-GSS software.^[72] Finally, it should be mentioned that the convergence of the TtSTO-3G expansions for radius r_c lower than 2.5 Bohr is exceptionally difficult to achieve. Fortunately, it should be of very scarce use for the study of solvent effects.

Conclusions

- As was already pointed out by Hsu et al.,^[28] the effect of electronic confinement is an important factor in the calculation of the molecular properties in solution that must be taken into account in the calculations based on the self-consistent reaction field models. The more or less indirect procedures habitually used to introduce this effect in the Self Consistent Reaction Field (SCRF) type calculations of solvent effects should be completed (even, perhaps, substituted) by the direct introduction of the adequate boundary conditions in the calculation of the solute wavefunctions. These boundary conditions can be taken into account—at least from a qualitative point of

view—through the Gaussian expansions that we have developed in this work.

- Although the appropriate boundary conditions to be used in SCRF-type calculations are not easy to elucidate, they could be simulated by simple hard box conditions. We have found that the change of results induced by the use of this simple boundary condition, in the calculations used by us as a test, is important.
- We have found that the "exact" calculations achieved *in vacuo* by using Monte Carlo-type integration could be approximately substituted by those obtained via Gaussian expansions that can be directly introduced in standard PCM or COSMO calculations.
- We have found that the obtaining of the TSTO-nG or TtSTO-nG expansions is a problem much more difficult than the obtaining of the traditional STO-nG functions, due to numerical problems. Nevertheless, this difficulty can be reduced by using the procedure described in this work.
- At a qualitative level, the expansions of trimmed functions TSTO-3G can be replaced with expansions of truncated functions TtSTO-3G, which are easier to obtain than the TSTO-3G ones. Nevertheless, the results seem to be poorer than those obtained by using trimmed functions.
- When we use truncated functions, it is advisable to choose a different cavitation radius R_{cav} than the truncation radius r_c . In the case of the hydrogen atom, $r_c \simeq R_{cav} - 0.85$ a.u.
- The use of TSTO-nG or TtSTO-nG basis functions leads us to a dependence of energy with the cavitation radius that has a minimum at a value practically independent of the solvent used.

Keywords: confined systems · self consistent reaction field · polarizable continuum model · Gaussian expansions · trimmed and truncated Slater-type orbitals

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