**ORIGINAL PAPER**

# Distributed Gaussian orbitals for the description of electrons in an external potential

Léa Brooke[1] · Alejandro Diaz-Marquez[1] · Stefano Evangelisti[1] · Thierry Leininger[1] · Pierre-François Loos[1] · Nicolas Suaud[1] · J. A. Berger[1,2]

**Abstract**

In this work, we demonstrate the viability of using distributed Gaussian orbitals as a basis set for the calculation of the properties of electrons subjected to an external potential. We validate our method by studying one-electron systems for which we can compare to exact analytical results. We highlight numerical aspects that require particular care when using a distributed Gaussian basis set. In particular, we discuss the optimal choice for the distance between two neighboring Gaussian orbitals. Finally, we show how our approach can be applied to many-electron problems.

**Keywords** Basis set · Distributed Gaussians · Quantum chemistry

## Introduction

Expanding the electronic wavefunction in a set of one-electron basis functions is a standard technique to study many-electron systems [1]. In particular, Gaussian-type orbitals (GTO) are widely used in quantum chemistry calculations [2, 3]. In the case of molecular simulations, GTO are usually centered on nuclei, since this is a very effective way to describe the internal structure of the electronic wavefunction. Instead, for systems in which the electrons are subjected to a smooth effective potential, a basis set that consists of atom-centered Gaussians is, in general, not suitable to express the many-body wave function. Therefore, we have recently used distributed Gaussian orbitals in order to describe electrons confined in a quasi one-dimensional region of space [4]. This approach

✉ J. A. Berger
   arjan.berger@irsamc.ups-tlse.fr

   Stefano Evangelisti
   stefano.evangelisti@irsamc.ups-tlse.fr

1   Laboratoire de Chimie et Physique Quantiques, IRSAMC, CNRS, Université de Toulouse, Toulouse, UPS, France

2   European Theoretical Spectroscopy Facility (ETSF), https://www.etsf.eu/

seems to be very promising, in particular for the study of Wigner localization [5]. The use of evenly distributed orbitals, together with a small number of compact atom-centered orbitals, has also been investigated by some of us in the case of molecular calculations [6]. Alternatives are to use floating Gaussians [7–14] or spherical Gaussians [15]. Finally, we note that also other types of functions such as, e.g., delta functions, could be used. However, in the case of delta functions, results converge slowly [16]. In this work, we investigate to what extent Gaussian orbitals are suitable basis functions for the description of electronic systems.

Our ultimate goal is to study electronic properties of real systems, which can be either three-dimensional (3D) systems, or quasi-one-dimensional (1D) and quasi-two-dimensional (2D) systems. In particular, we are interested in studying quantum dots and quantum wires. For this reason, all Gaussian orbitals used for the expansion of the wavefunctions have been chosen to be *three-dimensional*. In the present work, the Gaussian orbitals have been chosen as 3D equally spaced Gaussians of *s* type having a common exponent. The Gaussian centers are placed on a regular grid, either in 1D, 2D, or 3D. Although different strategies for paving the space with Gaussian functions can be considered, for the sake of simplicity we will limit ourselves to an equidistant grid in 1D, a square grid in 2D and a simple cubic grid in 3D.

In this work, we investigate the efficiency of Gaussian basis sets to describe the wave function of electrons that are confined by a potential. This potential can be either

explicitly given, e.g., a harmonic potential, or implicitly generated by the Gaussians in the basis set, i.e., the electrons can only be present in the region of space that is spanned by the Gaussian orbitals. In order to validate our approach, we will mainly focus on one-electron systems because: (i) we can compare to exact analytical results; (ii) the conclusions can to a large extent be transferred to many-electron systems. First, we will study the requirements on the one-particle basis set to accurately describe the electronic wave function of a single electron confined by a potential. In particular, we will consider the cases of a particle-in-a-box and the harmonic oscillator, which are described by Hamiltonians that admit an analytical solution. Second, in order to show that a distributed Gaussian basis set can also be used for the treatment of interacting electrons, we will present and discuss some results for six electrons confined in a quasi-1D potential.

This article is organized as follows: In section "Theory" we briefly describe the model systems that we will study here. In section "Distributed Gaussian orbitals", the distributed basis set of Gaussian orbitals used to describe the wavefunction is defined. In section "A single electron in a quasi-1D potential", the particular case of quasi-1D systems is presented for both an explicitly given potential as well as a potential that is implicitly defined by the basis. In section "Results and discussion", we present results obtained with this basis for a particle in a box and an electron in a harmonic potential and we compare to exact results. We also show some results for systems with several electrons. Finally, in section "Conclusions", we draw our conclusions. We will use Hartree atomic units throughout.

## Theory

In order to keep this article self-contained, in this section we review some basic theory that will be useful in the remainder of this work. We will solve the time-independent Schrödinger equation with the following Hamiltonian,

$$\hat{H} = \hat{T} + \hat{V} + \hat{W}, \tag{1}$$

where the kinetic energy operator, the potential energy operator and the two-particle interaction are given by, respectively,

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_{\mathbf{r}_i}^2, \tag{2}$$

$$\hat{V} = \sum_{i=1}^{N} V(\mathbf{r}_i), \tag{3}$$

$$\hat{W} = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{4}$$

in which $V(\mathbf{r})$ is the external potential and $N$ is the number of electrons. In most of this work we will be interested in one-electron systems, in which case $\hat{W} = 0$.

