I. INTRODUCTION

The determination of the intermolecular potential between chemically nonbonding atoms and molecules is a problem of fundamental importance in the field of molecular physics. However, even in the case of the interaction between two helium atoms—the simplest inert gas pair—the problem is known to be difficult and has been the subject of numerous papers spanning a period from the late twenties to the present time (see, e.g., Ref. 1 for a historical review).

Two mainstreams in the methods of calculation can be distinguished: the supermolecular and the perturbational methods. In the supermolecular method the energy of interaction is obtained by subtracting from the total energy of the interacting molecules (the supermolecule) the sum of the energies of each monomer. Since the energies involved cannot be evaluated exactly one is confronted with the difficulty of obtaining a very small number as the difference of two huge numbers, both being known only approximately. As has been stated by van Lenthe et al.,2 for an accurate evaluation of the interaction energy using ab initio techniques three requirements should be fulfilled: saturation of the basis set, saturation of the configuration set, and effective elimination of the basis set superposition error. In practice, it turns out to be hard to meet these requirements, even for a relatively small system such as the helium dimer. Nevertheless, according to Liu and McLean,3 "... one seems to have come close to writing the end of the chapter on helium dimer potentials." Aziz and Slaman4 have fitted model potentials to the supermolecular ab initio energies of interaction calculated by Vos et al.5 and by Liu and McLean.3 With these potentials the prediction of a variety of accurate experimental data such as the second virial coefficient, viscosity and thermal conductivity was attempted. The agreement with experiment can be considered excellent,1 although, as has been stated by Aziz and Slaman,4 "... small failures nevertheless remain." In this context it is important to keep in mind the remark made by Anderson et al.,1 regarding a result given by Liu and McLean,3 "... that one should be a little nervous about the estimated uncertainty of ±0.03 K in the interaction potential when the calculated total energy is 1200 K above the exact total energy." Finally, van Mourik and van Lenthe6 very recently presented the results of full configuration interaction calculations for the helium dimer employing large basis sets, which contain up to h-type basis functions, including bond functions. Their results probably are the best at present for the He2 interaction energy. At the equilibrium distance, R=5.6 bohr, the interaction energy was calculated to be −34.67 μhartree with an error of ±0.03 μhartree.

Quantum Monte Carlo (QMC) methods also can be used to compute molecular energies. Lowther and Coldwell,7 using a variational QMC approach have calculated the energy of interaction for internuclear distances ranging from 4.5- to 15 bohr using a 189-term Hylleraas-type atomic wave function from which a fully correlated dimer wave function was constructed. They found a very good energy of interaction at the minimum of the potential of −35.5±1.5 μhartree which agrees well with the more recent values of −34.64 μhartree (Liu and McLean3), −34.42 μhartree (Vos et al.), and −34.67 μhartree (van Mourik and van Lenthe6). Exact QMC supermolecular calculations have been done by Ceperley and Partridge,8 for the small internuclear distances, ranging from 1.0–3.0 bohr, and by Anderson et al.,1 for distances greater than 3 bohr. The results obtained by Anderson1 fully agree with those of Liu and McLean,3 Vos et al., and van Lenthe.5 It should be emphasized that the difficult problems connected with the use of a basis set in ab initio calculations are...
absent in exact QMC calculations. The only input is the so-called trial wave function. It is important to realize that, although the statistical error is directly related to the quality of the trial wave function, the statistical estimate of the energy is not biased by a particular choice of the input trial wave function.

A very natural alternative approach to supermolecular methods is to consider the interaction energy as the result of a very small physical perturbation of the isolated monomers and thus to employ some kind of perturbational method. At this point, it is worthwhile to recall that, at the equilibrium distance of the helium dimer in which we are interested here, the interaction energy represents only approximately $6 \times 10^{-6}$ of the total dimer energy. Such a tiny fraction clearly justifies the use of perturbational methods. This line of research has been intensively followed during the last decades and has led to the so-called symmetry adapted perturbation theories (SAPT) for intermolecular interactions (see, e.g., Refs. 9, 10 or 11). Within this framework the intermolecular Coulomb potential is treated as a perturbation, and the interaction energy is directly given as a sum of perturbational components. This type of approach does not involve the typical difficulties of the supermolecular method mentioned above. Each perturbational component can be split into an exchange and a Rayleigh–Schrödinger (RS) or polarization contribution. A number of methods have been designed to calculate these contributions. A general feature is that exchange contributions are more difficult to obtain than the RS contributions since they require a wave function of good quality also in the outer region of the system, a region which is not necessarily very well described by wave functions obtained from a variational principle on the energy. Note that a quite complete review of the perturbation approach to van der Waals complexes has recently been published by Jeziorski, Moszynski, and Szalewicz. Unfortunately, the use of perturbational approaches is limited because the computation of the perturbational components is not easy to do. Even in the case of the helium dimer, only the first- and second-order contributions have been considered in practice. Of these two, the first-order term has been evaluated accurately since the wave function for the dimer is a simple product of the ground state monomer wave functions and these functions can be chosen to approximate the exact result very closely. Contrary to the first-order energy of interaction, the higher-order terms are given in sum-over-states representations and the excited-states must be known (explicitly or implicitly) to evaluate the sums. Accordingly, accurate evaluations of these terms are much more difficult to perform. In Sec. IV we will discuss this point in detail.

In this paper we present exact calculations of the first-, second-, and third-order RS interaction energies of the He–He interaction for internuclear distances ranging from 1.5- to 7.0 bohr. In order to do that, we resort to a recently proposed QMC method to compute perturbational quantities. In this approach the perturbational quantities are expressed as multitime integrals of some well-defined autocorrelation functions of the perturbing potential. The correlation functions are defined along the stochastic trajectories of some generalized diffusion process associated with the unperturbed system. In practice, to construct these trajectories only a good approximate trial wave function for the unperturbed Hamiltonian is required. It is important to emphasize that the results obtained are essentially exact within their statistical errors. In particular, the complete intramonomer correlation contribution is included. The QMC perturbational approach has been applied to the helium dimer in the original work of Caffarel and Hess. However, the numerical results presented in their work were obtained only for very short distances (1.5- to 2.0 bohr), and only for the first- and second-order interaction energies. Here, we make a much more systematic study including the short, intermediate, and large distances. In particular, we focus our attention on the region of the potential well which is the region of physical interest. The third-order RS term is also computed here and is found to play a significant role. As has been already stated above when discussing ab initio SAPT techniques, exchange contributions responsible for the repulsive part of the potential energy curve, are in general difficult to evaluate. This is particularly true for QMC. In fact, the results of the calculations presented here show that it is not realistic to expect quantitative results for the longer distances. In order to illustrate this we will report some calculations of the first-order exchange interaction energy using a high-quality approximate formula. The results are compared with accurate ab initio values and are found to agree within large statistical errors. In principle, it is possible to write exact expressions for the exchange components but, due to these large statistical fluctuations, they will be of no practical use and, therefore, will not be considered further.

