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Quantum Monte Carlo perturbation calculations of interaction energies

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A method of evaluating perturbational components of intermolecular interaction energies by using quantum Monte Carlo (QMC) techniques is presented. It is shown how the nth-order Rayleigh-Schrödinger (RS) perturbation term may be expressed in a very compact way in terms of suitably defined stochastic autocorrelation functions of the perturbing operator (the intermolecular interaction potential). The resulting formula is very general (not restricted to intermolecular interactions) and corresponds in fact to an alternative way of expressing RS perturbation theory in any order. As concerns the exchange contribution responsible for repulsion at small distances, an approximate expression for the first-order exchange interaction energy (by far the leading component) is given. Both advantages and drawbacks of the proposed QMC approach with respect to more conventional *ab initio* perturbational treatments are discussed. Some test calculations for the interaction of two helium atoms at small distances are presented. Results are systematically compared to those obtained with *ab initio* perturbation calculations using large Gaussian basis sets.

I. INTRODUCTION

Evaluating interaction energies between atoms and molecules is an important goal of molecular physics. Today, the most commonly employed method for such calculations is certainly the so-called supermolecule method[1] in which the interaction energy is obtained by subtracting from the total energy of the interacting molecules (the supermolecule) the sum of the total energies of each monomer, all energies being calculated by using the same method, generally some form of the configuration-interaction (CI) method. Difficulties associated with such an approach are well known and have been discussed in many places.[1] They can be summarized as follows.

(1) The problem of evaluating a very small quantity, the interaction energy, as a difference of two large and approximately evaluated quantities. Generally, it is very difficult to know whether errors made in calculating the total energies of the monomers and of the dimers are of comparable quality or not.

(2) Difficulties associated with the occurrence of the basis-set superposition error (BSSE), see, e.g., Refs. 2–5.

(3) Rapid increase of memory and CPU time requirements as a function of the size of the system studied.

An alternative approach to the supermolecule method consists in calculating interaction energies from perturbation theory using the intermolecular potential as perturbating operator. When the intermolecular distance R is large, one is dealing with the usual Rayleigh-Schrödinger perturbation theory. In this case, the complete set of excited states of the unperturbed Hamiltonian involved in perturbational components is simply chosen to be the products of monomer wave functions: due to the large separation between monomers no antisymmetrization of the factorized wave functions is necessary. In contrast, for shorter distances, such as, for example, distances corresponding to the region around the equilibrium configuration, the usual Rayleigh-Schrödinger theory must be generalized[6] in order to take into account the exchange of electrons between the interacting monomers (the introduction of exchange terms). This may be done by making use of one of the versions of the so-called symmetry-adapted perturbation theories (SAPT) in which the fermionic antisymmetry of the whole dimer is imposed within the perturbational expansion through the use of intersystem antisymmetrizers (see, e.g., Refs. 7 and 8). By using perturbation theory the basic difficulties of the supermolecule method listed above are essentially avoided: a direct evaluation of the small interaction energy is done, the BSSE is avoided, and calculations are generally much less expensive (the problem of having a high level of accuracy on total energies of each system is removed). However, a number of difficulties are still present. First, in order to perform the infinite summations over intermediate states involved in perturbational quantities, exact eigensolutions of monomers are required. Unfortunately, it is known that exact or even accurate correlated wave functions for atomic and molecular systems are in general not available. Consequently, approximate wave functions must be used. Generally, they are obtained from a self-consistent-field (SCF) calculation, so that the intramonomer electron correlation of monomers is neglected. However, it should be pointed out that by using the decomposition of the exact Hamiltonian of each monomer into the complete Fock operator and into the residual two-electron operator accounting for the electron correlation (Moller-Plesset-type decomposition), and by applying the usual Rayleigh-Schrödinger perturbation theory, one can express in principle each perturbation contribution (with respect to the intermolecular interaction potential) as an infinite series of perturbation corrections due to internal correlation.[9] In practice, such a procedure is generally limited to the calculation of 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. 10). Another difficulty associated with *ab initio* perturbation theory is the problem of summing efficiently infinite sums involved in perturbational expressions. In particular, as pointed out by Jeziorski and van Hemert[11] summations defined over the infinite set of unoccupied orbitals belonging to the continuous spectrum are practically inexecutable integrations. To overcome this difficulty, suitable variation-perturbation schemes have been proposed.[11] In practice, the achievement of a complete basis set is an obvious shortcoming of such procedures. An additional well-known difficulty common to any *ab initio* framework (supermolecular as well as perturbational approaches) is the problem of adequately choosing the basis set to use for a given physical problem. Due to the great sensitivity of perturbation quantities with basis set, the use of judiciously chosen basis sets turns out in fact to be essential. Finally, it is known that computational aspects of *ab initio* techniques are not favorable. Codes are important, complex, and many practical difficulties arise from calculation, storage, and manipulation of huge numbers of bielectronic integrals (with a very fast increase of the number of these integrals with the number of electrons treated).

In the present work, a method of evaluating perturbation quantities by using quantum Monte Carlo (QMC) techniques (e.g., Refs. 12–17 and references therein) is presented. The basic idea of this approach is to express perturbational quantities of interest in terms of suitably defined stochastic averages. The underlying stochastic process from which averages are taken is a pure diffusion process (a generalized Brownian process) constructed in a simple way from some reference wave function (a detailed presentation of this aspect may be found in Ref. 17). It is demonstrated how the nth-order Rayleigh-Schrödinger (RS) term $\Delta E_{\mathrm{RS}}^{(n)}$ can be expressed as an $(n-1)$-time integral of the connected (cumulant) n-time autocorrelation function of the perturbing potential (the intermolecular interaction potential) with respect to the diffusion process constructed from the exact ground-state wave function of the unperturbed Hamiltonian (the Hamiltonian describing noninteracting dimer). It should be remarked that this formula is very general (not restricted to intermolecular interactions) and corresponds in fact to an alternative way of expressing RS perturbation theory in any order.[18] In addition, this new formulation appears to be particularly compact, in contrast with the usual Bloch-Brückner formulation of the RS perturbation theory.[19] By expressing stochastic averages defined from the generally unknown exact ground-state wave function of the unperturbed Hamiltonian in terms of stochastic averages defined from an approximate trial wave function, and by resorting to standard Langevin simulation techniques, it is shown how practical calculations of $\Delta E_{\mathrm{RS}}^{(n)}$ may be performed. As concerns the exchange contribution responsible for intermolecular repulsion at small distances an approximate formula for the first-order exchange interaction energy $\Delta E_{\mathrm{exch}}^{(1)}$ (by far the leading contribution of the total exchange interaction energy) is given.

An essential feature of the method presented here is that no basis-set expansions are used. Resulting difficulties described above are therefore avoided. Another remarkable point is that infinite summations involved in usual perturbational expressions do not appear in our QMC formalism (in fact, they only appear *implicitly*, see below). Accordingly, no approximate expressions for eigenfunctions of each monomer are required. In practice, the only quantity needed for making exact calculations of perturbational quantities is an *approximate* ground-state wave function for each monomer (e.g., a Hartree-Fock wave function or better an explicitly correlated wave function). Another basic point which deserves to be mentioned is that intramonomer correlation contributions to perturbational quantities may be exactly taken into account without basic practical difficulties. Finally, we would like to emphasize that the computational aspects of the method are quite favorable[20] (in fact, this is a very general feature of all Monte Carlo approaches): (1) memory requirements remain perfectly bounded (no calculation and storage of bielectronic integrals) and (2) codes are short, simple, and very well suited for vector and parallel computing.

In a more general perspective, let us mention that a recent proposal based on the renormalization-group approach for electronic structure[40,41] could lead to an alternative way of computing interaction energies. However, no realistic calculations (done at the level of the chemical accuracy) have been performed so far.

