Received: 3 April 2022 | Revised: 26 June 2022 | Accepted: 16 August 2022
DOI: 10.1002/qua.27043

RESEARCH ARTICLE

International Journal of QUANTUM CHEMISTRY WILEY

Few electron systems confined in Gaussian potential wells and connection to Hooke atoms

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Funding information
Eusko Jaurlaritza, Grant/Award Numbers: IT1254-19, IT1584-22, PGC2018-098212-B-C21, PGC2018-097529-B-100

Abstract

In this work, we have computed and implemented one-body integrals concerning Gaussian confinement potentials over Gaussian basis functions. Then, we have set an equivalence between Gaussian and Hooke atoms and we have observed that, according to singlet and triplet state energies, both systems are equivalent for large confinement depth for a series of even number of electrons $n = 2, 4, 6, 8$ and 10. Unlike with harmonic potentials, Gaussian confinement potentials are dissociative for small enough depth parameter; this feature is crucial in order to model phenomena such as ionization. In this case, in addition to corresponding Taylor-series expansions, the first diagonal and sub-diagonal Padé approximant were also obtained, useful to compute the upper and lower limits for the dissociation depth. Hence, this method introduces new advantages compared to others.

KEYWORDS
Gaussian potential, Hooke atom, Padé approximants, Yukawa screening

1 | INTRODUCTION

Gaussian potential wells have attracted attention in the scientific community in a wide range of fields. On the one hand, in theoretical condensed matter field for modeling and gaining further knowledge on Quantum Dots (QDs) in semiconductors (such as GaAs) and confined systems [1–4]. Recent works concerning two and three dimensional quantum dots study properties of these impurities such as Aharonov–Bohm oscillations [5], decoherence effects [6], thermo-magnetic properties [7–10], interactions with electric and laser fields [11–15], topological dependence on the stated properties [16, 17], quantum entanglement [18], mathematical modeling [19–21] and even few-electron systems confined in such potentials [22, 23]. On the other hand, Ali-Bodmer potentials for describing α particles interactions in nuclear physics [24] are still employed in nuclear structure calculations with α clustering [25–27].

In the latter field (in which only one-body equations are considered) the Gaussian shaped interactions are treated as such. However, in the condensed matter and electronic structure community (where many-body problems arise) these functions are approximated by using harmonic potentials also known as Hooke atoms. Some of such systems composed by two electrons have closed form solutions [28] which are employed as benchmarks when testing novel electronic structure methods [29–35]. Besides, there are plenty of works in the literature where high theoretical level computations have been performed for larger systems [36, 37].

Although harmonic potentials found in Hookean systems are a sensible approximation when describing bound states in QDs and artificial atoms, there are two main inconveniences. First, by using such potentials, one loses molecular structure since any linear combination of many centre harmonic potentials will give rise to a new harmonic potential (the degree two polynomia space is complete). Second, harmonic potentials have an infinite number of bound states, therefore, processes such as ionization and dissociation cannot be properly modeled.

Minding the gap between one-particle confined in a Gaussian-like potential problems and many-body systems confined in harmonic potentials, in this work we have computed the required one-body integrals for Gaussian potentials using, also, Gaussian basis functions so employed in quantum chemistry. By doing so, we have set sail in three paths concerning these systems: we have studied deeply confined (high values depth parameter V_0) atomic systems with even number of electrons ($n = 2, 4, 6, 8$ and 10) by computing their singlet-triplet gap and relating them to equivalent Hooke atoms studied in previous works. Besides, we have studied dissociation limits for two electron systems in singlet spin state with Yukawa-like screening interaction.

2 | COMPUTATIONAL METHODS

In this work we have studied systems of even number of electrons ($n = 2, 4, 6, 8$ and 10) confined within a three dimensional Gaussian potential and screened electron–electron interactions writing the one-center Hamiltonian as in 1. The two-body (four-center) integrals concerning the screened Yukawa-like inter-electronic interactions were already computed and implemented for Gaussian basis functions by our group [38] in GAMESS-US [39]. This time, we have computed and implemented the corresponding one-body integrals for Gaussian confinement potentials using the same basis set functions as in Section 2.1.

$$\widehat{H} = -\frac{1}{2}\sum_{i}^{n}\nabla_{r_i}^{2} - V_0\sum_{i}^{n} e^{-\frac{\omega^2}{2v_0}r_i^2} + \sum_{j>i}^{n}\frac{e^{-\lambda r_{ij}}}{r_{ij}} \tag{1}$$

The election of the exponent in the Gaussian confinement function in Hamiltonian 1 is not a fact of chance, indeed. It has been selected so that for any value of the depth parameter V_0, the curvature of the confinement function is kept constant to ½ω^2; by doing so, we have been able to relate these new calculations to former ones from the literature.