By using the exact QMC data presented here for the second- and third-order RS interaction energies, and the best ab initio values for the complete first-order and second-order exchange contributions we discuss the relative importance of the different perturbational contributions making up the total interaction energy of the helium dimer: The RS contributions of different orders, the intraatomic electron–electron correlation, the exchange effects. To our knowledge, this is the first example of an intermolecular interaction whose perturbational description is fully understood. Besides its own interest, it is clearly of general interest for the theory of intermolecular forces and their evaluation by perturbation theory.

The organization of the paper is as follows. Section II presents the basic equations of the QMC-perturbational approach used here. Section III contains the computational details. Finally, Sec. IV presents and discusses the numerical results for the perturbational components of the He–He interaction.

II. BASIC EQUATIONS
A. Rayleigh–Schrödinger interaction energies

Let us first consider the calculation of the first-, second-, and third-order RS interaction energies. The formulas presented here are some particular cases of a general nth order formula derived by Caffarel and Hess. Since the formalism presented in Refs. 15 and 16 is very general and not
commonly used, we have chosen to rederive the pertubational expressions using a more pedestrian approach. It is emphasized that the equations are valid for any perturbational problem and are, therefore, not limited to intermolecular forces.

In any perturbational treatment the full Hamiltonian, \( H \), is written as the sum of a reference Hamiltonian, \( H^{(0)} \), and a perturbing potential \( V \)

\[
H = H^{(0)} + V. \tag{1}
\]

In the present application, \( H \) is the Hamiltonian of the interacting helium dimer, \( H^{(0)} \) is the Hamiltonian of the noninteracting dimer: \( H^{(0)} = H^A + H^B \), where \( H^M \) represents the Hamiltonian of the isolated helium atom (\( M = A,B \)). \( V \) is the interatomic interaction operator

\[
V = \frac{1}{r_{13}} + \frac{1}{r_{23}} + \frac{1}{r_{14}} + \frac{1}{r_{24}} - \frac{2}{r_{1B}} - \frac{2}{r_{2B}} - \frac{2}{r_{3A}} - \frac{2}{r_{4A}} + 4 R_{AB}, \tag{2}
\]

where the indices 1 and 2 refer to the electrons of atom \( A \) and indices 3 and 4 to those of atom \( B \); \( r_{ij} \) is the distance between electrons \( i \) and \( j \), and \( R_{ij} \) the distance between electron \( i \) and nucleus \( M (M = A,B) \).

We are interested in computing the change in the ground state energy of the dimer due to the presence of the perturbing operator \( V \). Within the framework of perturbational treatments this change in energy is expressed as an infinite perturbation series

\[
\Delta E_{RS} = E_0 - E^{(0)}_0 = \sum_{n=1}^{\infty} E^{(n)}_{RS}, \tag{3}
\]

where \( E_0 \) denotes the exact ground state energy of \( H \) but calculated with the complete neglect of the interatomic exchange of electrons; \( E^{(0)}_0 \) is the ground state energy of the reference Hamiltonian: \( E^{(0)}_0 = E^A + E^B \) with \( E^M (M = A,B) \) is the energy of the isolated atoms. \( \Delta E_{RS} \) is the so-called Rayleigh–Schrödinger (RS) interaction energy, and \( E^{(n)}_{RS} \) represents the \( n \)th order RS component. In the literature this quantity is also often called the \( n \)th order polarization component. At this point, it is important to emphasize that the ground state energy of the interacting dimer obtained by Eq. (3) is not the true physical ground state energy of the actual interacting dimer. Indeed, the change of symmetry of the wave function with respect to the exchange of electrons between the noninteracting and interacting dimers must also be taken into account. Physically, this leads to the repulsive interaction at short distances. In practice, this important physical effect is described by introducing in the perturbational series the so-called exchange terms. We shall discuss the exchange contribution later.

Now, Caffarel and Hess\(^1\) have shown that the \( n \)th order RS contribution can be written in terms of a multitime integral of the \( n \)-point autocorrelation function of the perturbing potential along the stochastic trajectories of some diffusion process built from the reference Hamiltonian \( H^{(0)} \). Let us denote by \( \phi_i^{(0)} \) the eigenfunctions of the reference Hamiltonian with energies \( E_i^{(0)} \)

\[
H^{(0)} \phi_i^{(0)} = E_i^{(0)} \phi_i^{(0)}. \tag{4}
\]

The diffusion process associated with \( H^{(0)} \) is entirely defined by its transition probability density

\[
p(x \rightarrow y,t) = \frac{\phi_i^{(0)}(y)}{\phi_i^{(0)}(x)} \sum_{i} \phi_i^{(0)}(x) \phi_i^{(0)}(y) \times \exp[-t(E_i^{(0)} - E_0^{(0)})], \tag{5}
\]

where \( x \) and \( y \) represent two points in the configuration space \((x = (r_1, r_2, r_3, r_4) \) in the present application, and \( t \) is the time parameter. In other words, the transition probability density is, up to some factor involving the ground state wave function, connected to the imaginary time-dependent Green’s function of \( H^{(0)} \)

\[
p(x \rightarrow y,t) = \frac{\phi_i^{(0)}(y)}{\phi_i^{(0)}(x)} \langle y | \exp[-t(H^{(0)} - E_0^{(0)})] | x \rangle. \tag{6}
\]