The contents of this paper are as follows. In Sec. II we present the basic theoretical elements of the method. Section II A is devoted to the derivation of the basic formula expressing $\Delta E_{\mathrm{RS}}^{(n)}$ in terms of stochastic averages. In Sec. II B we present our approximate formula for calculating $\Delta E_{\mathrm{exch}}^{(1)}$. How to compute the stochastic averages involved in both formulas is presented in Sec. II C. The detailed theory including mathematical derivations may be found elsewhere.[17] Section II D briefly discusses how to correctly introduce Fermi statistics for monomers within the framework of the proposed method. Section III is devoted to the presentation of some numerical results for the interaction of two helium atoms at short distances (ranging from 1.5 to 2 a.u.). The essential motivation of such numerical application is to demonstrate the applicability of theoretical expressions derived in Sec. II and not to make a quantitative study of He-He interaction. In any case, at the short distances studied corresponding to a nonperturbative region of interaction, perturbational treatments for describing He-He interaction would fail (note that an exact treatment of this region of interaction has been made by Ceperley and Partridge[21] using a QMC supermolecular approach). Some calculations for $\Delta E^{(1)}_{\mathrm{RS}}$, $\Delta E^{(1)}_{\mathrm{exch}}$, and $\Delta E^{(2)}_{\mathrm{RS}}$ are presented. In order to check the validity of the method our calculations have been systematically compared to calculations performed with an *ab initio* perturbational program based on the Jeziorski–van Hemert approach.[11,22] The role of the intra-atomic correlation contribution on perturbational quantities (known to be particularly difficult to evaluate within *ab initio* frameworks) is briefly discussed. Finally, some concluding remarks are presented in Sec. IV.

II. THEORY

Consider two interacting systems A and B (atom or molecule). The total Hamiltonian of the complex, denoted as H, is decomposed as usual into three different parts

$$H = H^A + H^B + V^{AB} , \tag{1}$$

where H^M denotes the Hamiltonian of the noninteracting system M ($M = A,B$) and V^{AB} is the intermolecular interaction potential (atomic units are used)

$$V^{AB} = \sum_{\alpha\in A}\sum_{\beta\in B}\frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} - \sum_{\alpha\in A}\sum_{j\in B}\frac{Z_\alpha}{r_{\alpha j}} - \sum_{\beta\in B}\sum_{i\in A}\frac{Z_\beta}{r_{\beta i}} + \sum_{i\in A}\sum_{j\in B}\frac{1}{r_{ij}} , \tag{2}$$

where $r_{ab} = |\mathbf{r}_a - \mathbf{r}_b|$. Roman indices label electronic coordinates and Greek indices label nuclear coordinates. Z_μ is the charge number of nucleus μ belonging to molecule M ($M = A,B$). The normalized eigenfunctions of the Hamiltonian H^M of isolated system M ($M = A,B$) are denoted ϕ_i^M with the corresponding energies E_i^M, thus we write

$$H^M\phi_i^M = E_i^M\phi_i^M, \quad M = A,B . \tag{3}$$

The intermolecular interaction energy is defined as the difference between the total ground-state energy E_0^{AB} of the complex described by the Hamiltonian H and the total ground-state energy of the two noninteracting subsystems A and B,

$$\Delta E = E_0^{AB} - (E_0^A + E_0^B) . \tag{4}$$

As usual, the interaction energy is decomposed into two contributions corresponding to the so-called Rayleigh-Schrödinger and exchange parts of the interaction energy

$$\Delta E = \Delta E_{\mathrm{RS}} + \Delta E_{\mathrm{exch}} . \tag{5}$$

The Rayleigh-Schrödinger interaction energy corresponds to the interaction energy obtained when antisymmetry constraints on wave functions associated with the possibility of exchanging electrons between each subsystem are not considered. When full antisymmetry constraints are taken into account, the resulting increase in energy is given by the exchange part ΔE_{exch}. Let us first focus our attention on the Rayleigh-Schrödinger part of the interaction energy.

A. *n*th-order Rayleigh-Schrödinger interaction energy

Within the framework of perturbational treatments, ΔE_{RS} is expressed as an infinite perturbation series of the form

$$\Delta E_{\mathrm{RS}} = \sum_{n=1}^{+\infty} \Delta E^{(n)}_{\mathrm{RS}} , \tag{6}$$

where n corresponds to the order in V^{AB}. Let us show how the nth-order RS interaction energy $\Delta E^{(n)}_{\mathrm{RS}}$ may be expressed in terms of a suitably defined stochastic time-correlation function of the intermolecular interaction potential V^{AB}. For that purpose, it is first noticed that the RS interaction energy may be expressed in the following form:

$$\Delta E_{\mathrm{RS}} = -\lim_{t\to+\infty}\frac{\partial}{\partial t}\ln\langle \phi_0^A\phi_0^B|e^{-t(H-E_0^A-E_0^B)}|\phi_0^A\phi_0^B\rangle . \tag{7}$$

The validity of this expression is easily checked by making use of the spectral representation of operator e^{-tH}. It should be noted that the eigenvalue of H extracted by making the long-time limit is the lowest eigenvalue of H whose corresponding eigenfunction has a nonzero overlap with $\phi_0^A\phi_0^B$. This wave function obeys the same antisymmetry properties as $\phi_0^A\phi_0^B$ and the interaction energy obtained in Eq. (7) is therefore the RS interaction energy and not the true physical one as defined by Eq. (4).

Now, our essential step consists in invoking the so-called generalized Feynman-Kac (GFK) formula presented elsewhere.[17,20] Basically, this formula expresses the quantum matrix element of the right-hand side of Eq. (7) (actually, a slightly generalized version of the imaginary time-dependent Green's function associated with H) as an expectation value with respect to a suitable diffusion process. This basic formula is written here in the form

$$\langle \phi_0^A\phi_0^B|e^{-t(H-E_0^A-E_0^B)}|\phi_0^A\phi_0^B\rangle = \left\langle \exp\left[-\int_{-t/2}^{t/2} V^{AB}(\mathbf{X}(s))ds\right]\right\rangle_{\phi_0^A\phi_0^B} , \tag{8}$$

where $\langle\ \rangle_{\phi_0^A\phi_0^B}$ denotes the stochastic average over the infinite set of stochastic continuous trajectories $\mathbf{X}(s)$ [defined in the time interval $(-t/2,t/2)$] of the underlying diffusion process constructed from the wave function $\phi_0^A\phi_0^B$ (Refs. 17 and 20). Here, $\mathbf{X}(s)$ is a compact notation for representing a point (at time s) in the $3(N_A+N_B)$-dimensional configuration space, that is $\mathbf{X} = (\mathbf{r}_1^A,\ldots,\mathbf{r}_{N_A}^A,\mathbf{r}_1^B,\ldots,\mathbf{r}_{N_B}^B)$, where N_A and N_B are the numbers of electrons of molecule A and B, respectively. At this stage, we shall not define the exact meaning of this stochastic average and the way of computing it in a Monte Carlo simulation. This will be done in detail in Sec. II C.

Our next step consists in taking advantage of the fact that the previous stochastic average is a genuine average operation (in the Kubo sense, see Ref. 23) so that it is possible to resort to standard cumulant expansion methods. Applying a theorem due to Kubo (theorem II in Ref. 23), the averaged exponential in the right-hand side of formula (8) may be rewritten as the exponential of a cumulant expansion

$$\left\langle \exp\left[-\int_{-t/2}^{t/2} V^{AB}(\mathbf{X}(s))ds\right]\right\rangle_{\phi_0^A\phi_0^B} = \exp\left[\sum_{n=1}^{+\infty}(-1)^n\int_{-t/2}^{t/2}dt_n\int_{-t/2}^{t_n}dt_{n-1}\cdots\int_{-t/2}^{t_2}dt_1\langle V^{AB}(\mathbf{X}(t_1))\cdots V^{AB}(\mathbf{X}(t_n))\rangle^c_{\phi_0^A\phi_0^B}\right], \quad (9)$$

where $\langle\ \rangle^c_{\phi_0^A\phi_0^B}$ are the usual cumulant averages which are known to be expressed as some well-defined linear combination of products of same and lower-order moments (as pointed out by Kubo,[23] c may be as well understood as connected in the sense given to this word in the techniques of graphical representation). Note that for the sake of clarity a superscript notation for c is employed here instead of the more commonly used subscript notation. By making use of Eqs. (7), (8), and (9), the RS interaction energy takes the form

$$\Delta E_{\mathrm{RS}} = -\lim_{t\to+\infty}\frac{\partial}{\partial t}\sum_{n=1}^{+\infty}(-1)^n\int_{-t/2}^{t/2}dt_n\int_{-t/2}^{t_n}dt_{n-1}\cdots\int_{-t/2}^{t_2}dt_1\langle V^{AB}(\mathbf{X}(t_1))\cdots V^{AB}(\mathbf{X}(t_n))\rangle^c_{\phi_0^A\phi_0^B}. \quad (10)$$

