

An accurate and compact wave function for the ^4He dimer

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Abstract – We introduce a local measure of the quality of a trial wave function: the local variance. Using this tool we examine the pair function often adopted to construct wave functions for small helium clusters and apply it to a wave function for $^4\text{He}_2$ using the TTY interaction potential. Our analysis shows that this commonly employed functional form should be improved in the short-range region. We introduce a new model based on the short-range behaviour of the exact ground-state solution of a Morse potential. The resulting compact trial wave function for $^4\text{He}_2$ recovers 98% of the exact binding energy with only six variational parameters.

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Introduction. – In the last few decades weakly bound van der Waals noble gases clusters have attracted much attention from both theoreticians and experimentalists. The most intriguing one probably is the family of helium clusters, starting from $^4\text{He}_2$, due to their highly quantum features caused by the small atomic mass and the very weak interaction potential. Due to their peculiarities these systems can only be studied by fully quantum-mechanical many-particle methods.

The existence of a bound state for the smallest member of the family, the ^4He dimer, was debated for a long time from a theoretical point of view. Starting from the 1970s almost all realistic interaction potentials supported the existence of at least a very weakly bound state (see Kolganova *et al.* [1] for a recent review and references therein). However, it was only in 1993 that the elusive ^4He dimer was finally detected by Luo and coworkers [2] in an electron impact ionization experiment. In a subsequent and independent work the helium dimer and trimer were detected by Schöllkopf and Toennies [3,4] in a diffraction experiment using a transmission grating.

From the computational point of view the study of these weakly bound systems still presents some problems when compared to less peculiar molecular systems. Helium clusters show a high degree of delocalization even in their ground state, due both to the weakness of the interaction potential between their constituent atoms and to the light helium mass. For this reason an accurate expression of the potential energy surface is needed to

compute meaningful energies and other properties. When compared with heavier rare-gas systems the predictions based on a crude Lennard-Jones interaction potential show significant deviations from accurate results obtained using more recently developed potentials like the Tang, Toennies and Yiu (TTY) potential [5]. The TTY potential, based on perturbation theory, provides an accurate analytical expression of the van der Waals interactions between two helium atoms, in agreement with the best empirical and *ab initio* potentials. The interaction potential for a $^4\text{He}_N$ cluster is usually written as a sum of two-body terms,

$$V = \sum_{i<j}^N V_{\text{He-He}}(r_{ij}), \quad (1)$$

where r_{ij} is the distance between two helium atoms and $V_{\text{He-He}}(r)$ is the two-body interaction potential. For small helium clusters three-body terms are usually excluded since they are believed to be unimportant.

A critical issue in the study of helium clusters is represented by the choice of the trial wave function. A good and well-behaved trial wave function is necessary to accurately compute the structural properties of these systems. The wave function for $^4\text{He}_N$ is usually written in a pair-product form,

$$\Psi_T(\mathbf{R}) = \prod_{i<j}^N f(r_{ij}), \quad (2)$$

where \mathbf{R} is the complete set of atomic coordinates, r_{ij} is the distance between two ^4He and f is a two-body pair function. It is clear that the development of a compact

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and accurate two-body wave function is at the heart of any computational method that aims to predict accurate cluster energies and structural properties over a wide range of sizes. A reasonable request is that any proposed functional form should be able to provide even a good description of the helium dimer: not an easy task due to the peculiarities of this system.

Wave function form ${}^4\text{He}_2$ and larger clusters.

– In recent years many theoretical papers have been devoted to the study of ${}^4\text{He}_N$ clusters, using different computational methods to estimate their properties. A variety of functional forms has been used in the past for the two-body wave function [6,7], often in conjunction with quantum Monte Carlo methods since usually these wave functions are not amenable to analytical integration.

Rick, Lynch, and Doll [8] proposed for $f(r)$ the following analytical form:

$$f(r) = \exp\left(\frac{p_5}{r^5} + \frac{p_2}{r^2} + p_0 \ln(r) + p_1 r\right). \quad (3)$$

This function, called RLD in the following, has since gained popularity and has been used with success by several authors for the description of small pure and doped helium clusters. For example Lewerenz [7] studied small pure ${}^4\text{He}$ clusters, Bressanini *et al.* studied mixed ${}^3\text{He}/{}^4\text{He}$ clusters [9], while Casalegno *et al.* studied helium clusters doped by the hydrogen anion [10]. The development of accurate and compact trial wave functions for weakly bound systems is an active area of research. In a recent paper Geltman [11] tackled the problem of developing an accurate and compact analytical wave function for the ${}^4\text{He}$ dimer. For this system the Schrödinger equation can be solved numerically, as was done by Geltman using the TTY interaction potential, obtaining a numerical wave function and a ground-state energy of -4.183×10^{-9} a.u. Geltman then proceeded to develop an analytical wave function that mimicked as close as possible the exact numerical wave function choosing

$$\Psi_T(r) = \exp(-\alpha r) [1 - \exp(-\beta(r - r_0)^\gamma)]^\delta / r \quad (4)$$

as trial function. The parameters were optimized obtaining an upper bound to the exact ground-state energy of -3.548×10^{-9} a.u., recovering 85% of the binding energy. A good result for such a simple and compact wave function and this peculiar system, but there is obviously room for improvement.

