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Computing forces with quantum Monte Carlo

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We present a simple and stable quantum Monte Carlo approach for computing forces between atoms in a molecule. In this approach we propose to use as Monte Carlo estimator of the force the standard Hellmann–Feynman expression (local force expressed as the derivative of the total potential energy with respect to the internuclear coordinates). Invoking a recently introduced zero-variance principle it is shown how the infinite variance associated with the Hellmann–Feynman estimator can be made finite by introducing some suitably renormalized expression for the force. Practical calculations for the molecules H_2 , Li_2 , LiH , and C_2 illustrate the efficiency of the method. © 2000 American Institute of Physics. [S0021-9606(00)31330-7]

I. INTRODUCTION

Over the recent years quantum Monte Carlo (QMC) methods have become more and more successful in computing ground-state properties of atomic and molecular systems (see, e.g., Refs. 1–3). However, the vast majority of applications has been limited to the calculation of the ground-state total energy. Although this is clearly a most important quantity, other properties (dipole moments, forces, polarizabilities, etc.) are also of primary interest. In theory, there is no difficulty for computing such quantities within a QMC framework. However, in practice, the convergence of the Monte Carlo calculations is much more slower and, therefore, much more computationally demanding than the case of the energy. Thus, only a limited number of calculations of properties can be found in the literature. The fundamental point allowing very efficient and accurate calculations of the energy (compared to other properties) is the existence of a so-called “zero-variance” property for this special observable. To understand this point, let us first briefly recall how the energy is computed with QMC. In short, the energy is expressed as a simple average over some suitably chosen distribution

$$E_0 = \langle E_L \rangle, \quad (1)$$

where the brackets $\langle \dots \rangle$ denote the statistical average and E_L is a local function defined as

$$E_L(x) = H\psi_T / \psi_T, \quad (2)$$

and usually referred to as the local energy. Here, H denotes the Hamiltonian under consideration and ψ_T a trial wave function. The distribution for the average defines the type of quantum Monte Carlo calculation performed. In variational Monte Carlo (VMC) schemes, the distribution is constructed

to be proportional to ψ_T^2 and Eq. (1) is nothing but an estimate of the standard quantum-mechanical variational energy associated with the trial wave function. In diffusion Monte Carlo (DMC) schemes, the stochastic rules employed to generate configurations are essentially similar to those of VMC, except that a new step—a branching process—is added to pass from the VMC distribution to the so-called “mixed” distribution given by $\phi_0\psi_T$, where ϕ_0 denotes the exact ground-state wave function. In that case, Eq. (1) realizes an exact estimate of the energy. From expression (1) it is clear that the statistical error on the energy is directly related to the magnitude of the fluctuations of the local energy. In turn, such fluctuations depend on the “quality” of the trial wave function. The closer the trial wave function is to the exact one, the smaller these fluctuations are. In the limit of an exact trial wave function the local energy becomes strictly constant and the statistical error vanishes completely. This is the result which is known as the “zero-variance” property. In practice, this property is of great importance: very accurate calculations can be performed with a reasonable amount of computer time only if accurate enough trial wave functions are at our disposal. When no particular trial wave function is used [$\psi_T=1$ in the preceding formula, (1)] the local energy reduces to the total potential energy. In this case the statistical error on the energy is very important since the bare potential fluctuates enormously. Introducing a trial wave function can be viewed as defining a “renormalizing procedure” applied to the bare potential in order to reduce its fluctuations. Of course, such a process is allowed only because both the bare potential (the total potential energy) and the renormalized one (the local energy) have the same average.

Very recently, we have generalized this zero-variance property to any observable defined on the configuration space.⁴ Denoting O some rather arbitrary observable we have shown that it is possible to construct *in a systematic way* a renormalized observable $\tilde{O}$ verifying:

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$$\langle \tilde{O} \rangle = \langle O \rangle \quad (3)$$

and

$$\sigma^2(\tilde{O}) < \sigma^2(O) \quad (4)$$

where $\sigma^2(A)$ represents the variance of operator A

$$\sigma^2(A) \equiv \langle (A - \langle A \rangle)^2 \rangle. \quad (5)$$

When using $\tilde{O}$ instead of O as estimator of the observable, the convergence of the calculations can be improved since the statistical error on a finite Monte Carlo sample is directly proportional to the variance of the quantity to be averaged. As we shall see later, the renormalized observable depends on two auxiliary quantities, $\tilde{H}$ and $\tilde{\psi}$ which play a role similar to that played by H and ψ_T in the renormalized version of the bare potential, Eq. (2). Some preliminary classical and quantum Monte Carlo calculations on simple systems have shown that very important reduction of the computational effort can be achieved by using this general zero-variance principle.⁴ In the present paper we apply this idea to the problem of calculating forces between atoms in molecules. The calculation of forces is known to be a very difficult task for QMC methods.³ Some calculations limited to very small molecules (typically H_2 and LiH) have been reported.^{5,6} However, their extension to bigger systems is essentially not realistic. Note that very recently Filippi and Umrigar have presented a new method for computing forces.⁷ Their method is based on a special transformation coordinates and a correlated sampling approach. Here, we follow a quite different route. It is shown that forces can be computed in a very natural way by using the standard Hellmann–Feynman (HF) theorem. More precisely, the force is computed as the average of the local force, a quantity defined as the gradient of the potential energy with respect to the internuclear coordinates. In previous works (see, e.g., discussion in Ref. 3) such a possibility was excluded because of the uncontrolled statistical fluctuations associated with the bare force (infinite variance). Here, it will be shown that with the help of the generalized zero-variance principle, the pathological part of the force responsible for the infinite variance can be removed exactly in a simple and general way. Once this is achieved, it is possible to perform stable calculations of the forces by using standard variational and diffusion Monte Carlo methods. The first applications presented here illustrate the accuracy and efficiency of the method.

II. METHOD

To compute forces between atoms in a molecule we take advantage of the Hellmann–Feynman theorem. According to this theorem the average force defined as

$$\langle F_q \rangle \equiv -\nabla_q E_0(\mathbf{q}) \quad (6)$$

is given by the expectation value of the gradient of the potential (local force)

$$\langle F_q \rangle = \frac{\int d\mathbf{x} \phi_0^2(\mathbf{x}, \mathbf{q}) F_q(\mathbf{x}, \mathbf{q})}{\int d\mathbf{x} \phi_0^2(\mathbf{x}, \mathbf{q})}, \quad (7)$$

with

$$F_q(\mathbf{x}) \equiv -\nabla_q V(\mathbf{x}, \mathbf{q}). \quad (8)$$

In these formulas $\mathbf{q}$ represents the set of the $3N_{\text{nuc}}$ nuclear coordinates (N_{nuc} being the number of nuclei), V the total potential energy operator of the problem, $E_0(\mathbf{q})$ the total ground-state energy for a given molecular geometry, and ϕ_0 the corresponding ground-state wave function.

As remarked by a number of authors, one of the major difficulties in computing forces by QMC via formulas (7) and (8) is the presence of uncontrolled statistical fluctuations (see, e.g., Ref. 3). Indeed, the variance of the Hellmann–Feynman estimator of the force is infinite. This is a simple consequence of the fact that at short electron-nucleus distances r , the local force behaves as $F \sim 1/r^2$, so that $\langle F^2 \rangle = \infty$. Various solutions to this problem have been proposed. A common idea consists in introducing some sort of cutoff when the electrons approach the nuclei.⁶ However, by doing this a systematic error is introduced. In addition, to control this error is a very tricky problem since any extrapolation procedure (cutoff going to zero) is ill-defined.

To escape from this difficulty we propose to replace the standard expression of the local force $F_q(\mathbf{x})$ by a ‘renormalized’ expression, $\tilde{F}_q(\mathbf{x})$, having the same average but smaller fluctuations. It should be emphasized that the decrease in fluctuations will be dramatic here since, in contrast with the bare expression, the renormalized version will have now *finite* fluctuations. Let us give the explicit expressions for the renormalized quantities. We shall consider two different cases. The first case corresponds to variational Monte Carlo (VMC) calculations. The distribution of walkers in configuration space, $\pi(\mathbf{x})$ is given by

$$\pi_{\text{VMC}}(\mathbf{x}) \sim \psi_T^2(\mathbf{x}). \quad (9)$$

The second case corresponds to calculations within the diffusion Monte Carlo (DMC) approach. In that case the distribution employed is the so-called mixed distribution given by

$$\pi_{\text{DMC}}(\mathbf{x}) \sim \psi_T(\mathbf{x}) \phi_0(\mathbf{x}). \quad (10)$$