Note that expressions Eqs. (5) and (6) are identical only if all the eigenfunctions are real. This condition is satisfied since only real Hamiltonians will be considered (for such Hamiltonians a complete set of real eigenfunctions can always be constructed). As a consequence, no conjugation sign will appear in the formulas that follow. Eq. (5) defines a diffusion process consisting of a standard free diffusion part in configuration space plus a deterministic part corresponding to a drifted move with a drift vector given by

\[
b = -\nabla \frac{\phi_i^{(0)}}{\phi_i^{(0)}}. \tag{7}
\]

It can be verified by substitution that the previous transition probability density, Eq. (5), is the solution of the following (forward Fokker–Planck) diffusion equation

\[
\frac{\partial p}{\partial t} = \frac{1}{2} \nabla^2 p - \nabla \cdot [b(y)p] \tag{8}
\]

with the initial condition, \( p(x \rightarrow y,0) = \delta(x-y) \) (for a general presentation of diffusion processes, see, e.g., Refs. 19 and 20). In practice, stochastic trajectories of the diffusion process are generated using a discretized version of the Langevin equation

\[
\Delta x(t + \Delta t) = b(x(t)) \Delta t + \eta \sqrt{\Delta t}, \tag{9}
\]

where \( \eta \) is a random vector whose independent components are drawn from a Gaussian distribution with zero mean and unit variance (free diffusion process in a multidimensional space).

Next the different perturbational components can be written in terms of averages of the diffusion process just presented. The first order is given by the usual formula \( \langle \phi_i^{(0)} | V | \phi_i^{(0)} \rangle \) is supposed to be normalized

\[
E^{(1)} = \langle \phi_i^{(0)} | V | \phi_i^{(0)} \rangle, \tag{10}
\]

which can be written as

\[
E^{(1)} = \int dx \ p(x) V(x), \tag{11}
\]
where \( p(x) \) is given by
\[
p(x) = \langle \phi_0^{(0)}(x) \rangle^2.
\] (12)

In this formula, \( p(x) \) is the quantum-mechanical probability density associated with the ground state wave function of the reference Hamiltonian. In fact, \( p(x) \) is also the stationary density of the diffusion process. This property is easily checked by looking at the long-time behavior of the transition probability density, Eq. (5), or by verifying that \( p \) is the stationary solution of Eq. (8). Denoting by \( \langle \cdots \rangle \) the stochastic average along any trajectory or group of trajectories generated using the Langevin equation (these two methods of averaging are equivalent due to the ergodicity of the diffusion process, see Ref. 15), the first order is simply given by
\[
E^{(1)} = \langle V \rangle.
\] (13)

The derivation of the second order is more involved and explicitly makes use of the dynamics of the diffusion process. In what follows, we will use the reduced resolvent of \( H^{(0)} \) defined by
\[
R_0 = \sum_{i > 0} \frac{1}{E^{(0)}_0 - E^{(0)}_i} \langle \phi_i^{(0)} \rangle \langle \phi_i^{(0)} \rangle^*.
\] (14)

The usual expression for the second order is
\[
E^{(2)} = \sum_{i > 0} \frac{\langle \phi_i^{(0)} \rangle \langle \phi_i^{(0)} \rangle \langle \phi_i^{(0)} \rangle \langle \phi_i^{(0)} \rangle}{E^{(0)}_0 - E^{(0)}_i} ,
\] (15)

which can be written in the compact form
\[
E^{(2)} = \langle \phi_0^{(0)} \rangle V R_0 V \langle \phi_0^{(0)} \rangle.
\] (16)

Now, from the basic relation, Eq. (6), we can express the reduced resolvent, Eq. (14), in terms of the transition probability density in the following way:
\[
\int_0^{+\infty} dt [p(x-y,t) - p(y)] = - \frac{\phi_0^{(0)}(y)}{\phi_0^{(0)}(x)} \langle y | R_0 | x \rangle.
\] (17)

Using Eqs. (16) and (17) we get
\[
E^{(2)} = - \int_0^{+\infty} dt \left[ \int dx \; dy \; p(x)V(x)p(x-y,t)V(y) \right.
\]
\[
- \left[ \int dx \; p(x)V(x) \right]^2 ,
\] (18)

which can be viewed as the integral of the two time-centered autocorrelation function of the perturbing potential
\[
E^{(2)} = - \int_0^{+\infty} dt \; C_{VV}(t),
\] (19)

where the autocorrelation function \( C_{VV}(t) \) is given by
\[
C_{VV}(t) = \langle (V(0) - \langle V \rangle)(V(t) - \langle V \rangle) \rangle
\]
\[
= \langle V(0)V(t) \rangle - \langle V \rangle^2.
\] (20)

This is the final formula for the second-order interaction energy. Note that \( C_{VV} \) appears as a second-order cumulant of the perturbing potential. A similar formula can be obtained for the third-order RS component by starting from the usual expression of the third-order component in terms of the reduced resolvent
\[
E^{(3)} = \langle \phi_0^{(0)} | VR_0(V - E^{(1)}_0)R_0 | \phi_0^{(0)} \rangle ,
\] (21)

which can be written in the form
\[
E^{(3)} = \int_0^{+\infty} \int_0^{+\infty} dt_1 dt_2 \int \int dx \; dy \; dz \; p(x)V(x)
\]
\[
\times [p(x-y,t_1) - p(y)](V(y) - \langle V \rangle)
\]
\[
\times [p(y-z,t_2) - p(z)](V(z) - \langle V \rangle).
\] (22)

After some algebra, this formula can be rewritten as
\[
E^{(3)} = \int_0^{+\infty} \int_0^{+\infty} dt_1 dt_2 \langle (V(0)V(t_1)V(t_2))
\]
\[
- \langle V \rangle \langle V(0)V(t_1) \rangle \rangle - \langle V \rangle \langle V(t_1)V(t_2) \rangle
\]
\[
- \langle V \rangle \langle V(0)V(t_2) \rangle + 2 \langle V \rangle^3 ,
\] (23)

which can be used for practical Monte Carlo calculations. Note that, now, it is a third-order cumulant of the perturbing potential which appears in the formula. Quite naturally, the general formula for the general \( n \)th order in perturbation involves the \( n \)th order cumulant of the potential (see Ref. 15).