In this work, we want to demonstrate the efficiency of a basis set of distributed Gaussians. We will do this by studying quasi-1D systems, i.e., the Gaussian orbitals will be distributed along a line. In this way, the Gaussians do not span a strict 1D space [17] since the Gaussian orbitals are themselves three-dimensional. For this reason, we denote the space as quasi-1D. The main advantage of this approach is that the notation remains simple and we can compare to exact, analytical results for 1D model systems. Moreover, the conclusions we will obtain for the quasi-1D systems can be easily extended to 2D or 3D systems. However, due to the 3D nature of the Gaussian orbitals that we will use, the energy of a quasi-1D system has a contribution stemming from the two transverse components of the Gaussians, i.e., orthogonal to the line along which the Gaussians are placed. This contribution to the energy has to be removed in order to compare to the analytical results of 1D model potentials. We will discuss how to do this in the following.

In this work, we will consider the potentials related to the following two 1D models: (i) *The particle in a box*; (ii) *The harmonic oscillator*. Let us now briefly discuss the main details of these two models that are relevant to this work.

### Particle in a box

The solutions to the problem of a particle in a 1D box (PiB) of length $L$ are well known. We consider here a symmetric potential, i.e., $V(z) = 0$ between $-L/2$ and $L/2$ and $V(z) = \infty$ everywhere else. The eigenfunctions of this system are given by [18] (see also [19])

$$\psi_n(z) = \sqrt{\frac{2}{L}} \cos\left(\frac{n\pi x}{L}\right) \quad (n = 1, 3, 5, \cdots), \tag{5}$$

$$\psi_n(z) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad (n = 2, 4, 6, \cdots), \tag{6}$$

and the corresponding eigenenergies are

$$E_n(L) = \frac{n^2 \pi^2}{2L^2} \quad (n = 1, 2, 3, \cdots). \tag{7}$$

In order to simulate the external potential, one could use a continuous function of the form $V_k(z) = (2z/L)^{2k}$ where $k$ is a positive integer, and then take the limit $k \to \infty$ in order to simulate the presence of the box walls. In fact, we have $\lim_{k \to \infty} V_k(z) = 0$ if $|z| < L/2$ and $\lim_{k \to \infty} V_k(z) = +\infty$ if $|z| > L/2$. The problem is that such an approach should be combined with the use of basis functions that have compact support, i.e., functions that are identically zero for $|z| > L/2$. Unfortunately, Gaussians are different from zero everywhere, and therefore they do not have compact support. As a consequence, *all* the matrix elements of the

potential with two Gaussians diverge in the limit $k \to \infty$ and, therefore, also the eigenenergies will diverge.

Because of this difficulty, we propose an alternative procedure in which we *implicitly* define the box through the presence of the Gaussian functions. In fact, since the potential is zero within the box and infinite outside the box, we can solve a free-electron problem, i.e., $\hat{H} = -\frac{1}{2}\nabla^2$, in which the electron is confined to a box spanned by the orbital basis. However, as a consequence, the boundaries of the box are not sharp but fuzzy because the Dirichlet boundary conditions $\psi(-L/2) = \psi(L/2) = 0$ are not strictly satisfied [20].

## Harmonic oscillator

The second model system that we consider is the harmonic oscillator. In this case, the potential function given by $\frac{1}{2}kz^2$, with $k$ the force constant, is well defined for any value of $z$, and therefore a suitable number of Gaussian orbitals in the region of the minimum of the potential is well adapted to reproduce the eigenvectors associated to the low-lying part of the spectrum. The Hamiltonian operator is given by

$$\hat{H} = \hat{T} + \hat{V} = -\frac{1}{2}\nabla^2 + \frac{1}{2}kz^2. \tag{8}$$

The analytical solutions to the corresponding Schrödinger equation are well known. The eigenenergies are given by

$$E_n = \left(n + \frac{1}{2}\right)\omega, \tag{9}$$

where $\omega = \sqrt{k}$ is the angular frequency and $n$ is a non-negative integer, while the eigenfunctions are given by

$$\psi_n(z) = \frac{1}{\sqrt{2^n n!}}\left(\frac{\omega}{\pi}\right)^{1/4} e^{-\frac{\omega z^2}{2}} H_n\left(\sqrt{\omega}z\right), \tag{10}$$

in which $H_n$ are Hermite polynomials.

## The effective potential $\bar{V}$

In the case of the PiB, we implicitly defined the external potential through the basis set. In this section, we show how one can obtain an explicit expression for the potential for a given basis set by reverse engineering. For a given basis set, the one-particle wave function $\psi(z)$ that is an eigenstate of the Hamiltonian can be obtained by solving the free-electron problem. From the wave function we can obtain the corresponding potential that generated it. The Schrödinger equation for a single particle in an external potential $V(z)$ is given by

$$-\frac{1}{2}\frac{d^2\psi(z)}{dz^2} + V(z)\psi(z) = E\psi(z). \tag{11}$$

This means that a multiplicative potential $V(z)$ can be obtained via the relation

$$V(z) = \frac{1}{2\psi(z)}\frac{d^2\psi(z)}{dz^2} - E. \tag{12}$$

This equation is valid everywhere, except, possibly, at the nodes of $\psi(z)$. Therefore, if the ground-state wavefunction, as it often happens, is nodeless, the potential can be defined everywhere. We note that Eq. (12) gives the exact original potential $V(z)$ if both the wavefunction $\psi$ and the energy $E$ are exact. We now turn to approximated energies and wavefunctions. If these quantities are the result of an approximated calculation (let us indicate them by $\tilde{\psi}$ and $\tilde{E}$), we can define an effective potential $\tilde{V}(z)$ as

$$\tilde{V}(z) = \frac{1}{2\tilde{\psi}(z)}\frac{d^2\tilde{\psi}(z)}{dz^2} - \tilde{E}. \tag{13}$$

We have now that Eq. 13 *defines* the effective potential $\tilde{V}$, in such a way that

$$-\frac{1}{2}\frac{d^2\tilde{\psi}(z)}{dz^2} + \tilde{V}(z)\tilde{\psi}(z) = \tilde{E}\tilde{\psi}(z). \tag{14}$$

We use Eq. 13 in order to obtain the effective potential associated to the solution of the Schrödinger equation for a free particle, projected on a set of Gaussian orbitals.