In preceding works, we have optimized some even-tempered Gaussian basis functions for spherical harmonic potentials with curvature $\omega^2 = ½$ and even number of electrons ($n = 2, 4, 6, 8$ and 10) at Complete Active Space Self Consistent Field (CASSCF) and Second Order Multi Reference Many-body Perturbation (MRMP2) levels of theory using n electrons and 13 orbitals in the active space [40]. As it has been observed in this previous works concerning Hooke atoms, the most balanced (concerning accuracy and size) basis set was the one obtained for six electron systems with singlet spin state, namely ETBS-6 S basis. We have used the same basis and method throughout this paper conditioning the exponent of the Gaussian confinement function so that the curvature is kept as in the optimized Hooke system for each individual atom.

2.1 | One-body integrals concerning Gaussian confinements

We need to obtain the one-body integrals for N center external potentials defined as in (2); as it is commonly done in quantum chemistry, if we expand atomic orbitals as contracted Gaussian primitive functions, the inner integrals to be computed have the form (3).

$$V_{ext}(r) = -\sum_{i=1}^{N} V_{0,i} e^{-\beta_i (r - R_{0,i})^2} \tag{2}$$

$$\int G_1(\alpha_1, R_A, l_1, m_1, n_1) G_2(\alpha_2, R_B, l_2, m_2, n_2) e^{-\beta_i (r_1 - R_{0,i})^2} dr_1 \tag{3}$$

We take the next step by applying the Gaussian Product Theorem [41–43] upon the two basis functions $G_1$and G_2 so we obtain another Gaussian namely G_P:

$$G_P = K\sum_{l=0}^{l_1+l_2}\sum_{m=0}^{m_1+m_2}\sum_{n=0}^{n_1+n_2} f_l f_m f_n (x_1 - X_p)^l (y_1 - Y_p)^m (z_1 - Z_p)^n e^{-\gamma_P (r_1 - R_p)^2} \tag{4}$$

For which the characteristic constants and coefficients are defined as:

$$K = exp\left(-\frac{\alpha_1\alpha_2}{\gamma_P}(R_A - R_B)^2\right)$$

$$f_l = \sum_{i=0}^{l_1} \sum_{j=0}^{l_2} (X_P - X_A)^{l_1 - i} \binom{l_1}{i} (X_P - X_B)^{l_2 - i} \binom{l_2}{j}$$

$$f_l = \sum_{i=0}^{l_1} \sum_{j=0}^{l_2} (X_P - X_A)^{l_1 - i} \binom{l_1}{i} (X_P - X_B)^{l_2 - i} \binom{l_2}{j}$$

$$f_n = \sum_{i=0}^{n_1} \sum_{j=0}^{n_2} (Z_P - Z_A)^{n_1 - i} \binom{n_1}{i} (Z_P - Z_B)^{n_2 - i} \binom{n_2}{j}$$

As the potential energy function is yet a Gaussian function itself with zero angular momentum, we apply the Gaussian Product Theorem again upon the potential function and the Gaussian obtained in the previous step G_P. Then we obtain a new Gaussian, namely, G_Q given as:

$$G_Q = K' \sum_{l'=0}^{l} \sum_{m'=0}^{m} \sum_{n'=0}^{n} f_{l'} f_{m'} f_{n'} (x_1 - X_Q)^{l'} (y_1 - Y_Q)^{m'} (z_1 - Z_Q)^{n'} e^{-\gamma_Q \left(r_1 - R_{Q,i}\right)^2}$$

where the constants and the coefficients are:

$$K' = exp\left(-\frac{\beta_i \gamma_P}{\gamma_Q}(R_P - R_{0,i})^2\right), R_Q = \frac{\beta_i R_{0,i} + \gamma_P R_P}{\gamma_Q}, \gamma_Q = \beta_i + \gamma_P$$

$$f_l = \sum_{i=0}^{l'} (X_Q - X_{0,i})^{l' - i} \binom{l'}{i}$$

$$f_m = \sum_{i=0}^{m'} (Y_Q - Y_{0,i})^{m' - i} \binom{m'}{i}$$

$$f_l = \sum_{i=0}^{l'} (X_Q - X_{0,i})^{l' - i} \binom{l'}{i}$$

Now, using the properties of the exponential function and considering the distance squared dependency of the exponent, we can acknowledge the integral (3) is in fact composed by the product of three integrals; one for each spacial variable. It can, therefore, be written as in (5)