At this point, we have shown that, for a general Hamiltonian, it is possible to express any perturbational component as an integral of a stochastic autocorrelation function of the external potential. To compute this correlation function, only the ground state wave function has to be known. From this wave function the drift vector can be computed and, then, the stochastic trajectories can be generated using the Langevin equation, Eq. (9). In general, except for very simple cases, the ground state wave function is not known and stochastic trajectories corresponding to the true reference problem cannot be constructed. This problem is easily solved by making use of a slightly different diffusion process constructed from a very good approximation of the unknown ground state wave function. Of course, in that case, it is also necessary to change in some suitable way the integrands in the stochastic averages so that the perturbational expressions remain exact. Let us denote by \( \psi_T \) (T for trial wave function) this new approximate wave function. It is important to emphasize that, once a trial wave function is given, the diffusion process is entirely determined via the Fokker–Planck equation Eq. (8) and the drift vector Eq. (7) that is built from it. Doing this corresponds to choosing a new transition probability density whose expression is given by
\[
p_T(x-y,t) = \frac{\psi_T(y)}{\psi_T(x)} \langle y | \exp[-t(H_T^{(0)} - E_T^{(0)})] | x \rangle ,
\] (24)

where \( H_T^{(0)} \) is the Hamiltonian which has \( \psi_T \) as its ground state wave function, or
\[
H_T^{(0)} \psi_T = E_T^{(0)} \psi_T.
\] (25)

The important point is that this new approximate Hamiltonian is explicitly known.
\[ H_T^{(0)} = H^{(0)} - (E_L(x) - E_T^{(0)}) , \]

where \( E_L \) is the so-called local energy corresponding to the trial wave function
\[ E_L(x) = H^{(0)} \psi_T / \psi_T . \]

When the approximate wave function reduces to the exact one, the local energy reduces to the exact energy and the difference between \( H_T^{(0)} \) and \( H^{(0)} \) vanishes. Accordingly, the smoothness of the local energy is a measure for the quality of the trial wave function.

In the short time limit a relation between the exact and trial transition probability density can be found. Using Eqs. (6), (24), (26), and keeping the leading contribution in time, we get

\[ p(x \rightarrow y, \tau) \sim \tau_c p_T(x \rightarrow y, \tau) \exp[- \tau(E_L(x) - E_T^{(0)})] . \]

Essentially there are two different ways to take into account the additional exponential weight factor. A first method considers this factor as a simple weight and carries it along the stochastic trajectories. This method, which is usually referred to as the pure diffusion Monte Carlo (PDMC) method, is the method we shall employ here. The different aspects of this method have been presented elsewhere\(^{15-18} \) and will not be repeated here. The general expression used for the multi-time correlation functions is

\[
\langle V[x(u_1)] \cdots V[x(u_k)] \rangle = \lim_{t \to \infty} \frac{\langle V[x(u_1)] \cdots V[x(u_k)] \exp[ - \int_{-t/2}^{t/2} ds (E_L(x(s)) - E_T^{(0)})] \rangle}{\langle \exp[ - \int_{-t/2}^{t/2} ds (E_L(x(s)) - E_T^{(0)})] \rangle},
\]

where the \( u_i \)'s are some fixed time values in the interval \((-t/2, t/2)\). Note that the total exponential weight appearing in this formula is usually referred to as the Feynman–Kac weight.\(^{17,18} \)

A second possible approach is to simulate the exponential term using a birth–death process or branching process. In contrast with the pure diffusion method, the number of walkers varies during the simulation with some rate related to the magnitude of the exponential factor. This method is referred to as the diffusion Monte Carlo (DMC) method (see, e.g., Ref. 21 for a detailed presentation). Note that this method could be used here for computing correlation functions. However, its implementation is not straightforward because of the varying number of walkers. In order to compute the different multitime correlation functions we have to keep trace of all the death and birth events during a given period of time. This is a nontrivial accounting problem that is avoided here by using a PDMC approach.

### B. Exchange terms

As mentioned in Sec. I, this paper does not focus on the evaluation of the different exchange energy components with QMC. Indeed, large statistical fluctuations associated with very small exchange overlaps prevent accurate results being obtained. Let us just present the approximate formula of the first-order exchange contribution employed here.

The exact first-order energy of interaction is defined as

\[ E^{(1)} = \left< \frac{\phi_0^{(0)}}{\psi_T} \right| V \left| \frac{\phi_0^{(0)}}{\psi_T} \right> , \]

where \( \phi_0^{(0)} \) is the exact ground state wave function of the Hamiltonian \( H^A + H^B \). The operator \( \mathcal{A} \) denotes the antisym-metrizer for all electrons. The first-order energy can be split into two contributions: the first-order RS energy of interaction and the first-order exchange interaction

\[ E^{(1)} = E^{(1)}_{\text{RS}} + E^{(1)}_{\text{exch}} . \]

The first-order Rayleigh–Schrödinger has already been considered in the previous section. It is given by

\[ E^{(1)}_{\text{RS}} = \left< \frac{\phi_0^{(0)}}{\phi_0^{(0)}} \right| \frac{V \phi_0^{(0)}}{\phi_0^{(0)}} . \]

After integration over the spin coordinates, it is not difficult to obtain the following expression for the first-order exchange component:

\[ E^{(1)}_{\text{exch}} = \frac{\left< \mathcal{A} \right| V \left< \mathcal{A} \right> }{1 - \left< \mathcal{A} \right> } , \]

with \( \mathcal{A} = \frac{1}{2} (P_{13} + P_{14} + P_{23} + P_{24}) - P_{13}P_{24} \). \( P_{ij} \) denotes the transposition of electrons \( i \) and \( j \). The brackets indicate the stochastic average along stochastic trajectories of the diffusion process constructed from \( \phi_0^{(0)} \). In practice, our approximate expression for this quantity is obtained by using the stochastic trajectories of the approximate diffusion process built from the high-quality trial wave function \( \psi_T \). The present definition for the first-order energy exchange is in accordance with Rybak et al.\(^{13} \) and Caffarel and Hess\(^{15} \) but differs from that given by Conway and Murrell.\(^{22} \) As these authors split the total first-order energy in a different way into two components. The differences are, however, completely negligible for regions of small overlap.