Now, it is important to note that, due to the stationarity property of the diffusion process, all the cumulants involved in the preceding expression are only functions of the time differences t_i-t_{i-1}. It is therefore possible to perform a time-shift of length $t/2$ on each variable of integration and then to make the time derivative, one obtains

$$\Delta E_{\mathrm{RS}} = -\lim_{t\to+\infty}\sum_{n=1}^{+\infty}(-1)^n\int_0^t dt_{n-1}\int_0^{t_{n-1}}dt_{n-2}\cdots\int_0^{t_2}dt_1\langle V^{AB}(\mathbf{X}(t_i))\cdots V^{AB}(\mathbf{X}(t_{n-1}))V^{AB}(\mathbf{X}(t))\rangle^c_{\phi_0^A\phi_0^B}. \quad (11)$$

By making the following change of variables: $u_{i-1}-u_{i-2}=t_i-t_{i-1}$ ($i=2$ to n with $t_n\equiv t$ and $u_0\equiv 0$) and by invoking once more the stationarity property, the nth-order contribution of Eq. (11), $\Delta E^{(n)}_{\mathrm{RS}}$, may be finally written in the form

$$\Delta E^{(n)}_{\mathrm{RS}} = (-1)^{n+1}\int_0^{+\infty}du_{n-1}\int_0^{u_{n-1}}du_{n-2}\cdots\int_0^{u_2}du_1\langle V^{AB}(\mathbf{X}(0))V^{AB}(\mathbf{X}(u_1))\cdots V^{AB}(\mathbf{X}(u_{n-1}))\rangle^c_{\phi_0^A\phi_0^B}. \quad (12)$$

This is our final form for the nth-order RS perturbation term as a function of the n-time connected (cumulant) autocorrelation function of the intermolecular interaction operator with respect to the underlying diffusion process. It should be emphasized that this form is very compact, in contrast with the standard Bloch-Brückner formulation of the RS perturbation theory in any order (see, e.g., Ref. 19).

Let us briefly explain how to recover standard expression for $\Delta E^{(n)}_{\mathrm{RS}}$ from our formula (12). In order to make explicit the nth-order cumulant, kth-order correlation functions of the perturbing potential are needed ($k=1$ to n). Using the very basic definition of stochastic averages in terms of the underlying probability densities, the kth-order correlation function of V^{AB} is written

$$\langle V^{AB}(\mathbf{X}(0))\cdots V^{AB}(\mathbf{X}(u_{k-1}))\rangle_{\phi_0^A\phi_0^B} = \int d\mathbf{x}_0\cdots d\mathbf{x}_{k-1}p(\mathbf{x}_0)V^{AB}(\mathbf{x}_0)\prod_{i=1}^{k-1}p(\mathbf{x}_{i-1}\to\mathbf{x}_i,u_i-u_{i-1})V^{AB}(\mathbf{x}_i), \quad (13)$$

with $u_0\equiv 0$ and where $p(\mathbf{x})$ and $p(\mathbf{x}\to\mathbf{y},u)$ denote the stationary and transition probability densities of the diffusion process, respectively. These densities may be expressed in terms of the eigenfunctions $\phi_i^A\phi_j^B$ (with corresponding energies $E_i^A+E_j^B$) of the unperturbed Hamiltonian $H_0=H^A+H^B$ as follows [see Eqs. (2.7) and (2.13) in Ref. 17]:

$$p(\mathbf{x}) = (\phi_0^A\phi_0^B)^2(\mathbf{x}) \quad (14a)$$

and

$$p(\mathbf{x}\to\mathbf{y},u) = \frac{(\phi_0^A\phi_0^B(\mathbf{y})}{(\phi_0^A\phi_0^B)(\mathbf{x})}\sum_{i,j}(\phi_i^A\phi_j^B)(\mathbf{x})(\phi_i^A\phi_j^B)(\mathbf{y}) \times e^{-u(E_i^A+E_j^B-E_0^A-E_0^B)}. \quad (14b)$$

After having inserted expressions (13) and (14) into Eq. (12) time integrals may be easily performed. Once this is done, standard expanded expressions of Rayleigh-Schrödinger perturbational components in terms of combination of multiple summations over the complete set of eigenfunctions of the unperturbed Hamiltonian H^A+H^B are recovered. Let us derive the two first perturbational contributions. The first-order interaction energy is readily obtained; one has

$$\Delta E^{(1)}_{\mathrm{RS}} = \langle V^{AB}\rangle^c_{\phi_0^A\phi_0^B} = \langle V^{AB}\rangle_{\phi_0^A\phi_0^B}. \quad (15)$$

Now, since the stationary density of the diffusion process is nothing but the quantum-mechanical probability density associated with $\phi_0^A\phi_0^B$ [Eq. (14a)], the usual expression for $\Delta E^{(1)}_{\mathrm{RS}}$ is recovered:

$$\Delta E^{(1)}_{\mathrm{RS}} = \langle\phi_0^A\phi_0^B|V^{AB}|\phi_0^A\phi_0^B\rangle. \quad (16)$$

Applying the general formula (12) to the case $n=2$ and using expression of the second-order cumulant[23]

$$\langle X_1X_2\rangle^c = \langle(X_1-\langle X_1\rangle)(X_2-\langle X_2\rangle)\rangle, \quad (17)$$

the second-order RS interaction energy takes the form

$$\Delta E^{(2)}_{\rm RS}=-\int_0^{+\infty}du\,\langle(V^{AB}-\langle V^{AB}\rangle_{\phi_0^A\phi_0^B})(\mathbf{X}(0))(V^{AB}-\langle V^{AB}\rangle_{\phi_0^A\phi_0^B})(\mathbf{X}(u))\rangle_{\phi_0^A\phi_0^B}\,. \tag{18}$$

Using the basic definition of stochastic averages in terms of probability densities, one obtains

$$\Delta E^{(2)}_{\rm RS}=-\int_0^{+\infty}du\int\int d\mathbf{x}_0d\mathbf{x}_1p(\mathbf{x}_0)[V^{AB}(\mathbf{x}_0)-\langle V^{AB}\rangle_{\phi_0^A\phi_0^B}]p(\mathbf{x}_0\to\mathbf{x}_1,u)[V^{AB}(\mathbf{x}_1)-\langle V^{AB}\rangle_{\phi_0^A\phi_0^B}]\,. \tag{19}$$

By using Eqs. (14) and performing the time integral, expression (19) is finally found to be

$$\Delta E^{(2)}_{\rm RS}=\sum_{ij}{}'\frac{|\langle\phi_0^A\phi_0^B|V^{AB}|\phi_i^A\phi_j^B\rangle|^2}{E_0^A+E_0^B-(E_i^A+E_j^B)}\,, \tag{20}$$

which is nothing but the usual expression for the second-order term (here, the prime in $\sum'$ means as usual that the term corresponding to $i=0$ and $j=0$ is excluded from the summation). Higher-order perturbational terms would be recovered in the same way.

B. Exchange interaction energy

In this work, we shall limit ourselves to the calculation of the first-order exchange contribution which is by far the leading contribution of the exchange interaction energy. Following standard symmetry-adapted perturbation theories,[7,8] the complete first-order interaction energy is written

$$\Delta E^{(1)}=\frac{\langle\Phi_0^A\Phi_0^B|V^{AB}\underline{A}|\Phi_0^A\Phi_0^B\rangle}{\langle\Phi_0^A\Phi_0^B|\underline{A}|\Phi_0^A\Phi_0^B\rangle}\,, \tag{21}$$

where $\underline{A}$ is the full antisymmetrizer of the interacting supersystem (intra- and intersystem permutations are both considered) and where Φ_0^M $(M=A,B)$ denotes the complete exact wave function of system M (depending on *both* space and spin coordinates). Now, especially because $\underline{A}$ is a nonlocal operator mixing coordinates of each subsystem, to derive an *exact* expression of $\Delta E^{(1)}$ suitable for Monte Carlo simulation is not a trivial task (it involves off-diagonal matrix elements). In the present work, we did not investigate such a possibility. We shall content ourselves with giving a high-quality approximate expression for $\Delta E^{(1)}$. To do that, some approximate trial wave function Ψ_0^M $(M=A,B)$ for representing each monomer will be employed. Note that such an approximation is similar to that used when doing variational quantum Monte Carlo simulation for calculating total energies (see, e.g., Ref. 24). However, it should be emphasized that no variational property holds here for such a perturbational component. A well-known feature of any QMC approach is that no basic limitations on the form of the trial wave function to be used are required. Here, following previous works (e.g., Refs. 12–17), we shall use an explicitly correlated wave function for describing monomers:

$$\Psi_0^M=\underline{A}{}_N^M(\exp U_{\rm LS}^M\exp U_{\rm US}^M X_\alpha^M X_\beta^M),\quad M=A,B \tag{22}$$