$$I(x, y, z) = KK' I(x) I(y) I(z) \tag{5}$$

And each integral is given as:

$$I_i(x) = \sum_{l=0}^{l_1 + l_2} f_l \sum_{l'=0}^{l} f_{l'} \int_{-\infty}^{\infty} (x_i - X_Q)^{l'} e^{-\gamma_Q (x_i - X_Q)^2} dx_i$$

$$I_i(y) = \sum_{m=0}^{m_1 + m_2} f_m \sum_{m'=0}^{m} f_{m'} \int_{-\infty}^{\infty} (y_i - Y_Q)^{m'} e^{-\gamma_Q (y_i - Y_Q)^2} dy_i$$

$$I_i(z) = \sum_{n=0}^{n_1 + n_2} f_n \sum_{n'=0}^{n} f_{n'} \int_{-\infty}^{\infty} (z_i - Z_Q)^{n'} e^{-\gamma_Q (z_i - Z_Q)^2} dz_i$$

Notice we have exchanged the order of integration and summation and we are allowed to do so as both, the integral and summation, are totally convergent, the former because we are dealing with functions which live in the Schwartz space and the latter because the summation is finite. We may also notice that all three integrals are the momenta of a Gaussian distribution for which the general formula is given by Equation (6). Since the Gaussian distribution is even with respect to reflection plane where the point $t_1 = T_Q$ in contained, only even order momenta will be different from zero.

$$\int_{-\infty}^{\infty} (t_i - T_Q)^k e^{-\gamma_Q (t_i - T_Q)^2} dt_i = \frac{\Gamma\left(\frac{k+1}{2}\right)}{\gamma_Q^{(k+1)/2}}, k = 0,2,4 \tag{6}$$

One last remark concerns the evaluation of the gamma function obtained in Equation (6). As we have mentioned, the moment parameter *k* must be even for the integral not to vanish, using a property of the gamma function, we may evaluate it using a product as: *i*

$$\Gamma\left(n+\frac{1}{2}\right)=\sqrt{\pi}\frac{1\cdot3\cdot5\ldots(2n-1)}{2^n}, n\in\mathbb{N}$$

Thus, each of the three spatial components of the matrix element containing the *i*th center are given as simple nested sums and products as in (7).

$$I_i(x)=\sum_{l=0}^{l_1+l_2} f_l \sum_{l'=0}^{l,2} f_{l'} \frac{\sqrt{\pi}}{\gamma_Q^{(k+1)/2}} \prod_{l''=1}^{l'-1,2} \frac{l''}{2} \tag{7}$$

We have coded these integrals as a subroutine in FORTRAN70 in order to add them to the *source* file for the one body integral packages in the open code package GAMESS-US [39].

2.2 | Pseudocode for implementing one-body integrals

In order to implement these one-body integrals in GAMESS-US, we have edited the corresponding source file (namely int1.src). In this file, we have written the two required functions named GAUSS_INTEGRALS and ONE_DIM_INTEGRALS for which the pseudo-codes are given by Algorithms 1 and 2 respectively.

Once the required functions were incorporated, it was sufficient to call these functions instead of the nuclear attraction integrals every time one would compute one of such for all the electron-nucleus interactions. Hence, the centers of the Gaussian confinement potentials are given by the coordinates of the (now) dummy atoms. In addition, GAMESS-US aborts any calculation in which the distance between two atoms (centres) is smaller than 0.1 Å; in order to account for merging Gaussian potentials, we have deactivated the corresponding distance checking point.

Algorithm 1 GAUSS_INTEGRALS

```
Require: $\alpha_1$, $\alpha_2$, $l_1$, $m_1$, $n_1$, $l_2$, $m_2$, $n_2$, $\mathbf{R}_A$, $\mathbf{R}_B$, $V_{0,i}$, $\beta_i$, $\mathbf{R}_{0,i}$
    Compute the P and Q centres
    Compute the one-dimensional integrals ($I_x$,$I_y$,$I_z$)
    Compute the total integral $I = V_0 K_P K_Q I_x I_y I_z$
    Return the value of the integral $I$
```

Algorithm 2 ONE_DIM_INTEGRALS

```
Require: $\alpha_P$, $\alpha_Q$, $l_1$, $l_2$, $\mathbf{R}_P$, $\mathbf{R}_Q$
    Set INTX = 0.0
    for L = 0:($l_1 + l_2$) do
      Compute $f_l$
      Set SUMLP = 0.0
    if mod(L,2)==0 then for LP =0:L:2 do
      Compute sumation terms $S_{lp}$
        Set SUMLP = SUMLP + $S_{lp}$
       end for
      end if
      Set INX = INTX + $f_l$ * SUMLP
    end for
    Return the value of the integral INTX
```