## Distributed Gaussian orbitals

The primitive orbitals used to expand the wavefunction are chosen as 3D $s$-type Gaussian orbitals having a single common exponent, $\alpha$. For normalized orbitals, we get

$$\phi_i^\alpha(\mathbf{r}) = (2\alpha/\pi)^{\frac{3}{4}} \exp(-\alpha\|\mathbf{r} - \mathbf{R}_i\|^2), \tag{15}$$

where $\mathbf{R}_i$ indicates the center of the $i$-th Gaussian. Here we place the centers of the Gaussians on a regular linear grid along the $z$-axis. The centers $Z_i$ of the Gaussians are given by the expression

$$Z_i = i\delta \qquad (i = -g, -g+1, ..., 0, 1, ..., g), \tag{16}$$

where $g$ is a non-negative integer. Therefore, $M = 2g + 1$ is the total number of Gaussians. The overlap between two Gaussians having the same exponent $\alpha$, and centers placed at a distance $\delta$ is given by

$$\mathcal{S}(\alpha, \delta) = \exp(-\alpha\delta^2/2). \tag{17}$$

In the present investigation, the distance between two neighboring centers is related to the exponent of the Gaussian via the relation

$$\alpha = \frac{\xi}{\delta^2}, \tag{18}$$

where $\xi$ is a constant that characterizes the resolution of the basis set. This choice implies that the overlap $\mathcal{S}$ between two normalized Gaussians is a function of $\xi$ only. It is given by

$$\mathcal{S}(\xi) \,=\, \exp(-\xi/2). \tag{19}$$

One of the main goals of this work is to establish a range of optimal values for $\xi$. Before discussing numerical results in the next section, we can already establish a reasonable range for $\xi$ from qualitative arguments only.

Let us consider a set of $M$ equally spaced Gaussians, placed on a straight line along the $z$-axis. In this case, the matrix elements of the overlap matrix are of the form $S_{ij} = S(|i - j|)$, with $S(0) = 1$, $S(1) = \mathcal{S}$, and $S(k) > S(k + 1) > 0$ for any non-negative integer $k$ (here we dropped the dependence of $S(k)$ on $\xi$ to simplify the notation). The evaluation of the minimum eigenvalue $\lambda_M$ of the overlap matrix becomes particularly simple for an infinite number of Gaussians since in this case we can map the problem on that of a periodic system and use the Bloch theorem. The eigenvectors will be given by plane waves, and the eigenvector corresponding to the smallest eigenvalue will have elements given by $z_k = (-1)^k$. We thus obtain the following expression for $\lambda_\infty$,

$$
\begin{aligned}
\lambda_\infty(\xi) \,&=\, 1 + 2 \sum_{k=1}^{\infty} (-1)^k S(k) \\
&=\, 1 + 2 \sum_{k=1}^{\infty} (-1)^k \exp(-k^2\xi/2) \\
&=\, \vartheta_4(0, e^{-\xi/2}), \tag{20}
\end{aligned}
$$

where $\vartheta_4$ is a Jacobi theta function [21]. The lowest eigenvalue is particularly relevant for numerical applications, since if it is very small the problem becomes ill conditioned, and hence numerically unstable. For this reason, in most quantum chemistry packages a minimum eigenvalue of about $10^{-6}$ is set as a threshold. In Fig. 1, we report the values of $\lambda_\infty(\xi)$ as a function of $\xi$. We observe that for $\xi = 0.3$ the minimum eigenvalue is about $10^{-6}$. This means that for 1D systems $\xi = 0.3$ can be considered a lower limit. We can also make an estimate for the lower limit of $\xi$ in the case of 3D systems if we assume that $\lambda_\infty$ scales with the dimensionality. If this is the case, the threshold is about $10^{-2}$ for each of the three dimensions. From Fig. 1 we then conclude that for 3D systems $\xi = 0.75$ is the lower limit.

On the other hand, $\xi$ cannot be chosen too large since otherwise two neighboring Gaussians will not have a sufficient overlap. In particular, one can show that the sum of two Gaussians having identical weights becomes a double-peaked function for $\xi > 2$. So this value can be considered as an upper limit for $\xi$ in order to get a reasonable description of a smooth wavefunction.

Considering the above arguments, the parameter $\xi$ is limited to a narrow interval around the value $\xi = 1$.

## A single electron in a quasi-1D potential

We consider here the problem of the expansion of a general wavefunction via a set Gaussian orbitals in a quasi-1D situation. In this case, the potential in the Hamiltonian depends on $z$ only, i.e., $V(\mathbf{r}) = V(z)$. We expand the electron wavefunction in a set of $M$ Gaussian orbitals having the same exponent $\alpha$. The centers of the orbitals are equally spaced, and placed on a straight line along the $z$-axis, i.e., $\mathbf{R}_i = (0, 0, Z_i)$. The property of equal spacing of the Gaussian centers, although convenient from the computational point of view, can be relaxed without noticeable consequences. The use of a common exponent, on the other hand, is crucial for quasi-1D or quasi-2D systems, since it permits to factorize out the transverse components of the wavefunction, and therefore eliminate the spurious kinetic-energy terms stemming from the wavefunction confinement. Only in the case of fully 3D systems this constraint can be dropped. In the quasi-1D discussed in this work, the energy contribution due to the transverse components of the 3D Gaussians is equal to $\alpha$, the exponent of the Gaussian function. The derivation of this value can be found in the Appendix.