### III. SOME COMPUTATIONAL DETAILS

The trial wave function \( \psi_T \) used to describe the noninteracting dimer is constructed from a high-quality wave function for the helium atom
The total local energy associated with the trial wave function appears in the different formulas used to compute the exact correlation functions of the interatomic potential. Using Eqs. (27) and (34) we get

\[ E_L = H^A \psi^A_K / \psi^A_K + H^B \psi^B_K / \psi^B_K. \]  

(37)

The total local energy is the sum of two monomer local energies. In fact, the two terms of the sum are statistically independent. Each monomer local energy depends only on its own actual configuration but not on the internuclear distance or on the relative orientation with respect to the other monomer. This property was used to accelerate the calculations. The local energy of an atom, in a particular configuration, does not change if one of the operations of the full octahedral point group, \( O_h \), the symmetry group of the cube, is applied to the configuration. The point group contains 48 symmetry operations. Application of these operations to each monomer leads to 48\( \times 48 \) different configurations all having the same total local energy. Of these configurations there are 6\( \times 48 \) configurations leading to different values for the interatomic potential. These have been used in the calculations. No bias in the results is caused due to the application of the symmetry operations. In practice, the reduction in computation time achieved by considering these new configurations was approximately a factor of 10.

Let us now consider the practical computation of the correlation functions. Rewriting the one-point correlation function of the interatomic potential, Eq. (29), as an average along an arbitrary stochastic trajectory (this is possible because of ergodicity, see Refs. 15, 17, 18 for all details), the first-order is written as

\[ E_{RS}^{(1)} = \lim_{t \to \infty} \lim_{T \to \infty} \frac{\int_0^T d\tau \left[ \psi(x(\tau)) \exp(-\int_{\tau}^{\tau+T/2} ds \, E_L[x(s)]) \right] \left[ \psi(x(\tau+T)) \right]}{\int_0^T d\tau \left[ \psi(x(\tau)) \exp(-\int_{\tau}^{\tau+T/2} ds \, E_L[x(s)]) \right]}. \]

(38)

Here, \( T \) is related to the total time considered along the trajectory (actually, the total time is \( T + t \)) and \( x(\tau) \) is an arbitrary stochastic trajectory generated with the Langevin equation. The typical time step used in this work is \( \Delta t = 0.03 \) a.u. and \( T = 3000\Delta t \). The projection time \( t \) appearing in the Feynman–Kac weight is taken to be \( t = 449\Delta t \). This relatively large value of \( t \) is in fact not required for the calculation of the first-order RS energy (a much smaller value would be sufficient). However, this value is needed for the evaluation of the time correlation functions. The two- and three-point correlation functions from which the second- and third-order RS interaction energies are calculated, are

\[ C_{VV}(u) = \lim_{t \to \infty} \lim_{T \to \infty} \frac{\int_0^T d\tau \left[ \psi(x(\tau)) \exp(-\int_{\tau}^{\tau+T/2} ds \, E_L[x(s)]) \right] \left[ \psi(x(\tau+u)) \right]}{\int_0^T d\tau \left[ \psi(x(\tau)) \exp(-\int_{\tau}^{\tau+T/2} ds \, E_L[x(s)]) \right]}. \]

(39)

and

\[ \psi_T(r_1, r_2, r_3, r_4) = \psi_k^A(r_1, r_2) \psi_k^B(r_3, r_4). \]

(34)

The helium atom wave function \( \psi_k^M (M = A, B) \) is a six-term Hylleraas-type wave function optimized and parameterized by Koga and written as

\[ \psi_k^M = \exp(-\zeta s)(1 + c_1 u + c_2 t^2 + c_3 u^2 + c_4 s^2 u + c_5 s^3 u), \]

(35)

where \( s, t, \) and \( u \) are the Hylleraas coordinates defined by

\[ s = r_i + r_j, t = r_i - r_j, u = r_{ij}, \]

(36)

and where the exponent \( \zeta \) and the coefficients \( c_i \) are variational parameters. \( r_i \) is the distance of electron \( i \) to nucleus \( M(M = A, B) \), \( r_{ij} \) is the distance between the two electrons. The values of the parameters are listed in Table I. This atomic trial wave function gives an accurate total energy corresponding to 99.35% of the correlation energy. In addition, its very compact form is quite attractive since the calculation of its first (drift vector) and second derivatives (Laplacian appearing in the local energy) is not too time consuming, an important point since this calculation must be performed at each Monte Carlo step.

Besides the statistical error inherent to any statistical method, the only source of error is the use of a finite time step when integrating the Langevin equation, Eq. (9) (short-time approximation). In order to reduce this short-time error we have imposed the detailed balance property during the simulation. Detailed balancing is introduced via an acceptance/rejection step at each Langevin move in a way similar to what is done in the usual Metropolis algorithm. Such a procedure is presented in detail in Ref. 15. It is important to note that the time step used in this work has been chosen small enough so that short-time errors are smaller than the statistical fluctuations.

<table>
<thead>
<tr>
<th>TABLE I. Optimized 6-term Hylleraas wave function for the helium atom (atomic units).</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \xi )</td>
</tr>
<tr>
<td>( c_1 )</td>
</tr>
<tr>
<td>( c_2 )</td>
</tr>
<tr>
<td>( c_3 )</td>
</tr>
<tr>
<td>( c_4 )</td>
</tr>
<tr>
<td>( c_5 )</td>
</tr>
<tr>
<td>Energy</td>
</tr>
<tr>
<td>Correlation energy( ^b )</td>
</tr>
<tr>
<td>Best literature value for the energy( ^c )</td>
</tr>
<tr>
<td>Hartree–Fock energy( ^d )</td>
</tr>
</tbody>
</table>

\( ^a \)Not all figures displayed are significant. Some are displayed only to avoid round-off errors.

\( ^b \)Defined as the difference between the exact nonrelativistic energy and the Hartree–Fock energy.

\( ^c \)Reference 24.

\( ^d \)Reference 25.
respectively. Note that, because of the stationarity property of the diffusion process, \( C_{VV} \) depends only on one time interval \( u \) and \( C_{VVV} \) on two time intervals, \( u \) and \( v \). Figure 1 gives a typical example of the time-correlation function, \( C_{VV} \), as a function of the time interval \( u \) (\( C_{VV} \) is the centered time correlation function defined according to Eq. (20)). In order not to bias the final result it is important to take large enough values of \( u \) and thus of the projecting time \( t \). To get the second-order term the correlation function, Eq. (39), has to be integrated (in fact, the centered version of it). The integration has been done using Bode’s rule. Figure 2 shows the negative of the integral of the time correlation function as a function of the total integration time, also for \( R = 5.6 \) bohr. By taking sufficiently large values of the correlation time, we can reach a regime where the integral has converged within statistical error bars.