3 | RESULTS AND DISCUSSION

3.1 | Deeply confined one center systems with even number of electrons

We have performed Complete Active Space Self Consistent Filed (CASSCF) and Second Order Multi Reference Many-body Perturbation (MRMP2) calculations using $m = 10$, 11, 12 and 13 orbitals in the active space upon systems composed by small even number of electrons $n = 2$, 4, 6, 8 and 10 confined in a single three-dimensional Gaussian potential well as in Hamiltonian 1. In order to make sure that our new results are sensible and make a connection with former works on Hook atoms with these numbers of electrons, we have taken 30 values for the Gaussian depth parameter V_0 evenly spaced in the range $[-300.0, -10.0]$ (in *au*), set the screening parameter $\lambda = 0.0$ and the curvature parameter $\omega^2 = 1/4$. With the aim of gaining a deeper insight of the connection between Gaussian and Hookean systems, we have expanded the Gaussian potential energy function in a power series as in Equation (8). If we keep the first three terms in this Taylor expansion, we may notice that we assume an error in potential energy which is proportional to the inverse of the Gaussian potential depth as in Equation (9). If we further assume that kinetic energy and electron interaction energy do not depend strongly on potential depth (which is a sensible assumption for deep potentials), the Gaussian system energy E_G and the equivalent (in the sense of curvature) Hookean system energy E_H are related as in Equation 11 where (n, ω^2) is the average value of the first anharmonic term and depends on the number of electrons n and the curvature of the equivalent Hookean ω^2. In other words, the first anharmonic term is treated as a first-order perturbation for the Hooke atom. Even if the number of electrons, the depth and the curvature are kept constant, we may infer that spin state of the wave-function also plays a role since rather different one-body functions may take part in building the whole many-body wave functions; therefore, altering the third term average value in Equation (9).

$$V_G = -\sum_{i=1}^{n} \sum_{k=0}^{\infty} \frac{\left(-\frac{\omega^2}{2}\right)^k V_0^{1-k} r_i^{2k}}{k!} \tag{8}$$

$$V_G = -nV_0 + \frac{\omega^2}{2} \sum_{i=1}^{n} r_i^2 - \frac{\omega^4}{8V_0} \sum_{i=1^n} r_i^4 + O\left(\frac{n\omega^6}{V_0^2}\right) \tag{9}$$

Hereby, based on the power series representation for the potential energy function in Equation (8) and considering T and V_{ee} do not heavily depend on a specific V_0 but rather on the curvature of the potential ω^2, we may state that—just considering the first anharmonic term—the shifted energy of the Gaussian system $E_G + nV_0$ depends linearly on the inverse of the Gaussian potential depth $1/V_0$ and the (shifted) energy $(E_G + nV_0)$ cuts the ordinate (where $V_0 = 0$) at the Hookean system energy with curvature ω^2. We have performed several calculations as stated in the previous paragraph and we have obtained the Hookean energy E_H and the first anharmonic term (written for simplicity as g) by linear regression; all regression estimates are contained in Table 1.

We may observe that Hooke atom energies for singlet and triplet states agree with those obtained in former works at the same level of theory and in the worst case scenario, the Hookean energy has 1×10^{-5}*au* error obtained by error estimation in routine linear regression; thus, the calculation protocol error is larger than the one from the regression. As far as first anharmonic terms g are considered, they are obtained by taking the slope of the linear regression which—in the worst case scenario—has an error of 4×10^{-4}*au*. If we take a deeper insight of the g values, we may immediately notice that, for a given spin state either singlet or triplet, does not dramatically change with the size of the active space while it is highly dependent on the number of electrons n. Besides the number of electrons, this anharmonic term also depends on the spin state taking the two-electron system as the most notorious one. From the previously exposed theory this behavior was expected since g represents a sum over electrons of an averaged value of a quartic potential with respect to a many-body normalized wave-function; therefore, g condenses a lot of information about the system: the curvature, the number of electrons and the spin state.

In the worst case scenario, the one for CASSCF(8,10)(S)/ETBS-6 S calculations, the regression correlation parameter was $R^2 = 0.9623$. However, this is a pretty odd case and the average value for this statistic is $R^2 = 0.9991$. It can also be seen that even the Hooke atom energy is comparable to the ones obtained by other methods, the anharmonic contribution g is quite different even if we compare it to the one obtained by including dynamical correlation effects via perturbation methods at the same theory level. We have also observed that as soon as the active space size is augmented, the correlation parameter gets rapidly closer to 1 approaching perfect linear dependency.