Therefore, for the two quasi-1D systems considered here, the particle in a box and the harmonic oscillator the total energies will tend to, respectively,

$$E_n^\alpha(L) \,=\, \frac{n^2\pi^2}{2L^2} \,+\, \alpha, \tag{21}$$

$$E_n^\alpha(\omega) \,=\, \left(n + \frac{1}{2}\right)\omega \,+\, \alpha. \tag{22}$$

As a consequence, when we compare to the exact analytical values given in Eqs. 7 and 9 we should subtract $\alpha$ from our calculated values.

## Results and discussion

### One-particle systems

In order to assess the quality of the Gaussian expansion to describe quasi-1D wavefunctions, several calculations have been performed by using a set of $M$ equally spaced Gaussians with exponent $\alpha$.

### Particle in a box

In the absence of an external potential, the lowest approximated solutions will converge to the PiB results.

**Fig. 1** The minimum eigenvalue of the overlap matrix for a 1D even-spaced infinite set of identical Gaussians as a function of $\xi$. Zoom in the inset
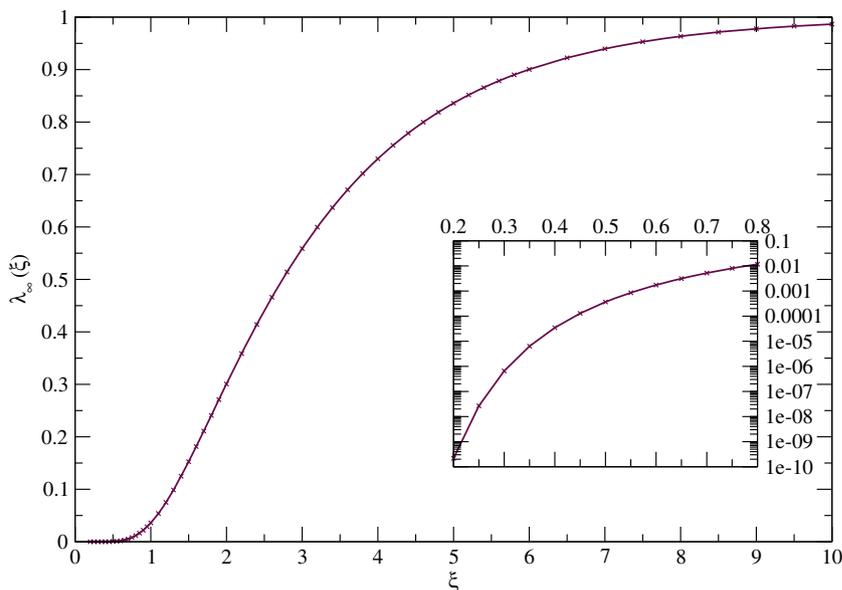
As a first step, the dependence of the energies on the $\xi$ parameter has been investigated. For this reason, the number of Gaussians has been fixed to a large value, i.e., $M = 401$. We keep the distance between the Gaussian centers fixed to $\delta = 1$ Bohr. We note that for this particular value of $\delta$, the parameter $\xi$ coincides with the exponent of the Gaussians $\alpha$. In Fig. 2, the longitudinal energy component of the lowest four eigenvalues are reported as a function of $\xi$, and compared to the exact energies of the PiB model, given in Eq. 7. It can be seen that the reported energies are very close to the exact values for $\xi \leq 1$, while the agreement quickly deteriorates for larger values of $\xi$. For small values of $\xi$, the calculated energies lie *below* the exact values, although by a very small amount, which implies that the energies are not variational approximations of the exact ones. For large values of $\xi$ the calculated energies lie well above the exact energies.

In fact, there are two sources of error stemming from the discretization procedure. The first one is that for large values of $\alpha$ a linear combination of Gaussians do not sufficiently overlap to be able to describe the smooth one-electron wave functions. Instead, it will lead to an oscillating function. The energies are, therefore, *above* the exact values, and this error can be estimated via the variational principle. The second source of error is due to the fact that the Gaussian orbitals do not vanish outside of the boundaries of the box. This error, which produces energies that are *below* the exact values, is more difficult to evaluate, and depends on both the number