where $X_\alpha^M=\prod_i\phi_i^M\alpha$ and $X_\beta^M=\prod_i\phi_i^M\beta$. The symbol $\underline{A}{}_N^M$ stands for the intramonomer antisymmetrizer acting on space and spin coordinates of the N electrons of system M; functions $U_{\rm LS}^M$ and $U_{\rm US}^M$ are some fully symmetric Jastrow-like pair-correlation factors introduced to allow explicitly for electron correlation in the wave function, subscripts LS and US being introduced in order to distinguish between like spin (LS) and unlike spin (UL) electron-electron correlation factors (for more details on wave functions see, e.g., Refs. 14, 15, and 24–26). Finally, $\{\phi_i^M\}$ is some set of one-particle atomic or molecular space orbitals and α and β represent usual spin functions. For the sake of clarity only expressions for two interacting closed-shell systems having the same number of electrons (here denoted N) will be derived. Generalizations to different numbers of electrons $N_A\neq N_B$ and/or to non-closed-shell systems do not involve particular difficulties. Now, since our Monte Carlo approach is defined within a spin-free framework, spin variables in Eq. (21) must be integrated out. Once this has been done, $\Delta E^{(1)}$ may be rewritten in the following form:

$$\Delta E^{(1)}=\frac{\langle\psi_0^A\psi_0^B|V^{AB}\tilde{A}|\psi_0^A\psi_0^B\rangle}{\langle\psi_0^A\psi_0^B|\tilde{A}|\psi_0^A\psi_0^B\rangle}\,, \tag{23}$$

where only space-dependent functions and space integrations are involved. Here, ψ_0^M $(M=A,B)$ denotes the space-dependent part of the trial wave function (22) and $\tilde{A}$ is an effective local operator depending only on space coordinates of monomers A and B [expression (27b) below]. To show this, we take advantage of the following equalities:

$$\underline{A}^2=\underline{A} \tag{24a}$$

and

$$\underline{A}\,\underline{A}{}_N^A\underline{A}{}_N^B=\underline{A}\,, \tag{24b}$$

and then rewrite $\Delta E^{(1)}$ in the form

$$\Delta E^{(1)}=\frac{\langle\underline{A}\Phi^{AB}|V^{AB}|\underline{A}\Phi^{AB}\rangle}{\langle\underline{A}\Phi^{AB}|\underline{A}\Phi^{AB}\rangle}\,, \tag{25a}$$

where

$$\Phi^{AB}=\exp(U_{\rm LS}^A+U_{\rm US}^A)\exp(U_{\rm LS}^B+U_{\rm US}^B)X_\alpha^AX_\alpha^BX_\beta^AX_\beta^B\,. \tag{25b}$$

Now, let us remark that $\Delta E^{(1)}$ as written in the form (25a) is nothing but the average of a spin-independent operator V^{AB} with respect to a properly antisymmetrized wave function for the dimer, $A\Phi^{AB}$. Spin integrations may be easily performed and the resulting expression includes only space antisymmetrizations over α and β electrons separately. More precisely, we have

$$\Delta E^{(1)}=\frac{\langle A_{N_\alpha}A_{N_\beta}\phi^{AB}|V^{AB}|A_{N_\alpha}A_{N_\beta}\phi^{AB}\rangle}{\langle A_{N_\alpha}A_{N_\beta}\phi^{AB}|A_{N_\alpha}A_{N_\beta}\phi^{AB}\rangle}\,, \tag{26a}$$

where ϕ^{AB} (depending only on space coordinates) is given by

$$\phi^{AB}=\exp(U^{A}_{\mathrm{LS}}+U^{A}_{\mathrm{US}})\exp(U^{B}_{\mathrm{LS}}+U^{B}_{\mathrm{US}}) \times\prod_{i=1}^{N_\alpha}\phi_i^A\phi_i^B\prod_{i=1}^{N_\beta}\phi_i^A\phi_i^B \; . \tag{26b}$$

Quantities A_{N_γ} $(\gamma=\alpha,\beta)$ refer here to *space*- antisymmetrizers with respect to the N_γ electrons of spin γ (belonging to *both* A and B monomers). Finally, $\Delta E^{(1)}$ may be written in the form (23) where ψ_0^M $(M=A,B)$ are usual space-dependent trial wave functions for monomers A and B:

$$\psi_0^M=\exp(U^{M}_{\mathrm{LS}}+U^{M}_{\mathrm{US}})A^{M}_{N/2}\prod_{i=1}^{N/2}\phi_i^M A^{M}_{N/2}\prod_{i=1}^{N/2}\phi_i^M, \quad M=A,B \tag{27a}$$

and $\tilde{A}$ the effective function is given by

$$\tilde{A}=\left[\frac{A_{N_\alpha}A_{N_\beta}\phi^{AB}}{\psi_0^A\psi_0^B}\right]^2 . \tag{27b}$$

In Eq. (27a) $A^{M}_{N/2}$ stands for the intramonomer antisymmetrizer acting on space coordinates of the $N/2$ electrons of system M with the same spin. It should be emphasized that in contrast with expression (27a) in which the total Jastrow factor is invariant under the action of $A^{M}_{N/2}A^{M}_{N/2}$ and then can be factorized out, the Jastrow factor involved in ϕ^{AB} [Eq. (26b)] is not invariant under $A_{N_\alpha}A_{N_\beta}$ (because of exchanges between electrons of same spin of systems A and B) and then cannot be factorized out when this operator is applied to ϕ^{AB}.

Now, by using the decomposition

$$\tilde{A}=1-\tilde{A}\,' , \tag{28}$$

the total first-order energy given by Eq. (23) may be expressed as a sum of two contributions corresponding to some approximate Rayleigh-Schrödinger first-order interaction energy and to the approximate first-order exchange interaction energy resulting from $\tilde{A}\,'$ in which we are interested here:

$$\Delta E^{(1)}_{\mathrm{exch}}=\frac{\langle\psi_0^A\psi_0^B|\tilde{A}\,'|\psi_0^A\psi_0^B\rangle\langle\psi_0^A\psi_0^B|V^{AB}|\psi_0^A\psi_0^B\rangle-\langle\psi_0^A\psi_0^B|V^{AB}\tilde{A}\,'|\psi_0^A\psi_0^B\rangle}{1-\langle\psi_0^A\psi_0^B|\tilde{A}\,'|\psi_0^A\psi_0^B\rangle} . \tag{29}$$

By rewriting quantum averages involved in Eq. (29) as one-time stochastic averages with respect to the approximate diffusion process constructed from $\psi_0^A\psi_0^B$ [admitting $(\psi_0^A\psi_0^B)^2$ as stationary density, see details of Sec. II C], $\Delta E^{(1)}_{\mathrm{exch}}$ takes the final following form suitable for Monte Carlo simulation:

$$\Delta E^{(1)}_{\mathrm{exch}}=\frac{\langle\tilde{A}\,'\rangle_{\psi_0^A\psi_0^B}\langle V^{AB}\rangle_{\psi_0^A\psi_0^B}-\langle V^{AB}\tilde{A}\,'\rangle_{\psi_0^A\psi_0^B}}{1-\langle\tilde{A}\,'\rangle_{\psi_0^A\psi_0^B}} . \tag{30}$$