As a comparison, using the TTY potential and the published parameters [7] for the ${}^4\text{He}_2$ RLD wave function (see table 1) we obtained a trial energy of $-1.842(14) \times 10^{-9}$ a.u., computed using the Variational Monte Carlo method, recovering only 44% of the binding energy.

Local analysis of the wave function quality. – Each term included in eq. (3) possesses a well-defined physical meaning. The term $\exp(p_5/r^5 + p_2/r^2)$ accounts for the short-ranged repulsive interaction between two

Table 1: Parameters and energies for the RLD, optimized RLD and DE wave functions.

Parameters	RLD original	RLD optimized	DE
p_5	-3280.0	-2887.25887	-1485.60098
p_2	-0.606	-9.255966	-6.146323
p_1	-0.005	-0.004148	-0.005390
p_0	-1.0	-1.079786	-1.013632
d_0			-76.371281
d_1			-1.007803
Energy ^(a)	$-1.842(14) \times 10^{-9}$	$-3.469(8) \times 10^{-9}$	$-4.107(2) \times 10^{-9}$

^(a)Energies are in a.u. In parenthesis the uncertainty on the last digits.

helium atoms, while the term $\exp(p_0 \ln(r) + p_1/r)$ describes the asymptotic behavior of the wave function when one atom is far from all the others. In order to improve this commonly used wave function for the helium dimer, and hopefully for higher clusters, we first need to know where it needs to be corrected the most. A commonly employed measure of the quality of a trial wave function $\Psi(\mathbf{R})$ is the variance of the local energy,

$$\sigma^2 = \langle H^2 \rangle - \langle H \rangle^2 = \langle E_L^2 \rangle - \langle E_L \rangle^2, \quad (5)$$

where $E_L = H\Psi(\mathbf{R})/\Psi(\mathbf{R})$ is the so-called local energy. For an exact wave function this quantity is equal to zero. For an approximate wave function the variance of the local energy is a measure of its overall quality. However, it is not very useful if one is trying to understand which part of the wave function should be modified to improve its quality since it gives no indication as to where $\Psi(\mathbf{R})$ is poor. We need an estimator of the local quality and this can be easily built and visualized for a two-particle system like the helium dimer. We start from the expression of the variance

$$\sigma^2 = \frac{\int \Psi (H - \langle H \rangle)^2 \Psi d\mathbf{R}}{\int \Psi^2 d\mathbf{R}} = \frac{\int \Psi^2 (E_L - \langle H \rangle)^2 d\mathbf{R}}{\int \Psi^2 d\mathbf{R}} \quad (6)$$

and choose a coordinate system suitable for ${}^4\text{He}_2$, integrating out the angular coordinates we obtain

$$\sigma^2 = \frac{\int_0^\infty r^2 \Psi^2(r) (E_L(r) - \langle H \rangle)^2 dr}{\int_0^\infty r^2 \Psi^2(r) dr} \quad (7)$$

where r is the interparticle distance. The integrand of the previous expression,

$$\sigma_L^2(r) = \frac{r^2 \Psi^2(r) (E_L(r) - \langle H \rangle)^2}{\int_0^\infty r^2 \Psi^2(r) dr}, \quad (8)$$

can be interpreted as a local variance that integrated over all space gives σ^2 :

$$\int_0^\infty \sigma_L^2(r) dr = \sigma^2. \quad (9)$$

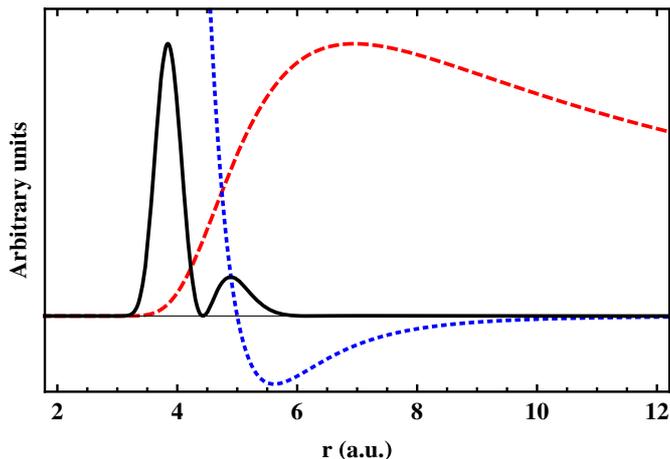


Fig. 1: (Colour on-line) ${}^4\text{He}_2$ wave function of RLD type (red dashed line), local variance (black thick line) and interatomic potential (blue dotted line) as a function of the interatomic distance.