**Fig. 2** Absolute energies for a particle in a box with 401 Gaussians as a function of $\xi$. Since $\delta = 1$ Bohr, in this case $\alpha = \xi$
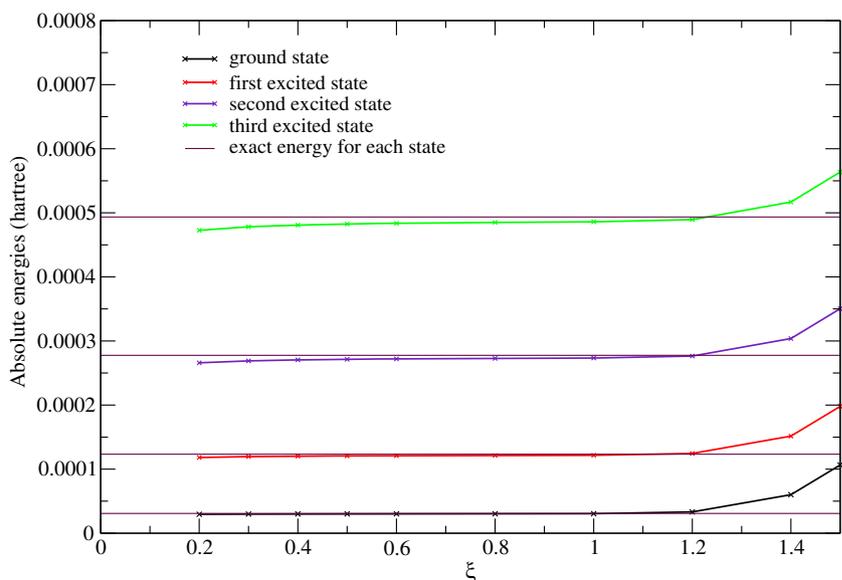
**Fig. 3** Relative energies with respect to the ground state $\epsilon_k/\epsilon_0$ ($k = 1, 2, 3$) for a particle in a box with 401 Gaussians, $L = 400$ Bohr, as a function of $\xi$. Since $\delta = 1$ Bohr, in this case $\alpha = \xi$
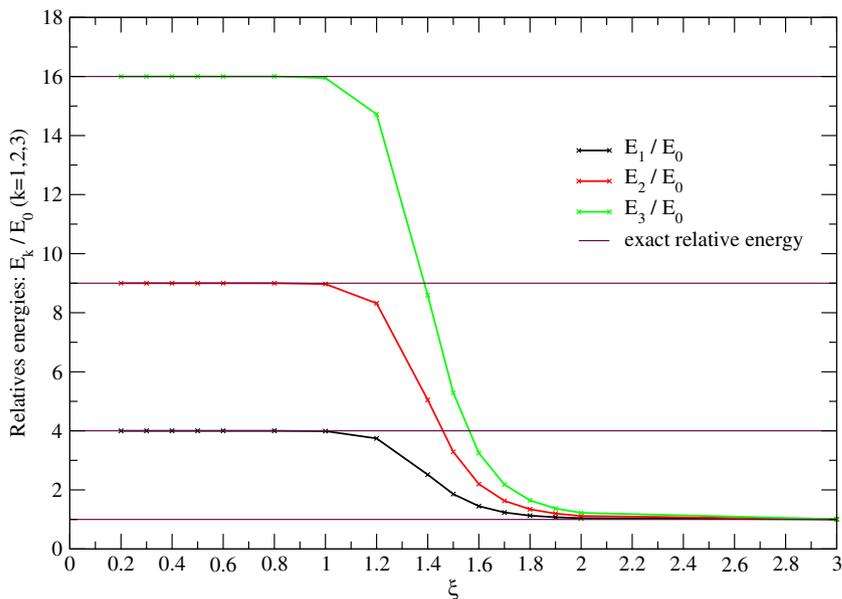
of Gaussians and their width. For a given box length, and a fixed value of $\xi$, one can show that the second error goes to zero as $1/M^2$ when $M \to \infty$.

Because of the incertitude about the (implicit) box length, a better way to assess the energy quality is to compute the *ratio* of the eigenvalues, since, according to Eq. 7, its value does not depend on $L$. This is shown in Fig. 3, where the ratios $\epsilon_n/\epsilon_1$ as a function of $\xi$ are plotted for $n = 2, 3, 4$. By looking at the exact energies, we see that the value of the ratio should be $n^2$. The calculated values are quite close to the exact ones for $\xi < 1$, then decrease dramatically, and converge to a common value $\epsilon_k/\epsilon_1 = 1$ in the limit $\xi \to \infty$. This means that the Gaussian basis set is well adapted to describe the exact eigenfunctions if $\xi < 1$. We note that,

as discussed before, in practical calculations one also has to pay attention to the problem of quasi-linear dependencies when $\xi$ is too small. Instead, in the limit $\xi \gg 1$, the Gaussians will essentially be isolated. The dominant effect in the energy will be the kinetic energy of the Gaussians, given by $\alpha/2$, regardless of the value of $k$. Therefore, the ratio $\epsilon_k/\epsilon_1$ converges to 1.

In Fig. 4, the lowest eigenfunction for a box of length $L = 10$ Bohr calculated with 1024 Gaussians is reported for different values of $\xi$. The presence of oscillations is visible when $\xi > 1$ which stems from the insufficient overlap between the Gaussians mentioned before. From the results in the inset of Fig. 4, we also see that the wave functions do not vanish beyond the boundaries of the box. This overflow

**Fig. 4** Ground-state wave function for a particle in a box along the $z$-axis as a function of the position $z$. Box with $L = 10$ Bohr and 1024 Gaussians, different values of $\xi$ are reported. *Inset*: zoom of the region close to the boundary of the box at $z = 5$ Bohr
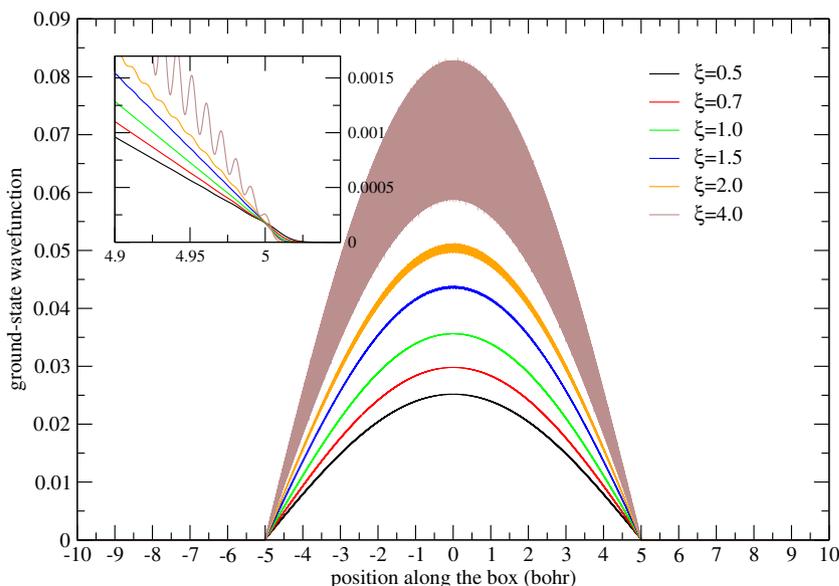
**Fig. 5** The ground-state wavefunction of a particle in a box along the $z$-axis as a function of the position $z$ for several values of $M$, the number of Gaussians. The box length is 10 Bohr and $\xi = 0.5$
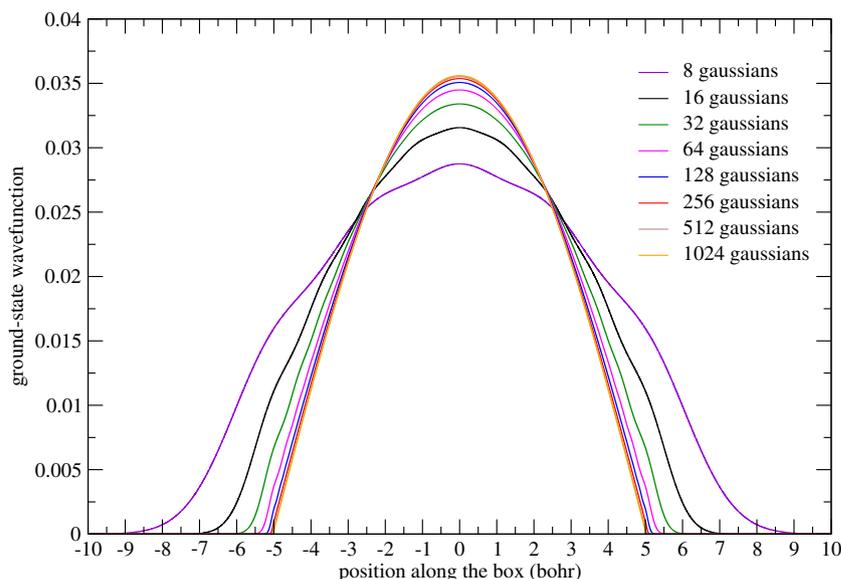
is bigger for the more diffuse Gaussians, i.e., those with small values for $\xi$.