3.2 | Loosely confined two electron systems with screened Coulomb interaction

Based on the fact that two electron systems with singlet spin state have at least one occupied bound state, we have been wondering at which point of Gaussian potential depth the whole systems dissociates ($E_G\,[V^d] = 0$). On top of this, we have also considered electron–electron interaction to be screened and in what measure it affects the loosely bound system's stability. Hence, we have modeled these systems using

TABLE 1 Hookean energy E_H (*au*) and *g* (*au*^{2}) terms obtained by linear regression using data obtained by CASSCF(*n*,*m*)/ETBS-6Sand MRMP2 (*n*,*m*)/ETBS-6 S calculations

S CAS				***S MRMP2***		***T CAS***		$E^{T}_{RMP2}{}^{M}$	
n	***m***	***EH***	***g***	***EH***	***g***	***EH***	***g***	***EH***	***g***
2	10	2.001718	0.3214578	2.000553	0.3214138	2.36111	0.4615673	2.359877	0.4623589
	11	2.001569	0.3220647	2.000541	0.3214695	2.359966	0.4629399	2.359749	0.4629238
	12	2.001353	0.3219344	2.000521	0.3214604	2.359883	0.4629516	2.359746	0.4629451
	13	2.001233	0.3221784	2.000509	0.3214931	2.35988	0.4629387	2.359746	0.4629558
4	10	6.41014	1.330105	6.391462	1.331209	6.369164	1.314156	6.353142	1.31538
	11	6.405534	1.329927	6.391097	1.331188	6.365399	1.315223	6.352794	1.315585
	12	6.401805	1.332317	6.390674	1.331675	6.361329	1.316371	6.352395	1.315823
	13	6.398952	1.331355	6.390306	1.331604	6.360014	1.305258	6.352244	1.314446
6	10	12.13421	2.784703	12.08499	2.786157	12.09482	2.767391	12.04846	2.768882
	11	12.12679	2.788366	12.0844	2.786919	12.08947	2.763241	12.04783	2.768251
	12	12.12125	2.788358	12.08397	2.786566	12.08349	2.770115	12.04719	2.768935
	13	12.11545	2.783258	12.08333	2.786984	12.07844	2.771766	12.04666	2.769276
8	10	19.07563	3.931056	19.00154	4.625022	19.36024	4.555748	19.27003	4.672289
	11	19.07066	4.728791	19.00104	4.728537	19.35476	4.703725	19.2721	4.905097
	12	19.06393	4.689791	19.00023	4.703367	19.34488	4.823247	19.27197	5.007794
	13	19.05414	4.735014	18.99894	4.729663	19.33712	4.901288	19.27023	4.921244
10	10	27.83390	7.339055	27.69036	7.533762	27.80165	7.224892	27.66912	7.522172
	11	27.81091	7.453328	27.68948	7.638288	27.78357	7.424963	27.66788	7.547430
	12	27.78987	7.5806211	27.69389	7.5958861	27.76885	7.5651956	27.66660	7.5712475

Hamiltonians as in Equation (10) where the confinement Gaussian potential has been defined as in the previous section and the electronic Coulomb interaction is replaced by a Yukawa-like potential with exponent $\lambda > 0$. We have taken 10 values for λ parameter in the evenly separated range [0.10, 1.00] and 20 values for V_0 also in a evenly separated range [−1.50, −0.50] at MRMP2(2,13)/ETBS-6 S level of theory for singlet states; the results for these calculations can be found in Figure 1.

Points with positive energies (above the gray line) in this plot are somehow meaningless since positive energies belong to dissociated systems (scattering states); nevertheless, energies are positive and real since the basis function themselves create the Dirichlet boundaries. At a first glimpse, one shall observe that the dissociation limit depth is smaller as λ is larger (therefore, electron–electron interaction is weaker).