Finally, in order to estimate the statistical error in each of the energy components, each calculation was split into a number of independent blocks. The final result was obtained as the mean value of the results obtained for the independent blocks, the error being obtained as the standard deviation of the mean. For \( R \) ranging from 3- to 7 bohr, we have used 38 blocks, each of them containing 50 trajectories. Taking into account the configurations generated with the symmetry as discussed above our statistics is based on approximately \( 1.6 \times 10^8 \) Monte Carlo events for each perturbational component and distance. For the shorter distances we have used 14 blocks.

IV. RESULTS AND DISCUSSION

A. First-order energy

In contrast with higher-order terms, the first-order perturbational energy depends only on the ground state wave functions of the constituent monomers. A high accuracy can then be achieved by expanding these wave functions over a sufficiently large set of basis functions. Table II reports the very accurate results obtained by Rybak et al.13 for both the RS part, denoted as \( E_{RS}^{(1)} \), and the exchange part, \( E_{exch}^{(1)} \). These results have been obtained using a 75-term GTG (Gaussian-type geminal) basis which reproduces 99.9976% of the helium correlation energy and properly represents the behavior of the electron density in the outer region of the helium atom. The error, in the interaction energy, is approximately 0.1 \( \mu \)hartree.13 Note that, even for the first-order terms, the convergence of the calculations with the size of the basis set, is not easy to achieve. As an illustrative example consider the very recent results of Tachikawa et al.14 Using quite a large basis set these authors obtained RS contributions being very similar to those given by Rybak et al.13 However, the first-order exchange contributions differ noticeably from those reported by Rybak et al.13 For example, at \( R = 5.6 \) bohr, the values of the polarization (RS) components almost equal ( \(-5.35\) and \(-5.37 \) \( \mu \)hartree), but the exchange contributions differ by approximately \( 1 \) \( \mu \)hartree (38.95 and 37.92 \( \mu \)hartree). To illustrate the effect of the intra-atomic correlation on the first-order energies, the SCF values, \( E_{RS}^{(0)} \) and \( E_{exch}^{(0)} \) as given by Tachikawa et al.14 also have been listed in Table II (as usual, the second superscript 0 indicates that the quantities are evaluated at the SCF level). When we regard the exponentially small first-order RS part (there are no permanent multipoles and this contribution results only from the penetration of the atomic wave functions) the contribution of the correlation energy is between 5% to 8%, except at the largest distance (\( R = 7 \) bohr) where it seems to be larger (however, care must be taken with the quality of the SCF value at such a large distance). The first-order exchange contribution is much more important and the effect of the intra-atomic correlation energy is a little stronger: between 6% to 12%. As for the RS component, the effect increases with the distance, showing that the tail of the atomic wave function seems to be sensitive to a

\[
C_{VVV}(u,v) = \lim_{t \to \infty} \lim_{\tau \to \infty} \frac{\int_0^T V[x(\tau)]V[x(\tau+u)]V[x(\tau+u+v)] \exp(-\int_{\tau+u}^{\tau+u+v} ds E[s(x)])}{\int_0^T \exp(-\int_{\tau}^{\tau+u} ds E[s(x)])}
\]

(40)
TABLE II. Quantum Monte Carlo and \textit{ab initio} perturbational components at various interatomic distance \(R\). Statistical errors on the last digit in QMC results are indicated in parentheses. Energies in |\textmu|hartree, distances in bohr.

<table>
<thead>
<tr>
<th>(R)</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
<th>5.6</th>
<th>6.0</th>
<th>7.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_{\text{RS}}(\text{1}))</td>
<td>283.09</td>
<td>22.79</td>
<td>4.94</td>
<td>1.78</td>
<td>0.138</td>
<td></td>
</tr>
<tr>
<td>(E_{\text{RS}}(\text{2}))</td>
<td>298.24</td>
<td>24.56</td>
<td>5.35</td>
<td>1.90</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>(E_{\text{RS}}(\text{3}))</td>
<td>3355(56)</td>
<td>25.6(6)</td>
<td>6.1(1)</td>
<td>3.2(2)</td>
<td>0.3(3)</td>
<td></td>
</tr>
<tr>
<td>(E_{\text{RS}}(\text{4}))</td>
<td>1752.71</td>
<td>155.85</td>
<td>35.52</td>
<td>13.11</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>(E_{\text{RS}}(\text{5}))</td>
<td>1854.16</td>
<td>168.14</td>
<td>38.95</td>
<td>14.55</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>(E_{\text{RS}}(\text{6}))</td>
<td>16932(604)</td>
<td>1381(313)</td>
<td>449(139)</td>
<td>300(269)</td>
<td>62(43)</td>
<td>1(1)</td>
</tr>
<tr>
<td>(E_{\text{RS}}(\text{7}))</td>
<td>520.11</td>
<td>114.38</td>
<td>55.27</td>
<td>33.25</td>
<td>11.97</td>
<td></td>
</tr>
<tr>
<td>(E_{\text{RS}}(\text{8}))</td>
<td>639.21</td>
<td>143.62</td>
<td>68.89</td>
<td>42.14</td>
<td>15.20</td>
<td></td>
</tr>
<tr>
<td>(E_{\text{RS}}(\text{9}))</td>
<td>4421(68)</td>
<td>703(17)</td>
<td>161(10)</td>
<td>74(1)</td>
<td>45(2)</td>
<td>15.9(4)</td>
</tr>
<tr>
<td>(E_{\text{RS}}(\text{10}))</td>
<td>96.05</td>
<td>8.13</td>
<td>1.894</td>
<td>0.723</td>
<td>0.067</td>
<td></td>
</tr>
<tr>
<td>(E_{\text{RS}}(\text{11}))</td>
<td>135.96</td>
<td>11.38</td>
<td>2.65</td>
<td>1.01</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>(E_{\text{RS}}(\text{12}))</td>
<td>1186(96)</td>
<td>46(22)</td>
<td>6(11)</td>
<td>2.2(2)</td>
<td>0.3(7)</td>
<td>0.13(3)</td>
</tr>
</tbody>
</table>

*a* Reference 14.