C. The calculation of stochastic averages

In this section the problem of computing stochastic averages introduced in the preceding sections [more precisely, kth-order correlation functions involved in Eq. (12) and one-time averages of Eq. (30)] is addressed. Let us first focus our attention on the computation of kth-order correlation functions as defined in Eq. (13). In principle, the computation of such quantities may be easily performed by merely averaging successive values of the product $V^{AB}(\mathbf{X}(0))\cdots V^{AB}(\mathbf{X}(u_{k-1}))$ along any stochastic trajectory of the underlying diffusion process constructed from the reference unperturbed Hamiltonian H^A+H^B,[17] that is

$$\langle V^{AB}(\mathbf{X}(0))\cdots V^{AB}(\mathbf{X}(u_{k-1}))\rangle_{\phi_0^A\phi_0^B} =\lim_{T\to+\infty}\frac{1}{T}\int_0^T V^{AB}(\mathbf{X}(\tau))\cdots V^{AB}(\mathbf{X}(u_{k-1}+\tau))d\tau , \tag{31}$$

where the infinite length stochastic trajectory $\mathbf{X}(s)$ is generated by using the Langevin equation associated with the underlying diffusion process, namely,

$$d\mathbf{X}(t)=\mathbf{b}(\mathbf{X}(t))dt+d\mathbf{W}(t) , \tag{32}$$

where $\mathbf{W}$ represents the multidimensional Wiener process and $\mathbf{b}$, the drift vector, depends only on the ground-state wave function of the unperturbed Hamiltonian $\phi_0^A\phi_0^B$ as follows:[17]

$$\mathbf{b}=\nabla\phi_0^A\phi_0^B/\phi_0^A\phi_0^B . \tag{33}$$

In practice, such a scheme is impossible to perform since the ground-state wave function of monomer M $(M=A,B)$ is generally unknown. To escape this difficulty we introduce a new diffusion process defined from a *known* trial wave function ψ_0^M $(M=A,B)$ for each monomer. For that purpose, let us construct a new reference Hamiltonian $H^{(0)M}$ admitting ψ_0^M as ground-state wave function. This may be trivially done as follows:

$$H^{(0)M} = -\tfrac{1}{2}\Delta + V^{(0)M} \tag{34a}$$

with

$$V^{(0)M} = \tfrac{1}{2}\Delta\psi_0^M/\psi_0^M + E_0^{(0)M}, \quad M = A,B \tag{34b}$$

where Δ denotes the $3N_M$-dimensional Laplacian operator, N_M being the number of electrons of monomer M, and $E_0^{(0)M}$ some arbitrary reference energy associated with $H^{(0)M}$. It is elementary to verify that

$$H^{(0)M}\psi_0^M = E_0^{(0)M}\psi_0^M, \quad M = A,B \ . \tag{35}$$

The complete Hamiltonian H^M of monomer M ($M = A,B$) may now be written in the form

$$H^M = H^{(0)M} + H^M\psi_0^M/\psi_0^M - E_0^{(0)M}, \quad M = A,B \ . \tag{36}$$

The basic quantity $H^M\psi_0^M/\psi_0^M$ is referred to in the following as the intramonomer local energy E_L^M associated with ψ_0^M:

$$E_L^M = H^M\psi_0^M/\psi_0^M, \quad M = A,B \ . \tag{37}$$

Roughly speaking, the magnitude of this quantity (actually, a function of all particle coordinates) is a measure of how much the unknown exact wave function ϕ_0^M and the used trial wave function ψ_0^M are different. Note that when the trial wave function is chosen to be identical with ϕ_0^M, the intramonomer local energy reduces to a constant (namely, the exact energy E_0^M) and one obtains $H^M = H^{(0)M}$. Now, by constructing the reference diffusion process from the trial wave function $\psi_0^A\psi_0^B$ and by making use of the GFK formula as explained in Ref. 17, the previously defined stochastic averages can be expressed as stochastic averages with respect to this new diffusion process. Let us write the quantity in which we are interested here, namely, the k-time autocorrelation function of the intermolecular interaction operator

$$\langle V^{AB}(\mathbf{X}(0)) \cdots V^{AB}(\mathbf{X}(u_{k-1})) \rangle_{\phi_0^A\phi_0^B}$$

$$= \lim_{t\to+\infty} \frac{\left\langle V^{AB}(\mathbf{X}(0)) \cdots V^{AB}(\mathbf{X}(u_{k-1}))\exp\left[-\int_{-t/2}^{t/2}(E_L^A + E_L^B - E_0^{(0)A} - E_0^{(0)B})(\mathbf{X}(s))ds\right]\right\rangle_{\psi_0^A\psi_0^B}}{\left\langle \exp\left[-\int_{-t/2}^{t/2}(E_L^A + E_L^B - E_0^{(0)A} - E_0^{(0)B})(\mathbf{X}(s))ds\right]\right\rangle_{\psi_0^A\phi_0^B}} \ , \tag{38}$$

with $-t/2 < 0 \le u_1 \le \cdots \le u_{k-1} < t/2$.

The main steps of our approach for practical computations of $\Delta E_{\mathrm{RS}}^{(n)}$ may be then summarized as follows.

(1) Use formula (12) to express $\Delta E_{\mathrm{RS}}^{(n)}$ in terms of a suitable combination of time-correlation functions with respect to the diffusion process constructed from $\phi_0^A\phi_0^B$.

(2) Resort to formula (38) to express stochastic averages defined over the diffusion process built from the generally unknown ground-state wave function $\phi_0^A\phi_0^B$ in terms of stochastic averages defined over the diffusion process built from the chosen trial wave function $\psi_0^A\psi_0^B$.

(3) Calculate stochastic averages involved in the right-hand side of Eq. (38) by resorting to the ergodic formula (31) (merely add the Feynman-Kac exponential weight), the stochastic trajectory being generated using a discretized version of the Langevin equation (32) in which the drift vector is constructed from $\psi_0^A\psi_0^B$. In actual fact, it is appropriate to introduce, instead of a single very long trajectory, a set of shorter trajectories since the corresponding set of time averages may be used for evaluating the variance using standard statistical methods.[27]

As concerns the computation of the first-order exchange interaction energy, it is readily done by taking one-time averages of the integrand involved in formula (30) along stochastic trajectories of the diffusion process constructed from the trial wave function $\psi_0^A\psi_0^B$.

D. Fermi statistics for monomers

Up to now, we did not pay attention to the problem of imposing fermion statistics for each monomer. In the preceding sections, formulas have been derived by implicitly assuming that a fixed-node approach for monomers was employed. Indeed, the trial wave function $\psi_0^A\psi_0^B$ was supposed to obey the correct antisymmetry properties with respect to internal exchange of electrons within each monomer (no intermonomer exchanges of electrons). In practice, such a condition may be fulfilled by antisymmetrizing independently electrons of spin up and down for each monomer (see Ref. 17 and references therein). When computing first-order observables (that is, mere one-time averages of local operators with respect to the trial wave function, the total energy for example), it is well known that such an approach generally introduces a bias in results due to an eventual error in the fixed location of the nodes of the trial wave function. The resulting approximation, known as the fixed-node approximation, has been extensively described in many works.[14,16,17] Here, it is important to realize that we are in somewhat different situation. In contrast with the usual case where only a very good approximation of the unknown ground-state wave function is needed, the computation of the k-time correlation functions implicitly requires the *com-*

plete set of eigenfunctions of the reference Hamiltonian constructed from the trial wave function [Hamiltonian defined by Eq. (34)]. To be more precise, let us write which transition probability density is introduced when a fixed-node framework for each monomer is used:

$$p(\mathbf{x}\rightarrow\mathbf{y},\tau)=\frac{\phi_0^{\mathrm{FN}}(\mathbf{y})}{\phi_0^{\mathrm{FN}}(\mathbf{x})}\sum_i \phi_i^{\mathrm{FN}}(\mathbf{x})\phi_i^{\mathrm{FN}}(\mathbf{y})e^{-\tau(E_i^{\mathrm{FN}}-E_0^{\mathrm{FN}})} \tag{39}$$

where $(\phi_i^{\mathrm{FN}},E_i^{\mathrm{FN}})$ denote the fixed-node eigensolutions of the reference Hamiltonian (34). These eigensolutions are those obtained by imposing *all* eigenfunctions of $H^{(0)M}$ to vanish wherever the ground-state wave function $\phi_0^{\mathrm{FN}}=\psi_0^M$ vanishes. In particular, excited states obtained in that way may be very different from the correct ones which actually have no reason to vanish at the same locations as ϕ_0^{FN}. Accordingly, a *wrong* dynamics for the underlying diffusion process is introduced and an *a priori* uncontrolled error for correlation functions is made. It is quite important to stress that such an error *does* exist, even if *exact* nodes for the trial wave function would be used. As a consequence, it is never *a priori* justified to use a fixed-node framework for computing multiple-time correlation functions.[28] To escape this difficulty, projection methods or some form of them[15,17,29,30] (simple projection method, release-node projection, or nodal relaxation methods) must be used. This type of approach has already been described elsewhere.[17,29] In a few words, the essence of these methods consists in using a bosonic-type nonvanishing wave function as trial wave function and to remove bosonic components by making use of projection functions having correct fermionic antisymmetry properties. Let us denote as f and g two such projection functions; the exact nonbiased autocorrelation function of V^{AB} is then written

$$\langle V^{AB}(\mathbf{X}(0))\cdots V^{AB}(\mathbf{X}(u_{k-1}))\rangle_{\phi_0^A\phi_0^B} = \lim_{t\rightarrow+\infty}\frac{\left\langle f(\mathbf{X}(-t/2))V^{AB}(\mathbf{X}(0))\cdots V^{AB}(\mathbf{X}(u_{k-1}))g(\mathbf{X}(t/2))\exp-\int_{-t/2}^{t/2}(E_L^A+E_L^B--E_0^{(0)A}-E_0^{(0)B})(\mathbf{X}(s))ds\right\rangle_{\psi_0^A\psi_0^B}}{\left\langle f(\mathbf{X}(-t/2))g(\mathbf{X}(t/2))\exp-\int_{-t/2}^{t/2}(E_L^{(A)}+E_L^{(B)}-E_0^{(0)A}-E_0^{(0)B})(\mathbf{X}(s))ds\right\rangle_{\psi_0^A\psi_0^B}} \tag{40}$$

where $\psi_0^A\psi_0^B$ is a bosonic (nonvanishing) trial wave function. From a practical point of view, it is important to recall that Monte Carlo procedures based on projection methods are much less stable than those based on a fixed-node approach. We shall return to this point in our final discussion of the concluding section.