Let us try to make sense of the obtained results. As in the previous section, we have expanded our Gaussian systems energy now taking an additional term as in Equation (11) where the anharmonic contributions g_1 and g_2 are generally taken as positive despite the fact the sign is alternating in the original Taylor-like series. Now, we shall obtain E_H, g_1 and g_2 from data using linear regression (omitting all E_G >0 data) via small squares minimisation; from the residues, we may notice that they follow an expected cubic polynomial trend due to the fact that we have trimmed the Taylor-like series at that order.

$$H = -\frac{1}{2}\sum\nolimits_{i=1}^{2}\nabla_i^2 - V_0\sum\nolimits_{i=1}^{2} e^{-\frac{\omega^2}{2V_0}r_i^2} + \frac{e^{-\lambda r_{12}}}{r_{12}} \tag{10}$$

$$E_G + 2V_0 = E_H + \frac{g_1}{V_0} + \frac{g_2}{V_0^2} + O\left(\frac{\omega^8}{V_0^2}\right); g_1 = \frac{\omega^4}{8}\left\langle \sum\nolimits_{i=1}^{2} r_i^4 \right\rangle; g_2 = \frac{\omega^6}{36}\left\langle \sum\nolimits_{i=1}^{2} r_i^6 \right\rangle \tag{11}$$

Once we have obtained the coefficients we can solve the Equation (11) for E_G as in Equation (12) where we still have a Taylor-like series. Now, we can exploit an interesting property of the energy function: in the Taylor-like series signs are alternating, therefore it is a Stiljies function. That means if we obtain the main Padé sequence (i.e., the sequence containing the diagonal and lower diagonal Padé approximants $P_N^N\left(V_0^{-1}\right)$ and $P_{N+1}^N\left(V_0^{-1}\right)$, respectively), we shall obtain physically relevant values such as the dissociation limit of the system. Since we only have obtained the first three coefficients of the Taylor-like series, the highest order main Padé sequence we shall obtain is the one composed by the diagonal approximant $P_1^1\left(V_0^{-1}\right)$ and the subdiagonal approximant $P_2^1\left(V_0^{-1}\right)$ given in Equations (13) and (14), respectively. It is known that the sequence

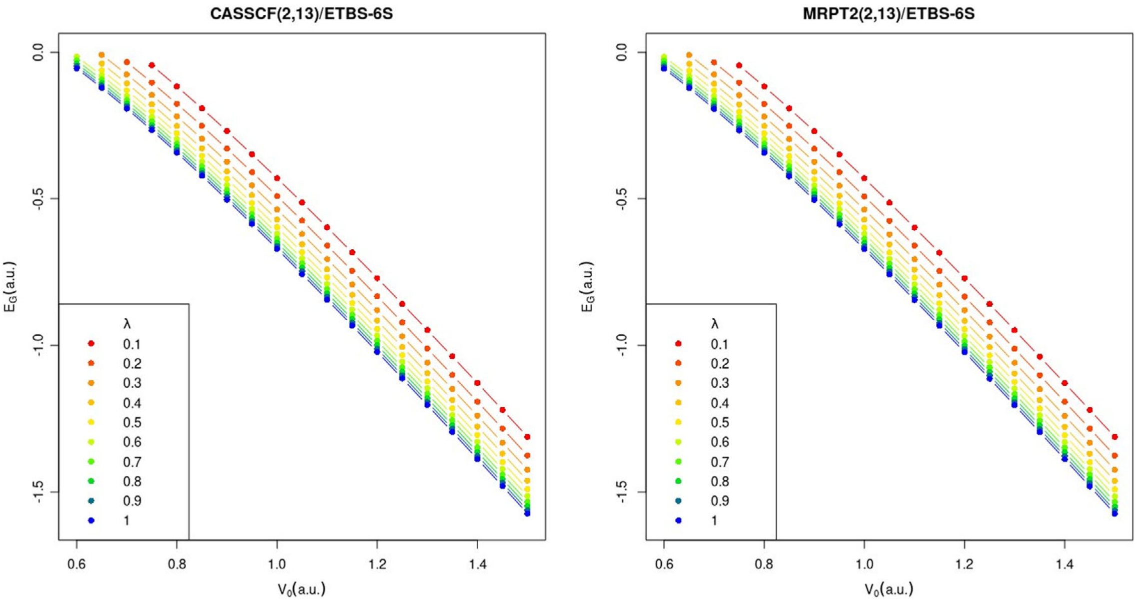

FIGURE 1 Energies for Gaussian confinement with two electrons in singlet spin state for several screening parameter λ values

TABLE 2 Hooke atom energy (E_H), first anharmonic terms (g_1, g_2) and bound dissociation limits obtained for several screening parameter values for two-electron systems with singlet spin state at CASSCF(2,13)/ETBS-6 S and MRMP2(2,13)/ETBS-6 S levels