The subscript L indicates that we are dealing with the local variance of the local energy weighted over the probability distribution $\Psi^2(r)$. We choose this function to measure the local accuracy of a trial wave function with the assumption that by lowering its fluctuations, it should be possible to enhance the accuracy of the expectation values of the energies. This assumption is mainly motivated by the fact that the local energy is a constant with a local variance of zero for the exact ground-state wave function. Therefore, a two-body wave function that shows small fluctuations in the local variance is expected to provide good results. Figure 1 shows $\sigma_L(r)$ as a function of r for a RLD-type function employed in the past [7,8], along with the wave function itself and the TTY interaction potential. The local variance shows its largest fluctuations for small values of r , in the repulsive region of the potential. We expect that a better wave function could be obtained by tuning its short-range behavior.

Wave function improvement. – Since the original RLD ${}^4\text{He}_2$ wave function was poorly optimized we performed a full numerical optimization using the *Mathematica*® software package. After reoptimization (see table 1) we obtained an improved energy of $-3.469(8) \times 10^{-9}$ a.u., recovering 83% of the exact binding energy, a percentage similar to Geltman’s wave function. Also the local variance (see fig. 2) has been reduced somewhat but there are still deficiencies at short range. To gain a further improvement the wave function form must be modified. The RLD pair function was originally introduced to mimic the exact ground-state wave function for the Lennard-Jones potential, often employed in computational studies on rare-gases van der Waals clusters. Since the repulsive part of the helium-helium potential is not well described by a Lennard-Jones interaction, it is not surprising that this kind of wave function does not behave well at small distance. To have

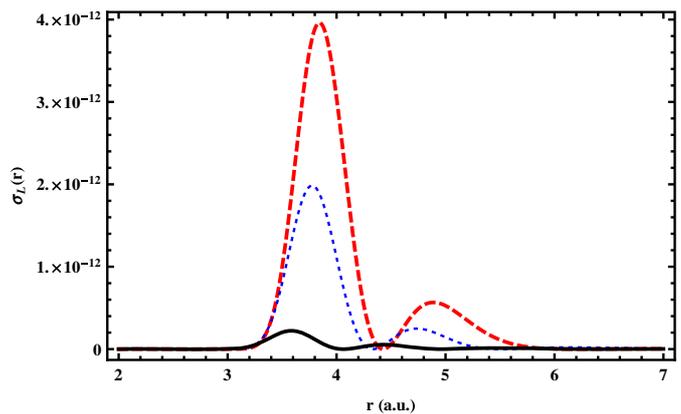


Fig. 2: (Colour on-line) local variances of the original RLD wave function (red dashed line), reoptimized RLD wave function (blue dotted line) and DE wave function (black thick line).

an indication on how to improve it at short distances we turned to the ground-state analytical solution of the Schrödinger equation for the Morse potential [12]:

$$V(r) = D_0 \left\{ 1 - e^{-\alpha(r-r_0)} \right\}^2, \quad (10)$$

that is

$$\Psi(r) = A \exp\left(-k e^{-\alpha(r-r_0)} - \beta r\right). \quad (11)$$

At short range the wave function is described by a double exponential. We introduced this term into eq. (3) to mimic the short-range behavior of the Morse function obtaining a new model, called DE in the following owing to the presence of the double exponential term:

$$\Psi_T(r) = \exp\left(d_0 e^{-d_1 r} + \frac{p_5}{r^5} + \frac{p_2}{r^2} + p_0 \ln(r) + p_1 r\right). \quad (12)$$

We optimized the parameters (see table 1) and estimated its energy using the Variational Monte Carlo method, obtaining an energy of $-4.107(2) \times 10^{-9}$ a.u. recovering a remarkable 98% of the exact ground-state energy estimated by Geltman of -4.183×10^{-9} a.u. [11]. As expected the local variance, shown in fig. 2, has been greatly reduced showing at the same time the validity of the local variance as an indicator of the local quality of a trial wave function.

To our knowledge this function is the most accurate compact analytical wave function for ${}^4\text{He}_2$ with the TTY interaction potential. The simple investigation we have carried out on the helium dimer has shown that the double exponential term provides a substantial gain in energy and a better description of the short-range region so we expect it to be useful also for bigger helium clusters where the average interatomic distance is smaller than in ${}^4\text{He}_2$.

Conclusions. – Using the local variance as a tool we analyzed the quality of a trial wave function for ${}^4\text{He}_2$ as a function of the interatomic distance. We found out that where the potential is repulsive the wave function behaves

badly. Using the exact solution of a Morse potential as a guide we included a double exponential term in the wave function describing in a more correct way the short-range correlation effects. The optimized wave function has been greatly improved recovering 98% of the binding energy. Work is underway to test this newly developed trial wave function to the helium trimer and higher helium clusters.

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