III. NUMERICAL APPLICATIONS

In order to demonstrate the applicability of formulas derived in the preceding sections, some test calculations for the interaction of two helium atoms at small distances have been performed. Results have been systematically compared to those obtained by using standard *ab initio* techniques. In what follows, two different trial wave functions for the helium atom are employed. The first trial wave function is the Hartree-Fock wave function proposed by Clementi and Roetti,[31]

$$\psi_0^M(\mathbf{r}_1,\mathbf{r}_2)=1s_M(r_1)1s_M(r_2),\quad M=A,B \tag{41}$$

where the optimized $1s_M$ orbital (centered at nucleus M) is built as a linear combination of five Slater orbitals, namely,

$$1s_M(r)=\sum_{i=1}^{5} c_i e^{-\lambda_i r},\quad M=A,B\ . \tag{42}$$

Coefficients and exponents may be found in the tables of Clementi and Roetti.[31] Our second trial wave function is a more sophisticated wave function which explicitly contains the interelectron coordinate r_{12} to properly describe the electron-electron interaction at small distances. It is written in the form

$$\psi_0^{(M)}(\mathbf{r}_1,\mathbf{r}_2)=\exp\left[\frac{0.5r_{12}}{1+ar_{12}}\right]\exp\left[-\left[\frac{2+br_1^M}{1+b_1^M}\right]r_1^M\right]\times\exp\left[-\left[\frac{2+br_2^M}{1+br_2^M}\right]r_2^M\right],\quad M=A,B \tag{43}$$

where r_i^M denotes the distance between electron i $(i=1,2)$ and nucleus M $(M=A,B)$. By employing this form, it should be remarked that all two-particle cusp conditions are fulfilled, namely $(1/\psi)(\partial\psi/\partial r_{12})|_{r_{12}=0}=\frac{1}{2}$ (electron-electron cusp condition for unlike spins) and $(1/\psi)(\partial\psi/\partial r_i)|_{r_i=0}=-Z$ (electron-nucleus cusp condition for an infinite mass nucleus of charge number Z). In addition, a Padé form for both correlated and Slater parts of the trial wave function has been chosen. Parameters involved in Eq. (43) have been adjusted in an exact QMC calculation of total energy of the He atom so as to achieve the lowest variance on the estimator of the ground-state energy. Some features of both trial wave functions are presented in Table I. In the following, electrons labeled 1 and 2 (respectively, 3 and 4) are arbitrarily assigned to atom A (respectively atom B). Using this convention, the intermolecular interaction operator V^{AB} is written

$$V^{AB}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4)=\frac{4}{r_{AB}}-\frac{2}{r_{1B}}-\frac{2}{r_{2B}}-\frac{2}{r_{3A}}-\frac{2}{r_{4A}}+\frac{1}{r_{13}}+\frac{1}{r_{14}}+\frac{1}{r_{23}}+\frac{1}{r_{24}}\ . \tag{44}$$

TABLE I. Some features of trial wave functions used.[a]

Properties	Hartree-Fock wave function[b]	Correlated wave function[c]
E_0	$-2.861\,68$	$-2.8983(1)$
Correlation energy[d]	0%	87%
$\langle r_{12} \rangle$	1.362(1)	1.4247(6)

[a] All quantities are given in atomic units. Statistical uncertainties on QMC results are indicated in parentheses.

[b] Equations (41) and (42), see Ref. 31.

[c] Equation (43) with $a=0.3$ and $b=0.1$.

[d] Defined as the difference between the exact nonrelativistic and Hartree-Fock total energies.

TABLE II. Hartree-Fock first-order RS interaction energy.[a]

R[b]	$\Delta E_{\rm RS}^{(1)}$ (QMC)[c]	$\Delta E_{\rm RS}^{(1)}$ (*ab initio*)[d]	$\Delta E_{\rm RS}^{(1)}$ (exact)[e]
1.5	$-0.0805(4)$	-0.0807	-0.0806
1.6	$-0.0686(4)$	-0.0688	-0.0686
1.7	$-0.0575(5)$	-0.0577	-0.0575
1.8	$-0.0477(4)$	-0.0478	-0.0476
1.9	$-0.0390(3)$	-0.0392	-0.0391
2.0	$-0.0318(2)$	-0.0319	-0.0318

[a] All quantities are given in atomic units.

[b] Interatomic separation.

[c] Using Eq. (45a). Statistical uncertainties are indicated in parentheses.

[d] *Ab initio* calculation using ten Gaussian functions for representing 1*s* orbital (42).

[e] Exact analytical evaluation of Eq. (45a).

A. First-order interaction energy

Let us first present some approximate calculations of first-order Rayleigh-Schrödinger and exchange interaction energies. For that we shall set the intramonomer local energies [Eq. (37)] to zero. Such an approximation consists in neglecting internal fluctuations due to the nonexactness of the trial wave function $\psi_0^A\psi_0^B$ used. As already pointed out, this approximation is similar to the approximation made when doing variational quantum Monte Carlo simulations for calculating total energies, except that no variational property holds here for such variational components. Rewriting Eq. (15) by replacing the exact ground-state wave function by the approximate trial wave function, and Eq. (30), the following expressions for $\Delta E_{\rm RS}^{(1)}$ and $\Delta E_{\rm exch}^{(1)}$ are obtained:

$$\Delta E_{\rm RS}^{(1)} = \langle V^{AB} \rangle_{\psi_0^A\psi_0^B} , \tag{45a}$$

$$\Delta E_{\rm exch}^{(1)} = \frac{\langle \tilde{A}' \rangle_{\psi_0^A\psi_0^B} \langle V^{AB} \rangle_{\psi_0^A\psi_0^B} - \langle V^{AB} \tilde{A}' \rangle_{\psi_0^A\psi_0^B}}{1 - \langle \tilde{A}' \rangle_{\psi_0^A\psi_0^B}} . \tag{45b}$$

Expectation values involved in Eqs. (45) may be evaluated as one-time averages with respect to the diffusion process constructed from $\psi_0^A\psi_0^B$. It should be remarked that they are simply six-dimensional integrals and therefore it would be possible here to resort to any efficient integration procedure to calculate them. However, let us emphasize that such procedures would no longer be useful when considering calculation of exact quantities (such as the exact first- and second-order RS interaction energies). A practical difficulty encountered when using a finite time step for integrating the Langevin equation (32) is the occurrence of the well-known short-time approximation.[14,16,17,32] Indeed, the transition probability density used to generate stochastic trajectories (corresponding to a discretized form of the Langevin equation) is only an approximate version of the exact one, for example, in the simple Gaussian approximation,

$$p(\mathbf{x} \to \mathbf{y}, \Delta t) = \frac{1}{(2\pi\Delta t)^{1/2}} \exp\left[-\frac{[\mathbf{y}-\mathbf{x}-\mathbf{b}(\mathbf{x})\Delta t]^2}{2\Delta t} \right] , \tag{46}$$

and therefore calculated stationary averages are subject to a finite time-step error. One possible way of removing this error consists in imposing the detailed balance condition in the Monte Carlo simulation. Doing that, a nonbiased stationary density is constructed. In practice, detailed balancing is ensured by accepting moves from $\mathbf{x}$ to $\mathbf{y}$ with a probability $P_{\rm accept}$ given by[33]

$$P_{\rm accept} = \min\left[1, \frac{(\psi_0^A\psi_0^B)^2(\mathbf{y}) p(\mathbf{y} \to \mathbf{x}, \Delta t)}{(\psi_0^A\psi_0^B)^2(\mathbf{x}) p(\mathbf{x} \to \mathbf{y}, \Delta t)} \right] , \tag{47}$$

where $p(\mathbf{x} \to \mathbf{y}, \Delta t)$ is the short-time Gaussian approximation (46) of the exact unknown transition probability density. This procedure may be viewed as a generalized version of the well-known Metropolis algorithm in which the usual initial random displacement is replaced by a Langevin move generated through Eq. (46).