From the above results, we conclude that values between $\xi = 0.5$ and $\xi = 1$ are a good choice for quasi-1D systems. We will now study the convergence behavior with respect to the number of Gaussians. In Fig. 5, the calculated ground-state wavefunction obtained with different numbers of Gaussians are shown using $\xi = 0.5$. With a large number of Gaussians, i.e., $M \geq 256$, the agreement is excellent. Instead, for smaller values of the number of Gaussians, small oscillations are visible, and the wavefunction has relatively large nonzero values outside the boundaries of the box.

Finally, we will have a look at the effective potential that is implicitly defined by the Gaussian basis set using the approach outlined in section "The effective potential $\bar{V}$". In Fig. 6, the effective potential is reported for several values of $M$ i.e., $M = 8, 16, 32,$ and $\xi = 1$. The potential is close to zero inside the box, and grows parabolically beyond the boundaries of the box. Close to the boundaries, there are oscillations that become more pronounced if the number of Gaussians is increased. There are also small oscillations inside the box, as can be seen from the inset in Fig. 6. We note that the small oscillations inside the box correspond to the positions of the Gaussian centers. In Fig. 7 we report the effective potential obtained with more diffuse



**Fig. 6** The effective potential $\tilde{V}$ along the $z$-axis, $\xi = 1.0$, for $M = 8, 16, 32$
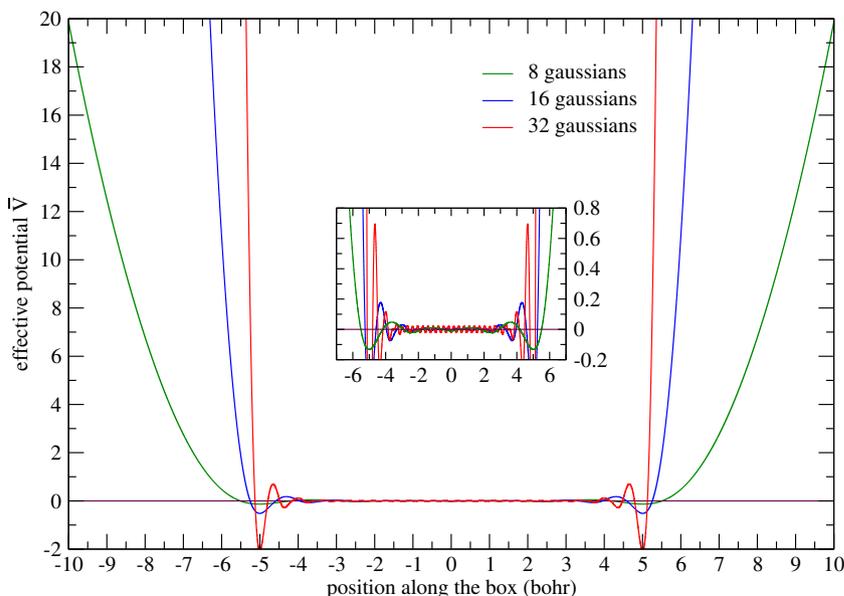
**Fig. 7** The effective potential $\tilde{V}$ along the z-axis, $\xi = 0.5$, for $M = 8, 16, 32$
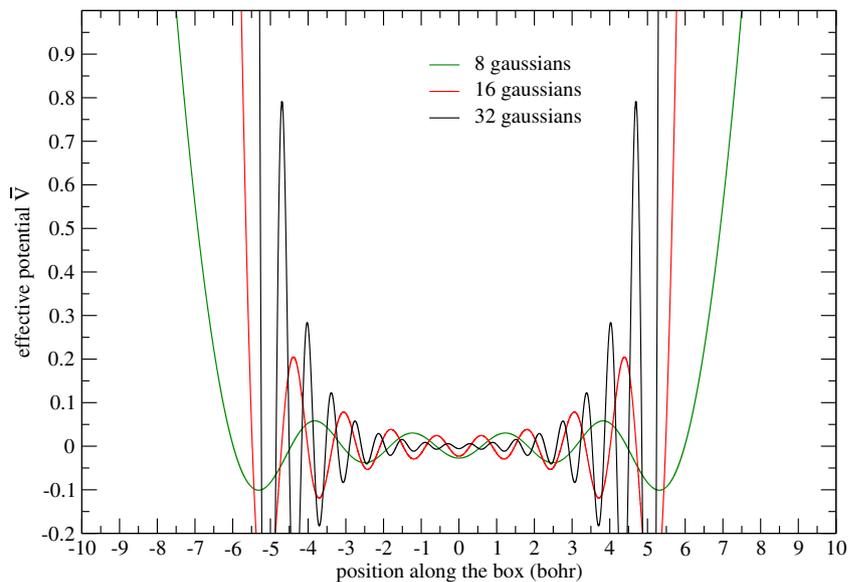