*b* Reference 13.

*c* Approximate QMC first-order exchange energy, Eq. (33) with trial wave function Eq. (34).

*d* Reference 27.

Proper description of the intra-atomic correlation. We also present our QMC evaluation of the first-order components, \(E_{\text{RS}}\) for \(\text{RS-QMC}\) and \(E_{\text{RS}}\) for \(\text{RS-QMC}\). The first-order RS energy has been computed using the exact expression Eq. (38), whereas the first-order exchange energy has been calculated using the approximate expression Eq. (33). The first-order QMC results are given to show that they are in rough agreement with the much more accurate \textit{ab initio} results. For the RS component the statistical fluctuations are 5% for \(R=4\) bohr, 17% at the equilibrium distance, \(R=5.6\) bohr, and essentially 100% at the largest distance, \(R=7\) bohr, where the first-order RS component is very small. As has been mentioned already, the situation for the first-order exchange energy is even worse. Statistical fluctuations range from 23% to 100%. For the shorter distances the situation is more favorable. Table III lists the results. It is seen that, in this region, accuracies of say, 1% to 2% are obtained. Hence, in what follows we shall use the accurate \textit{ab initio} values, for the longer distances, as reference values for the first-order energy. As we discuss below, QMC results for the higher orders are much more interesting.

**B. Second- and third-order interaction energies**

Perturbational components beyond the first-order have been obtained, so far, by using \textit{ab initio} frameworks where the monomer wave functions (ground and excited states) are expanded over a more or less extended set of basis functions. As is well known, a number of difficulties are present in such calculations. First, in order to perform the infinite summations, present in the perturbational expressions, the entire set of the exact eigenfunctions of the monomers is needed. These functions are in general not known and approximate wave functions have to be used. In general, these functions are issued from a self-consistent-field (SCF) calculation in which the intra-atomic electron correlation is neglected. Very recently, a great deal of attention has been focused on the calculation of intramonomer correlation contributions to the interaction energy components.\cite{14,27–35} The usual approach consists in decomposing the monomer Hamiltonians as a sum of the Fock operator and some residual intramonomer correlation operators (Möller–Plesset partitioning) and, then, to resort to a double perturbation theory (in the correlation operators of each monomer) using a many-body expansion framework. However, such calculations are not so easy to do and are limited, in practice, to the calculation of some leading corrections (e.g., up to second order in the internal correlation) and/or to some partial infinite-order summation corresponding to specific classes of diagrams (see, e.g., Ref. 36). Second, there is the problem of efficiently evaluating the infinite sums present in the perturbational expressions. In particular, the summations corresponding to the continuous part of the spectrum are in practice almost inexecutable integrations (see, Ref. 37). To solve this problem, variation-perturbation schemes have been proposed in which the perturbed wave function is interpreted as the solution of a variational problem (Hylleraas variational procedure). Then,

**TABLE III. Quantum Monte Carlo perturbational components at short intermolecular distances \(R\). Statistical errors on the last digit are indicated in parentheses. Energies in |\textmu|hartree, distances in bohr.**

<table>
<thead>
<tr>
<th>(R)</th>
<th>1.5</th>
<th>1.6</th>
<th>1.7</th>
<th>1.8</th>
<th>1.9</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_{\text{RS}}(\text{1}))</td>
<td>-0.0813(6)</td>
<td>-0.0694(6)</td>
<td>-0.0583(6)</td>
<td>-0.0484(5)</td>
<td>-0.0398(5)</td>
<td>-0.0323(5)</td>
</tr>
<tr>
<td>(E_{\text{RS}}(\text{2}))</td>
<td>0.576(7)</td>
<td>0.462(6)</td>
<td>0.370(6)</td>
<td>0.297(6)</td>
<td>0.239(5)</td>
<td>0.191(5)</td>
</tr>
<tr>
<td>(E_{\text{RS}}(\text{3}))</td>
<td>-0.125(1)</td>
<td>-0.099(1)</td>
<td>-0.0784(9)</td>
<td>-0.0620(8)</td>
<td>-0.0495(8)</td>
<td>-0.0390(7)</td>
</tr>
<tr>
<td>(E_{\text{RS}}(\text{4}))</td>
<td>-0.077(2)</td>
<td>-0.059(2)</td>
<td>-0.045(1)</td>
<td>-0.035(1)</td>
<td>-0.028(1)</td>
<td>-0.021(1)</td>
</tr>
</tbody>
</table>
the total second order is very small \( \beta \); perturbational quantities are very sensitive to the basis set and by Jeziorski et al. variational space. Finally, as in any \textit{ab initio} standard sets of basis functions can be used to describe the
b Reference 14.
d Reference 27.

In Table II we show the \textit{ab initio} second-order RS interaction energies obtained very recently by Tachikawa et al.\textsuperscript{14} and by Jeziorski et al.\textsuperscript{27} To our knowledge, these values are the best \textit{ab initio} values calculated so far. It is worth remarking that, for \( R = 5.6 \) bohr, both SCF and correlated values of \( E_{\text{RS}} \) differ by approximately 2 \( \mu \text{hartree} \) between the two sets of results (the values given by Tachikawa et al.\textsuperscript{14} are \(-52.93 \mu \text{hartree} \), at the SCF level, and \(-66.91 \mu \text{hartree} \) at the correlated level, to compare with the better results of Jeziorski et al.\textsuperscript{27} presented here). These large differences illustrate the difficulties in obtaining converged values with \textit{ab initio} techniques.