Tables II and III present Hartree-Fock calculations performed by using form (41) of the trial wave function. Quantum Monte Carlo results for $\Delta E_{\rm RS}^{(1)}$ and $\Delta E_{\rm exch}^{(1)}$ (second column of Tables II and III, respectively) are compared to *ab initio* calculations performed with a large Gaussian basis set (ten Gaussian functions for represent-

TABLE III. Hartree-Fock first-order exchange interaction energy.[a]

R[b]	$\Delta E_{\rm exch}^{(1)}$ (QMC)[c]	$\Delta E_{\rm exch}^{(1)}$ (*ab initio*)[d]
1.5	0.508(11)	0.513
1.6	0.412(6)	0.415
1.7	0.334(8)	0.335
1.8	0.268(4)	0.270
1.9	0.215(4)	0.218
2.0	0.172(5)	0.175

[a] All quantities are given in atomic units.

[b] Interatomic separation.

[c] Using Eq. (45b). Statistical uncertainties are indicated in parentheses.

[d] *Ab initio* calculation using ten Gaussian functions for representing 1*s* orbital (42).

TABLE IV. First-order RS interaction energy using different wave functions.[a]

R[b]	HF wave function[c]	Correlated wave function[d]	Exact wave function[e]
1.5	−0.0805(4)	−0.0818(4)	−0.080(4)
1.6	−0.0686(4)	−0.0693(4)	−0.068(3)
1.7	−0.0575(5)	−0.0578(3)	−0.057(3)
1.8	−0.0477(4)	−0.0476(2)	−0.048(3)
1.9	−0.0390(3)	−0.0388(2)	−0.039(2)
2.0	−0.0318(2)	−0.0314(2)	−0.032(2)

[a] All quantities are given in atomic units. Statistical uncertainties are indicated in parentheses.

[b] Interatomic separation.

[c] Equations (41) and (42), see Ref. 31.

[d] Equation (43) with $a=0.3$ and $b=0.1$.

[e] Equation (48).

TABLE V. First-order exchange interaction energy using different wave functions.[a]

R[b]	HF wave function[c]	Correlated wave function[d]
1.5	0.508(11)	0.566(12)
1.6	0.412(6)	0.450(10)
1.7	0.334(8)	0.358(10)
1.8	0.268(4)	0.284(9)
1.9	0.215(5)	0.226(8)
2.0	0.172(5)	0.178(7)

[a] All quantities are given in atomic units. Statistical uncertainties are indicated in parenthesis.

[b] Interatomic separation.

[c] Equations (41) and (42), see Ref. 31.

[d] Equation (43) with $a=0.3$ and $b=0.1$.

ing 1*s* orbital taken from the van Duijneveldt tables[34]). Gaussian basis-set calculations are presented in the third columns of Tables II and III. In addition, exact results for $\Delta E^{(1)}_{\rm RS}$ obtained by performing space integrals involved in Eq. (45a) are given (last column of Table II). Of course, such exact integrations are possible only because the Hartree-Fock wave function (41) has a very simple structure. Agreement between exact and/or *ab initio* results and QMC results is excellent (within statistical errors). Calculations of first-order RS and exchange interaction energies with the explicitly correlated wave function (43) are displayed in Tables IV and V, respectively. It is seen that using a highly correlated wave function for describing each monomer does not change significantly the Hartree-Fock results obtained for $\Delta E^{(1)}_{\rm RS}$, at least for the small distances studied. Such a conclusion will be confirmed below from exact calculations of $\Delta E^{(1)}_{\rm RS}$. In contrast, $\Delta E^{(1)}_{\rm exch}$ appears to be slightly more sensitive to intra-atomic correlation. For all distances, the effect of correlation seems to be to increase Hartree-Fock results. It should be noted that a similar conclusion has been obtained within the framework of *ab initio* calculations using CI wave functions,[35,36] for larger distances (R ranging from 3.0 to 7.0 a.u.).

Let us now present some exact calculations of the first-order RS interaction energy. The basic expression for practical calculation of $\Delta E^{(1)}_{\rm RS}$ is obtained by rewriting expression (15) in terms of stochastic averages with respect to the diffusion process built from $\psi_0^A\psi_0^B$ [Eq. (38)] and by resorting to the property of ergodicity of the diffusion process [Eq. (31)]. One gets

$$\Delta E^{(1)}_{\rm RS}=\lim_{t\to+\infty}\ \lim_{T\to+\infty}\frac{\dfrac{1}{T}\displaystyle\int_0^T V^{AB}(\mathbf{X}(\tau))\exp\left[-\int_{-t/2+\tau}^{t/2+\tau}(E_L^A+E_L^B-E_0^{(0)A}-E_0^{(0)B})(\mathbf{X}(s))ds\right]d\tau}{\dfrac{1}{T}\displaystyle\int_0^T \exp\left[-\int_{-t/2+\tau}^{t/2+\tau}(E_L^A+E_L^B-E_0^{(0)A}-E_0^{(0)B})(\mathbf{X}(s))ds\right]d\tau}\ , \tag{48}$$

where $\mathbf{X}(s)$ is an arbitrary stochastic trajectory of the diffusion process built from $\psi_0^A\psi_0^B$. In contrast with preceding approximate evaluations of $\Delta E^{(1)}_{\rm RS}$ which were based only on the use of the stationary density, formula (48) also makes use of the dynamical properties of the diffusion process. Accordingly, exact calculations of $\Delta E^{(1)}_{\rm RS}$ [using Eq. (48)] are subject to the short-time error resulting from the nonexact form of the transition probability density used. The usual way of handling this problem is to repeat calculations for different values of the time step Δt and then to extrapolate results to zero time step by using a more or less sophisticated extrapolation procedure (see, e.g., Refs. 14, 17, and 32). Exact calculations of $\Delta E^{(1)}_{\rm RS}$ displayed in the last column of Table IV have been obtained with $\Delta t=0.01$ a.u. For such a time step, the short-time error turned out to be smaller than statistical fluctuations. Accordingly, results of Table IV may be essentially considered as exact within the statistical noise. It is seen by comparing the second and last columns of Table IV that for distances ranging from $R=1.5$ to 2.0 a.u., no differences appear between Hartree-Fock and exact results (up to statistical fluctuations). It is therefore concluded that intra-atomic correlation contribution to $\Delta E^{(1)}_{\rm RS}$ is certainly negligible at these small distances.

B. Second-order Rayleigh-Schrödinger interaction energy

Calculation of the second-order RS interaction energy is based on Eq. (18):

$$\Delta E^{(2)}_{\rm RS}=-\int_0^{+\infty}C^c(u)du\ , \tag{49}$$

where $C^c(u)$ is the connected two-time autocorrelation function of V^{AB} with respect to the diffusion process constructed from $\phi_0^A\phi_0^B$, namely,

$$C^c(u)=\langle \overline{V^{AB}}(\mathbf{X}(0))\overline{V^{AB}}(\mathbf{X}(u))\rangle_{\phi_0^A\phi_0^B}\ , \tag{50}$$

where $\overline{V^{AB}} \equiv V^{AB}-\langle V^{AB}\rangle_{\phi_0^A\phi_0^B}$. By expressing the stochastic average in terms of stochastic averages with respect to the diffusion process constructed from $\psi_0^A\psi_0^B$ [Eq. (38)] and by making use of the ergodic property (31), the following expression suitable for computational purposes is obtained:

$$C^c(u)=\lim_{t\to+\infty}\lim_{T\to+\infty}\frac{\frac{1}{T}\int_0^T \overline{V^{AB}}(\mathbf{X}(\tau))\overline{V^{AB}}(\mathbf{X}(\tau+u))\exp\left[-\int_{-t/2+\tau}^{t/2+\tau}(E_L^A+E_L^B-E_0^{(0)A}-E_0^{(0)B})(\mathbf{X}(s))ds\right]d\tau}{\frac{1}{T}\int_0^T \exp\left[-\int_{-t/2+\tau}^{t/2+\tau}(E_L^A+E_L^B-E_0^{(0)A}-E_0^{(0)B})(\mathbf{X}(s))ds\right]d\tau}\ , \tag{51}$$

and the numerical evaluation of this expression is performed as usual. On the other hand, by using the basic definition of stochastic averages in terms of probability densities [Eq. (13)] and by resorting to expressions (14) for these densities, the following form for $C^c(u)$ is obtained:

$$C^c(u)=\sum_{i,j}|\langle \phi_0^A\phi_0^B|(V^{AB}-\langle V^{AB}\rangle)|\phi_i^A\phi_j^B\rangle|^2 \times e^{-u(E_i^A+E_j^B-E_0^A-E_0^B)}\ . \tag{52}$$