Gaussians ($\xi = 0.5$). The oscillations of the potential close to the box borders tend to increase when $\xi$ is reduced. It is remarkable that despite this oscillating potential, the calculated eigenvalues are so close to the exact ones. This is probably due to the fact that the wavefunction vanishes at the boundaries of the box. Therefore the value of the potential has little influence on the wavefunction. We note that similar oscillations can be observed for the one-electron density within the Thomas-Fermi approximation [22].

### Harmonic oscillator

We will now show results obtained with an explicit external potential, namely that of the harmonic oscillator. Since the exact ground-state wave function is a Gaussian, one might think that the harmonic-oscillator model can be easily described with a basis set of Gaussian functions. However, for a given basis set, only for one specific value of the force constant $k$ does one Gaussian function suffice to describe the wave function. Moreover, none of the excited states are Gaussians. Here we set the force constant $k$ to unity. This means that the exact eigenvalues of the ground state and the first two excited states are 0.5, 1.5, and 2.5 Hartree, respectively. We set the box length equal to $L = 12$ Bohr.

In Fig. 8, the errors with respect to these exact values are reported as a function of $\xi$ for 13, 25, and 241 Gaussians. We conclude that the error can be reduced to very a small value (below $10^{-10}$ Hartree) if a suitable value of $\xi$ and

**Fig. 8** The absolute error with the exact energy for a harmonic oscillator, with 13,25 and 241 Gaussians
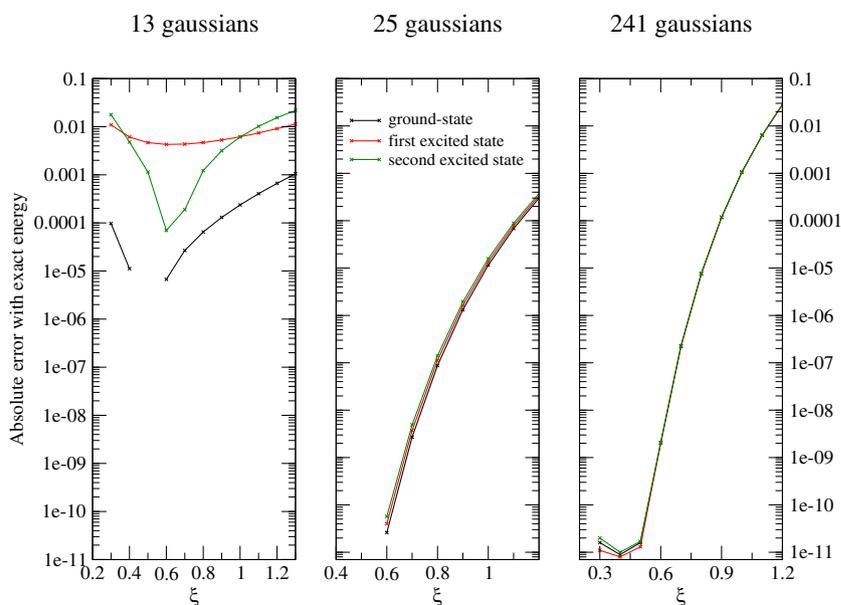
**Fig. 9** The normalized electron density of six electrons confined in a 1D box as a function of the position for several values of the Wigner–Seitz radius $r_s$
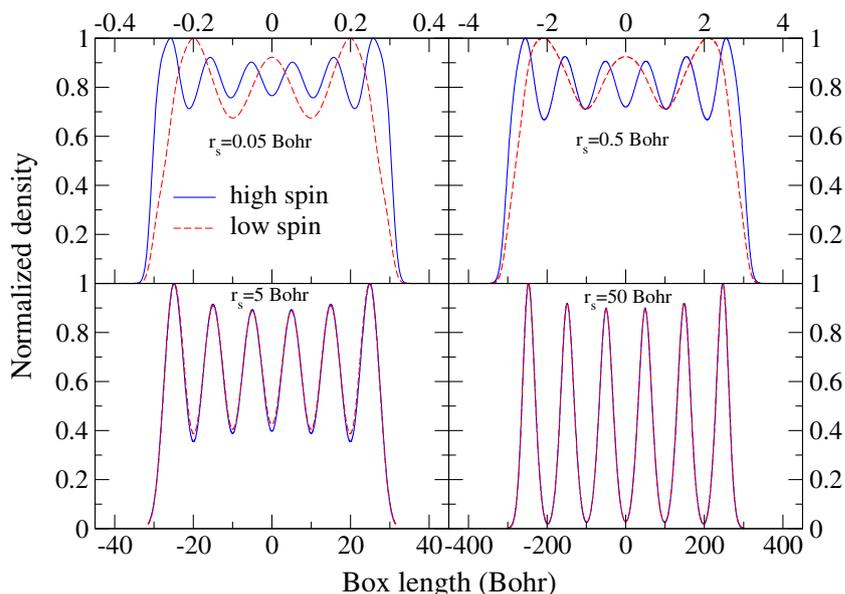


$M$ is chosen. Even with only 13 Gaussians it is possible to reproduce the exact energy of the two lowest states with an error that is below one mHartree. We note that the error for the ground-state energy using 13 Gaussians at $\xi = 0.5$ is not reported because for this particular value of $\xi$ the error is identically zero since the basis set contains the exact ground-state wave function.