In order to discuss the role of the intra-atomic electron correlation Table IV shows some of its perturbational contributions to the second-order components for \( R = 5.6 \) bohr. The differences between RS and \textit{ab initio} values on one hand, and QMC values on the other, are due to the intra-atomic electron correlation effects. In Table IV the first superscript gives the order in the interatomic perturbation, while the second superscript indicates the perturbational order in the Möller–Plesset expansion with respect to the intraatomic electron correlation operator. Note also that the second-order energy is decomposed as usual into an induction and dispersion part (see, e.g., Ref. 9). It may be clear that this distinction is specific to SCF and \textit{ab initio} calculations but is meaningless within our QMC framework. For \( R = 5.6 \) bohr, the exact QMC value is \(-74 \mu \text{hartree} \) with a statistical error of only 1 \( \mu \text{hartree} \) or approximately 1%. The SCF second-order RS energy, \( E_{\text{RS}} \), is quite different from our exact value, \( E_{\text{QMC}} \), which shows that the intra-atomic effect is strong. It is interesting to compare this result with the Möller–Plesset perturbational estimates of the same contribution presented by Jeziorski et al.\textsuperscript{27} Note that the induction contribution to the total second order is very small [penetration contribution behaving as \( \exp(-aR) \)] and only the contribution of the correlation effect to the dispersion part has been considered. At the first-order level 53% of the correlation contribution is recovered. The second-order gives some additional 21% so that the total contribution recovered is 74%. The remaining correlation contribution represents 14% of the total interaction energy. This illustrates the fact that any accurate evaluation of the intramonomer correlation effects must incorporate contributions beyond second-order. Note that the error in the QMC result is small enough (only 5% of this correlation effect) to validate this conclusion.

As noticed in previous works (e.g., Refs. 27 and 39) the second-order exchange effects in intermolecular interactions are in general not negligible. Here, this contribution is 8% of the total interaction energy. The correlation contribution to the second-order exchange part is small but significant (2% of the total interaction energy).

We have computed the exact second-order RS energy for various internuclear distances. The relative statistical error grows slowly with the distance (see Tables II and III). Even for the largest distance the error is only 3%, which is a satisfactory result. For the large distances the QMC results for \( E_{\text{QMC}} \) are compatible with a behavior as \( c_6/R^6 \) as it should be for a van der Waals dimer. Note that a QMC evaluation of the van der Waals coefficient, \( c_6 \), has been presented elsewhere.\textsuperscript{38}

The results for the third-order interaction energy are presented in Tables II and III. To the best of our knowledge there are no quantitative estimates of these values published so far. At the small distances this contribution is found to be negative, while at larger distances it corresponds to a repulsive contribution. It changes sign between \( R = 5.5 \) and 5.6 bohr. At the equilibrium distance, we find a repulsive contribution of 2.2 \( \mu \text{hartree} \) with a statistical error of 10%. This contribution is clearly significant since it represents 6% of the total interaction energy. In particular, it gives a contribution almost equal to the second-order exchange energy.

**C. Total interaction energy**

We are now in position to summarize the previous results and to discuss the relative importance of each perturbational component making up the complete interaction energy of the helium dimer. Within the framework of perturbational treatments (symmetry adapted perturbation theories (SAPT), the total interaction energy can be written as

\[
\Delta E_{\text{int}} = E_{\text{RS}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{RS}}^{(2)} + E_{\text{exch}}^{(2)} + E_{\text{RS}}^{(3)}.
\]

In this expansion all contributions occurring at first- and second-order in perturbation are taken into account. The neglected contributions are the third-order exchange effects and all contributions beyond the third-order. Putting together all these contributions according to Eq. (41) we get the values for the perturbational sum as listed in Table V. At the minimum of the potential the value of \(-35.0 \pm 1.2 \mu \text{hartree} \) for the total interaction energy of the helium dimer is found. This result is in good agreement with the very recent full CI interaction energy of van Mourik and van Lenthe\textsuperscript{6} which was calculated to be \(-34.68 \pm 0.03 \mu \text{hartree} \). It is also in accor-
TABLE V. Sum of perturbational contributions to the total interaction energy at various internuclear distances $R$. Statistical errors on the last digit in QMC results are indicated in parentheses. Energies in $\mu$hartree, distances in bohr.

<table>
<thead>
<tr>
<th>$R$</th>
<th>4.0</th>
<th>5.0</th>
<th>5.6</th>
<th>6.0</th>
<th>7.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E^{(1)} = E^{(1)}<em>{\text{exch}} + E^{(1)}</em>{\text{exch}}$</td>
<td>1555.92</td>
<td>143.58</td>
<td>33.60</td>
<td>12.65</td>
<td>1.08</td>
</tr>
<tr>
<td>$E^{(2)}_{\text{RS-QMC}}$</td>
<td>$-703(17)$</td>
<td>$-161(10)$</td>
<td>$-74(1)$</td>
<td>$-45(2)$</td>
<td>$-15.9(4)$</td>
</tr>
<tr>
<td>$E^{(2)}_{\text{ch}}$</td>
<td>135.96</td>
<td>11.38</td>
<td>2.65</td>
<td>1.01</td>
<td>0.09</td>
</tr>
<tr>
<td>$E^{(2)}_{\text{LM2M2}}$</td>
<td>$-46(22)$</td>
<td>$-6(11)$</td>
<td>2.2(2)</td>
<td>0.3(7)</td>
<td>0.13(3)</td>
</tr>
<tr>
<td>Perturbational sum</td>
<td>942.39</td>
<td>12.21</td>
<td>35.12</td>
<td>31.22</td>
<td>14.54</td>
</tr>
<tr>
<td>Full CI$^c$</td>
<td>933.88</td>
<td>0.709</td>
<td>34.67</td>
<td>30.60</td>
<td>14.62</td>
</tr>
<tr>
<td>VVVVR$^d$</td>
<td>934.5</td>
<td>0.507</td>
<td>34.58</td>
<td>30.56</td>
<td>14.62</td>
</tr>
<tr>
<td>LM2M2$^d$</td>
<td>927.7</td>
<td>-1.23</td>
<td>34.73</td>
<td>30.63</td>
<td>14.54</td>
</tr>
<tr>
<td>Supermolecular QMC$^e$</td>
<td>-1.3(25)</td>
<td>-34.9(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reference 13, ab initio calculations.
$^b$Reference 14, ab initio calculations.
$^c$Reference 6.
$^d$References 4 and 3.
$^e$References 4 and 40.

The perturbational expansion limited to the complete first- and second-order, plus the Rayleigh–Schrödinger third-order energy is sufficient to reproduce the total interaction energy of the helium dimer at intermediate and large distances.

Beyond this particular application it is clear that these conclusions are also important for the general theory of intermolecular forces and their evaluation by perturbation theory.

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