In the variational case and for a particular component q we consider the following renormalized expression:

$$\tilde{F}_q(\mathbf{x}) = F_q(\mathbf{x}) + \left[\frac{\tilde{H}\tilde{\psi}}{\tilde{\psi}} - \frac{\tilde{H}\psi_T}{\psi_T} \right] \frac{\tilde{\psi}}{\psi_T}, \quad (11)$$

where $\tilde{H}$ is some rather arbitrary auxiliary Hermitian operator and $\tilde{\psi}$ an arbitrary auxiliary function (supposed to be square-integrable). Note that the choice of the auxiliary quantities depends on the particular component q considered. Because $\tilde{H}$ is Hermitian we have $\langle \psi_T | \tilde{H} | \tilde{\psi} \rangle = \langle \tilde{\psi} | \tilde{H} | \psi_T \rangle$ and it is an elementary exercise to check that the average value of the bare and renormalized expressions over the VMC distribution (9) are identical

$$\langle \tilde{F}_q \rangle = \langle F_q \rangle. \quad (12)$$

Note that this result requires that both the trial function and its first derivatives are continuous over the whole configuration space. These conditions are fulfilled by the trial wave functions used in VMC schemes. Now, regarding the variances we have the following expression:

$$\sigma^2(\tilde{F}_q) \equiv \langle (\tilde{F}_q - \langle \tilde{F}_q \rangle)^2 \rangle = \sigma^2(F_q) + 2\langle F_q \Delta H w \rangle + \langle \Delta H^2 w^2 \rangle, \quad (13)$$

where, for the sake of simplicity, we have used the following notations:

$$\Delta H \equiv \left[\frac{\tilde{H}\tilde{\psi}}{\tilde{\psi}} - \frac{\tilde{H}\psi_T}{\psi_T} \right] \quad (14)$$

and

$$w \equiv \frac{\tilde{\psi}}{\psi_T} \quad (15)$$

Now, let us show that, from an arbitrary auxiliary function $\tilde{\psi}$, we can always construct a renormalized expression having a smaller variance. For that we consider the multiplicative constant of $\tilde{\psi}$, denoted here α , as a variational parameter. Minimizing the variance $\sigma^2(\tilde{F}, \alpha)$ with respect to α we get the following optimal value:

$$\alpha_{\text{opt}} = -\langle F_q \Delta H w \rangle / \langle \Delta H^2 w^2 \rangle \quad (16)$$

and, therefore,

$$\sigma^2(\tilde{F}, \alpha_{\text{opt}}) = \sigma^2(F) - \langle F \Delta H w \rangle^2 / \langle \Delta H^2 w^2 \rangle, \quad (17)$$

In general, the quantity $\langle F \Delta H w \rangle$ will not be equal to zero. As a consequence, equation (17) shows that, whatever the quality of the auxiliary function $\tilde{\psi}$ chosen, the use of the optimized prefactor (16) always leads to a decrease of the statistical fluctuations. Clearly, this gain in variance can be small but let us emphasize that it is a systematic gain. Of course, this is only by choosing appropriate auxiliary functions that large gains can be expected.

In the case of a diffusion Monte Carlo scheme the stationary distribution, Eq. (10), is no longer known analytically since it involves the unknown exact wave function which is stochastically sampled, and our general procedure which supposes the knowledge of the distribution cannot be readily applied to. However, in the particular case of the mixed distribution, a renormalized expression can still be defined.⁴ A natural choice is

$$\tilde{F}_q(\mathbf{x}) = F_q(\mathbf{x}) + \left[\frac{H\tilde{\psi}}{\tilde{\psi}} - E_0 \right] \frac{\tilde{\psi}}{\psi_T}, \quad (18)$$

where E_0 is some unbiased estimator of the exact ground-state energy. In this case also, it is quite easy to verify that the averages of the bare and renormalized estimators over the mixed distribution (10) are equal

$$\langle \tilde{F}_q \rangle = \langle F_q \rangle. \quad (19)$$

It should be emphasized that this result is valid only if the wave function ϕ_0 and its first derivatives are continuous everywhere. This is true for the exact solution of the problem. However, in general it will not be the case for the approximate solution obtained with a fixed-node diffusion Monte Carlo calculation. We shall return to this important point in the next section.