Accordingly, it is seen that $C^c(u)$ is written as an infinite sum of real exponentials with true excitation energies of the noninteracting systems as exponents, and squared centered transition moments of V^{AB} as amplitudes. Due to this form, it is natural to fit the calculated function C^c by a function expressed as a sum of a finite number of real exponentials, namely,

$$C^c(u)=\sum_{i=1}^{N}c_i e^{-\lambda_i u}\ . \tag{53}$$

At the distance studied ($R=2$ a.u.), this fit was performed from a set of 50 calculated values of C^c uniformly distributed in the time interval (0,2). The method used to perform the fit is a recently proposed method based on a Padé analysis of the Laplace transform (or eventually other integral transforms) of the function to analyze. This method is presented in detail elsewhere (see Ref. 37). We found out that a three-real-exponentials description was sufficient to correctly describe our data. The following amplitudes and exponents have been obtained:

$$c_1=0.033\,77,\quad \lambda_1=1.7539\ ,$$

$$c_2=0.080\,87,\quad \lambda_2=5.4948\ ,$$

$$c_3=0.063\,04,\quad \lambda_3=19.025\ .$$

Having an analytical expression of the autocorrelation function, $\Delta E_{\mathrm{RS}}^{(2)}$ is readily obtained from Eqs. (49) and (53); one obtains

$$\Delta E_{\mathrm{RS}}^{(2)}=-\sum_{i=1}^{N}\frac{c_i}{\lambda_i}\ . \tag{54}$$

The autocorrelation function obtained for the intraatomic distance $R=2$ a.u. is presented in Fig. 1. Note that the statistical fluctuations for all data are rather small, except at the initial time value $u=0$. This feature is explained as follows. From expression (52) of $C^c(u)$, it is seen that $C^c(0)$ is nothing but the average of the squared centered potential $C^c(0)=\langle \phi_0^A\phi_0^B|(\overline{V^{AB}})^2|\phi_0^A\phi_0^B\rangle$. When a particle of A (respectively, B) is close to a particle of B (respectively, A), this latter quantity is essentially given by $\langle 1/r^2\rangle$, where r is the interparticle distance. This average has a well-defined value but an infinite variance. Special techniques for handling this difficulty could be used (such as the introduction of a cutoff as made in Ref. 38). However, it should be noted that this difficulty occurs only for $u=0$. Accordingly, in order not to bias our analysis, we decided to remove the initial point from the set of data used to perform the fit. However, it should be noted that the initial value was correctly recovered by the fit function (53). The result obtained for $\Delta E_{\mathrm{RS}}^{(2)}$ at $R=2$ is presented in Table VI and is compared with an *ab initio* SCF perturbational calculation of the same quantity (method presented

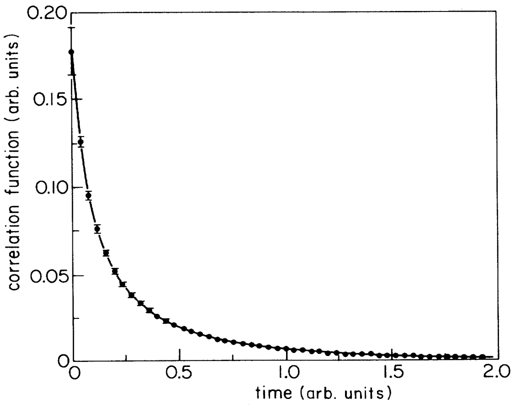

FIG. 1. The autocorrelation function of the intermolecular potential computed by Monte Carlo simulation vs the time u [Eq. (50)].

TABLE VI. Second-order RS interaction energy.[a]

R[b]	$\Delta E_{\mathrm{RS}}^{(2)}$ (QMC)[c]	$\Delta E_{\mathrm{RS}}^{(2)}$ (SCF)[d]
2	$-0.0375(11)$	-0.030

[a] All quantities are given in atomic units.

[b] Interatomic separation.

[c] Equations (49) and (51). Statistical uncertainites are indicated in parentheses.

[d] *Ab initio* SCF calculation, see text.

in Refs. 11 and 22). The numerical calculation was carried out by using an $(8s,3p,2d)$ Gaussian basis set. The major conclusion resulting from comparison between exact and Hartree-Fock calculations of $\Delta E_{\mathrm{RS}}^{(2)}$ is that intraatomic correlation contribution to $\Delta E_{\mathrm{RS}}^{(2)}$ is important. At the distance studied ($R=2$ a.u.), it accounts for more than 20% of the exact value. It is therefore essential to take account of such a contribution in any accurate calculation of interaction energies.

IV. DISCUSSION

Let us summarize what has been done in the present work. First, a very compact expression for the nth-order Rayleigh-Schrödinger perturbational energy has been derived within the framework of diffusion processes [Eq. (12)]. This formula expresses the nth-order component of the energy as an $(n-1)$-time integral of a connected correlation function of the perturbing operator. It should be stressed that it is a very general formula which can be used in any problem for which a perturbational approach is desired. However, in the present work we focused our attention on a specific application: the calculation of perturbational components in intermolecular interactions. In order to be able to compute the main part of the exchange interaction energy (a contribution resulting from the change of antisymmetry properties between the monomer and the interacting dimer), a high-quality approximate expression for this quantity (defined beyond the commonly used Hartree-Fock approximation) has been derived. In order to demonstrate the feasibility of our new approach we have carried out some test calculations for the interaction of two helium atoms at small distances. For this small system comparisons with more standard calculations using *ab initio* techniques are very satisfactory. Potential advantages of this new approach with respect to commonly employed *ab initio* methods may be summarized as follows.

(1) No basis-set expansions are used. Accordingly, well-known difficulties associated with basis-set calculations are avoided.

(2) Infinite summations appearing in the usual Bloch-Brücker formulation of perturbational components are not performed. Consequently, good representations of the infinite (continuous) set of excited wave functions and calculations of transition matrix elements of the perturbing operator between all intermediate states are not needed. Actually, the resolvent of the unperturbed Hamiltonian (responsible for the occurrence of infinite sets of intermediate wave functions in the usual formalism) is implicitly taken into account through the transition probability density [see Eq. (14b)] of the underlying diffusion process. In practice, the transition probability density may be easily simulated [from Langevin equation (32)] only by using an approximate expression of the ground-state wave function of the unperturbed Hamiltonian.

(3) Quantities difficult to evaluate within *ab initio* frameworks, such as intramonomer correlation contributions or high-order perturbational terms (third order, for example) are in principle easy to evaluate.

However, a number of potential difficulties may also exist.

(1) When applying formula (12) to systems involving fermions, it has been seen that the fixed-node procedure must be avoided, whatever the quality of the nodes of the trial wave function used. By making use of a projection approach, this problem may be in principle solved. However, it is known that such approaches are in general quite unstable numerically due to the sign problem. Only realistic calculations on bigger systems will permit one to give a precise answer about the feasibility of such a proposal. However, let us once more emphasize that this problem disappears when bosonic-type systems (or more generally when no change of symmetry between the unperturbed and total Hamiltonian occurs) are treated.

(2) It is not clear at this stage what the dependency is of statistical fluctuations on the order of the perturbational component considered. Here also the importance of such a difficulty could be very dependent on the system treated and on the quality of the trial wave function used.

The next step of this work will be to make calculations for interaction of bigger systems [such as $(\mathrm{LiH})_2$, Be_2, or $(\mathrm{H_2O})_2$, for example]. Expected practical limitations of the method result essentially form present limitations of QMC methods for treating monomers. Indeed, it is known that a serious increase of statistical fluctuations with the number of electrons treated is observed for atomic and molecular systems (see, e.g., discussion in Ref. 39). In the present method, this means that an increase of statistical fluctuations on intramonomer local energies must be expected when treating systems of increasing size. In practice, calculating interaction of systems having up to ten electrons should be considered as a reasonable limit at the present time. However, it is clear that any future improvement in the efficiency of quantum Monte Carlo methods for treating electronic structure would directly improve the practical possibilities of the present method.

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