EH			$g1$		$g2$		V^{d-}		V^{d+}	
λ	CASSCF	MRMP2	CASSCF	MRMP2	CASSCF	MRMP2	CASSCF	MRMP2	CASSCF	MRMP2
0.1	1.9379	1.9372	−0.3839	−0.3839	0.0163	0.0164	0.731	0.730	0.771	0.770
0.2	1.8719	1.8712	−0.3829	−0.3830	0.0200	0.0201	0.689	0.688	0.731	0.731
0.3	1.8204	1.8197	−0.3802	−0.3803	0.0232	0.0233	0.657	0.657	0.701	0.701
0.4	1.7770	1.7753	−0.3712	−0.3691	0.0232	0.0220	0.635	0.634	0.680	0.680
0.5	1.7397	1.7394	−0.3578	−0.3587	0.0203	0.0208	0.618	0.617	0.664	0.663
0.6	1.7143	1.7135	−0.3568	−0.3569	0.0233	0.0234	0.603	0.603	0.649	0.648
0.7	1.6902	1.6890	−0.3487	−0.3482	0.0223	0.0222	0.593	0.592	0.639	0.638
0.8	1.6702	1.6686	−0.3418	−0.3406	0.0215	0.0211	0.584	0.584	0.630	0.630
0.9	1.6532	1.6514	−0.3354	−0.3339	0.0206	0.0201	0.578	0.577	0.624	0.624
1.0	1.6376	1.6369	−0.3280	−0.3281	0.0192	0.0192	0.573	0.572	0.619	0.618

Note: All values are given in atomic units.

$P_1^1(V_0^{-1})$ will converge to the right energy from bellow while $P_2^1(V_0^{-1})$ will converge from above. For obtaining the dissociation limit, we take these Padé approximants solve them for V_0 obtaining the lower and upper limit of the dissociation depths V^{d-} and V^{d+} respectively in terms of the physical quantities E_H, g_1 and g_2 for a given screening parameter λ. All obtained results are condensed in Table 2.

$$\frac{E_G}{V_0} = -2 + \frac{E_H}{V_0} + \frac{g_1}{V_0^2} + \frac{g_2}{V_0^3} + O\left(\frac{\omega^8}{V_0^4}\right) \tag{12}$$

$$P_1^1\left(V_0^{-1}\right) = -\frac{2g_1 + E_H - 2E_H V_0}{g_1 - E_H V_0} \tag{13}$$

$$P_2^1\left(V_0^{-1}\right) = \frac{(4g_1 + 2E_H)V_0^2 - (4g_2 + 4g_1E_H)V_0}{-\left(E_H^2 + 2g_1\right)V_0^2 + (g_1 + 2g_2 + E_H)V_0 + \left(g_2E_H - g_1^2\right)} \tag{14}$$

If we focus our attention upon a given λ value and study a given estimated physical property, we shall notice that including dynamic correlation effects via perturbation methods does not quite make a big difference with respect to the same quantity obtained by regular CASSCF method.