## Many-electron systems

To demonstrate that our approach is suitable for many-electron systems, we also studied a quasi-1D system with six electrons [4]. Since the kinetic energy scales as $1/r_s^2$ and the electron-electron repulsion as $1/r_s$, where $r_s$ is the Wigner–Seitz radius, we expect that at small $r_s$ (large density) the system behaves as six non-interacting electrons since the kinetic energy is dominant. Instead, at large $r_s$ (low density) we expect that the electrons will localize since in this case the electron-electron repulsion is dominant.

In Fig. 9, we report the full configuration interaction (FCI) electron density for both the low-spin (LS) and high-spin (HS) wave functions, and for four values of $r_s$, namely 0.05, 0.5, 5, and 50 Bohr [4]. We used $\xi = 1$ and $M = 25$. We verified that the results are converged using these values. We observe that for $r_s = 0.05$ and $r_s = 0.5$, the density is close to being a constant. It is comparable to the density profile of six non-interacting electrons in a 1D box. We note that while six peaks can be observed in the HS case, only three peaks are visible for the LS case. This stems from the double occupation of the orbitals.

The density distribution completely changes going from $r_s = 0.5$ to $r_s = 5$ Bohr. In the case of $r_s = 5$ Bohr there are six peaks for both HS and LS. Moreover, the peaks

are divided by deep valleys. In the case of the largest $r_s$ that we report, $r_s = 50$ Bohr, the density almost vanishes between the peaks. We, therefore, observe that the electrons indeed localize for large $r_s$. Moreover, the HS and LS density profiles are indistinguishable for large $r_s$, as one would expect, since the spin coupling is not important for localized electrons. Finally, we note that the results in Fig. 9 are not influenced by the underlying basis of distributed Gaussians, i.e., the density profiles are smooth. We conclude that our approach, based on distributed Gaussians, is well suited to study electron localization in many-electron systems.

## Conclusions

We have demonstrated the viability of using distributed Gaussian orbitals as a basis set for the calculation of the properties of electrons subjected to an external potential. We have validated our method by studying one-electron systems for which we could compare to exact analytical results. We have highlighted the numerical aspects that require particular care when using a distributed Gaussian basis set.

We have also shown how our approach can be applied to many-electron problems. In the future, we plan to use this formalism for a systematic *ab initio* investigation of the physics of few-electron systems confined in quasi-1D regions, and possibly subjected to an external potential.

## Appendix: Energy contribution from the transverse components of the Gaussians

In this appendix, we derive the contribution to the energy due to the transverse components of the 3D Gaussian functions.

The electron wavefunction $\psi^\alpha(\mathbf{r})$ is expanded as a linear combination of the $\phi_i^\alpha$ orbitals:

$$\psi^\alpha(\mathbf{r}) = \sum_i C_i \phi_i^\alpha(\mathbf{r}). \tag{23}$$

By inserting Eq. 15 into Eq. 23, we obtain

$$\psi^\alpha(\mathbf{r}) = \sum_i C_i \exp(-\alpha\|\mathbf{r} - \mathbf{R}_i)\|^2) =$$

$$= \exp(-\alpha(x^2 + y^2)) \sum_i C_i \exp(-\alpha(z - Z_i)^2). \tag{24}$$

By acting on $\psi^\alpha(\mathbf{r})$ with the Hamiltonian, given in Eq. 8, and scalar multiplying the resulting equation by $\langle\phi^\alpha(\mathbf{r})|$ one finally gets, after a separation of variables, the three independent equations

$$\langle\exp(-\alpha x^2)|T_x|\exp(-\alpha x^2)\rangle = E_x\langle\exp(-\alpha x^2)|\exp(-\alpha x^2)\rangle, \tag{25}$$

$$\langle\exp(-\alpha y^2)|T_y|\exp(-\alpha y^2)\rangle = E_y\langle\exp(-\alpha y^2)|\exp(-\alpha y^2)\rangle, \tag{26}$$

$$\langle\exp(-\alpha(z - Z_j)^2)|T_z + V_z|\sum_i C_i \exp(-\alpha(z - Z_i)^2)\rangle = E_z\langle\exp(-\alpha(z - Z_i)^2)|\sum_i C_i \exp(-\alpha(z - Z_i)^2)\rangle. \tag{27}$$

The first two equations have the solution $E_x = E_y = \alpha/2$. This can be easily verified by explicitly performing the second derivative contained in the kinetic energy, and integrating the resulting expression. Alternatively, we note that a one-dimensional Gaussian with exponent $\alpha$ is the ground-state eigenfunction of a harmonic oscillator with eigenvalue $\alpha$. Because of the virial theorem, the mean value of the kinetic energy is equal to the mean value of the potential energy, and hence equal to one half of the total energy, i.e., $E_x = E_y = \alpha/2$.

The third equation corresponds to the projection of a true 1D eigen-equation for $H_z$ onto the set of non-orthogonal basis functions $|\exp(-\alpha(z - Z_i)^2)\rangle$. This means that the wavefunction is expressed as the product of three independent functions, depending on $x$, $y$, and $z$, respectively. Since the Hamiltonian is separable, the time-independent Schrödinger equation will have an energy given by the sum of three independent terms. The functions $\psi^\alpha(x)$ and $\psi^\alpha(y)$ do not contain any parameter, and their energy contributions will be those of a single Gaussian. The $\psi^\alpha(z)$ function can be computed, via the variational principle, by minimizing its energy. In the limit $M \to \infty$, $\psi^\alpha(z)$ will be an arbitrary function on the $[0, L]$ interval, vanishing in all points $z \notin [0, L]$.

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