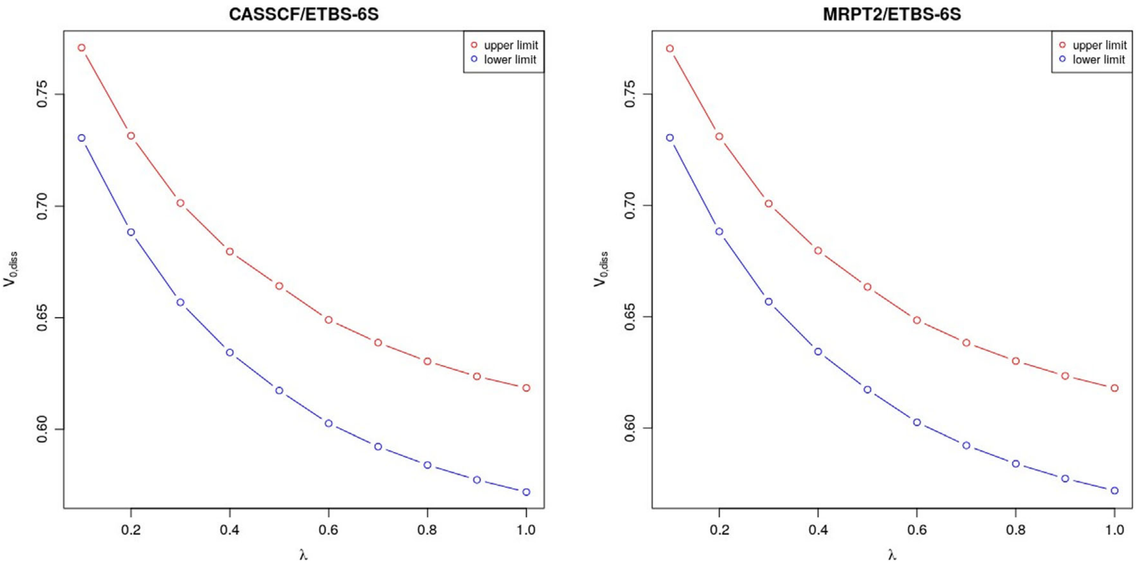

FIGURE 2 Limit dissociation potentials for several λ values

Now, as far as E_H is concerned, this energy is smaller as λ increases which is to be expected for Hooke atoms [40]. In contrast to the stated former results, in this very work, we obtained a Hooke two electron singlet atom energy for $\lambda = 0.2$, 0.4, 0.8 and 1.0 to be $E_H = 1.8459$, 1.7502, 1.6881, 1.6458 and 1.6159 *au*, respectively, at CASSCF/ETBS-6 S while in Table 2 the obtained energies are in average 0.025 *au* higher in energy. As we have discussed in the previous section, accurate Hooke energies are obtained for deep potentials, nevertheless, in this section we have been dealing with loosely confined systems. Therefore, on the basis of this approximation, we may state that our estimations are rather reasonable and both regimes have pretty unique features.

As for the anharmonic terms, g_1 we may obverse it also gets smaller as λ increases. We may hypothesize that as electron-electron interaction gets weaker, correlation effects are also turned off and electrons are more likely found in the center of the potential well, thus this first anharmonic term becomes smaller. On the other hand, the second anharmonic term g_2 gets a maximum for $\lambda = 0.6$ and then decreases.

Finally, the lower and upper bounds for the limit ionization potentials have in the worst-case scenario a 0.046 *au* amplitude as we may observe that we have predicted their behavior in terms of physical constants by setting the corresponding Padé approximants 18 and 19 to zero and solving for V_0. We shall see that these limit potentials are shallower and asymptotic to a limit value at which only one-body interactions are relevant. Thus, we get an obvious conclusion, as electron–electron interaction is turned off the potentials does not need to do so much "work" to confine the interacting particles and shallower potentials are still able to confine them. We may find a visual summary in Figure 2.

4 | CONCLUDING REMARKS

In this work, we have computed and implemented the required one-body integrals for quantum particles confined in Gaussian potential wells for which the center of the basis function and the center of the potentials do not need to coincide. Such implementation has been interfaced to electronic structure software GAMESS-US so that we can make use of its quantum chemical computation machinery to study systems of electrons confined in dissociative potentials. Firstly, we have performed computations on deeply confined systems (large V_0 parameter) with controlled width parameter such that the curvature of the potential at the minimum point was $\omega^2 = 0.25$. Since previous results on harmonic potentials have been well established for $n = 2, 4, 6, 8$ and 10 electrons, by means of Taylor series we have shown our calculations are compatible with the former ones.

Finally, we have studied dissociative systems composed by two electrons in which the conventional Coulomb operator was substituted by Yukawa potentials. In this case, we have not only obtained the corresponding Taylor-series expansion but also the first diagonal and sub-diagonal Padé approximant which were useful to compute the upper and lower limits for the dissociation depth for several screening parameters λ.

AUTHOR CONTRIBUTIONS

Xabier Telleria-Allika: Conceptualization; investigation; methodology; validation; writing – original draft; writing – review and editing. **Jose M. Mercero:** Formal analysis; supervision; visualization. **Jesus M. Ugalde:** Conceptualization; supervision; writing – review and editing. **Xabier Lopez:** Conceptualization; formal analysis; investigation; supervision; writing – original draft. **Jon M. Matxain:** Conceptualization; formal analysis; investigation; supervision; validation; writing – original draft; writing – review and editing.

ACKNOWLEDGMENTS

This research was funded by Eusko Jaurlaritza (the Basque Government), through Consolidated Group Project No. IT1254-19. Technical and human support provided by IZO-SGI, SGIker (UPV/EHU, MICINN, GV/EJ, ERDF and ESF) is gratefully acknowledged.

FUNDING INFORMATION

This research was funded by Eusko Jaurlaritza (the Basque Government), through Consolidated Group Project No. IT1254-19 and IT1584-22. Technical and human support provided by IZO-SGI, SGIker (UPV/EHU, MICINN, GV/EJ, ERDF and ESF) is gratefully acknowledged.

DATA AVAILABILITY STATEMENT

Research data are not shared.

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How to cite this article:

X. Telleria-Allika, J. M. Mercero, J. M. Ugalde, X. Lopez, J. M. Matxain, *Int. J. Quantum Chem.* **2023**, *123*(5), e27043. https://doi.org/10.1002/qua.27043