To make the connection with the variational case, remark that the latter expression can be rewritten as

$$\tilde{F}_q(\mathbf{x}) = \tilde{F}_q^{\text{VMC}}(\mathbf{x}) + [E_L - E_0]w, \quad (20)$$

where E_L represents the local energy function associated with the trial wave function ψ_T , Eq. (2), and $\tilde{F}_q^{\text{VMC}}(\mathbf{x})$ is the variational Monte Carlo expression of the renormalized force, Eq. (11). Note that the correction between the VMC and DMC estimators in formula (20) consists of a product of two quantities, namely $E_L - E_0$ and w . The quantity $E_L - E_0$ has a vanishing average and its statistical fluctuations are in general much smaller than those of w . Accordingly, it is quite efficient to introduce a centered version of the variable w . Indeed, it can be easily shown that the fluctuations of the product are in this way greatly reduced. Our final version of the DMC force used in our calculations is therefore

$$\tilde{F}_q(\mathbf{x}) = \tilde{F}_q^{\text{VMC}}(\mathbf{x}) + [E_L - \langle E_L \rangle][w - \langle w \rangle]. \quad (21)$$

Finally, it should be noted that the force calculated according to the preceding formulas are not exact since the DMC distribution is the mixed distribution instead of the exact one. This point is discussed later.

Now, in order to illustrate the method we consider the case of a diatomic molecule AB consisting of an atom A (nucleus charge Z_A) located at $(R, 0, 0)$ and an atom B (nucleus charge Z_B) located at the origin. Note that the general case corresponding to an arbitrary number of nuclei does not involve particular difficulties. It can be obtained by straightforward generalization of what is presented below. For a diatomic molecule we have the following expression of the force: $\mathbf{F} = (F, 0, 0)$, with

$$F(\mathbf{x}) = \frac{Z_A Z_B}{R^2} - Z_A \sum_{i=1}^{N_{\text{elect}}} \frac{(x_i - R)}{|\mathbf{r}_i - \mathbf{R}|^3}, \quad (22)$$

where N_{elect} is the total number of electrons and $\mathbf{r}_i$ represents the position of electron i . The second term on the right-hand side of Eq. (22) is responsible for the infinite variance contribution. Let us now show that this contribution can be exactly removed. In what follows we shall write the auxiliary function as

$$\tilde{\psi}(\mathbf{x}) = Q \psi_T, \quad (23)$$

where Q is some arbitrary function. Using this form it can be verified that the simplest form for Q canceling the pathological part of the bare force is the following:

$$Q = Z_A \sum_{i=1}^{N_{\text{elect}}} \frac{(x_i - R)}{|\mathbf{r}_i - \mathbf{R}|^3}. \quad (24)$$

Finally, we get for the renormalized force in the variational case [Eq. (11)]:

$$\tilde{F}(\mathbf{x}) = \frac{Z_A Z_B}{R^2} - \nabla Q \cdot \nabla \psi_T / \psi_T, \quad (25)$$

with a similar expression in the DMC case [see Eqs. (18) and (20)]. It can be checked that this latter expression has now a finite variance.

As already mentioned the QMC calculations presented here are done at two different levels of approximation. First, we present variational Monte Carlo calculations of the force. The average of the force is then obtained as

$$\langle \mathcal{F} \rangle_{\text{VMC}} = \frac{\int d\mathbf{x} \psi_T^2(\mathbf{x}) \mathcal{F}(\mathbf{x})}{\int d\mathbf{x} \psi_T^2(\mathbf{x})}, \quad (26)$$

where ψ_T is the trial wave function, and $\mathcal{F}$ represents here either the bare force, $\mathcal{F}=F$, Eq. (7), or the renormalized one, $\mathcal{F}=\tilde{F}$, Eq. (11). We also consider averages over the mixed distribution as obtained in a diffusion Monte Carlo scheme:

$$\langle \mathcal{F} \rangle_{\text{mixed}} = \frac{\int d\mathbf{x} \phi_0(\mathbf{x}) \psi_T(\mathbf{x}) \mathcal{F}(\mathbf{x})}{\int d\mathbf{x} \phi_0(\mathbf{x}) \psi_T(\mathbf{x})}, \quad (27)$$

where ϕ_0 is the exact wave function. Here, $\mathcal{F}$ is given either by Eq. (7) or by Eq. (18). In order to get a more accurate approximation of the unbiased exact force, corresponding to the density ϕ_0^2 , we shall also have recourse to the following ‘‘hybrid’’ formula:

$$\langle \mathcal{F} \rangle \approx 2\langle \mathcal{F} \rangle_{\text{mixed}} - \langle \mathcal{F} \rangle_{\text{VMC}}. \quad (28)$$

This formula is constructed so that the first-order contributions in the difference $\phi_0(\mathbf{x}) - \psi_T(\mathbf{x})$ for the quantities $\langle \mathcal{F} \rangle_{\text{mixed}}$ and $\langle \mathcal{F} \rangle_{\text{VMC}}$ compensate exactly (see, e.g., Ref. 3). From a practical point of view, expression (28) is particularly interesting. Both quantities involved can be straightforwardly computed in routine DMC and VMC calculations. Note that in principle it is also possible to get an exact estimate of $\langle \mathcal{F} \rangle$ but it requires some more elaborate scheme involving some kind of forward-walking.^{3,8} We shall not consider here such calculations, but let them for future publication.

III. A FEW REMARKS REGARDING THE PRACTICAL IMPLEMENTATION

As seen in the preceding section we use both VMC and DMC approaches in our actual computations. Regarding variational Monte Carlo no particular difficulties arise. In practice, the main weakness of the VMC approach lies in the fact that the average force obtained according to Eq. (26) is quite dependent on the trial wave function used. This is particularly true since ψ_T is optimized in order to improve the total electronic energy but not its derivatives with respect to the internuclear coordinates. However, as illustrated by the practical calculations presented below (see Table II), combining DMC and VMC calculations of the force according to the hybrid formula, Eq. (28), seems to represent a simple but accurate solution to this problem.

Let us now consider the specific difficulties associated with DMC calculations. In order to avoid the famous ‘‘sign problem’’ for fermions⁹ all calculations presented here are done using the stable but approximate fixed-node (FN) method. In this approach the Schrödinger equation is solved *separately* in each nodal domain (or ‘‘pocket’’) where ψ_T has a definite sign. When the trial wave function satisfies the tiling property^{10,11} all nodal domains are equivalent and related by the permutational symmetry. When this is not the case, energies associated with each nodal domain can be dif-

ferent and the FN solution corresponds to the eigensolution defined in the domain corresponding to the lowest energy. Without entering more into the details of the fixed-node approach (for that, see, e.g., Refs. 12 and 3) we just remark that a most important point with FN calculations is that the sampled fixed-node solution displays in general some discontinuous derivatives at the nodes (zeroes of ψ_T). Because of that, some mathematical care is necessary when integrating quantities (energy, derivatives of the energy, etc.) that are defined over the entire configuration space; in other words, the various nodal domains must be properly connected. A first example illustrating this remark is the problem of the validity of the Hellmann–Feynman (HF) theorem in fixed node QMC calculations, a point which has raised some discussion very recently.^{13–15} Due to the presence of the discontinuity at nodes the HF theorem is not true in general in that case. It can be shown that the theorem is valid only when the derivative of the total fixed-node energy with respect to the coordinate q is done without changing the nodes of the trial wave function when varying q .¹⁴ However, since in the present work no finite difference expressions for the fixed-node energy are used, this point is in fact of no practical importance. Let us just mention that the average force obtained in our fixed-node DMC calculations corresponds to the Hellmann–Feynman force we would obtain by performing such finite differences fixed-node calculations with the nodes kept fixed.

A second example of difficulties, which is here of fundamental importance, concerns the validity of the equality between the bare and renormalized expressions, Eq. (19). To clarify this point let us have a closer look at the condition we would like to fulfill. Using expression (18) the condition can be written as

$$\langle \tilde{F} \rangle - \langle F \rangle = \langle \phi_0^{\text{FN}} | \frac{(H - E_0^{\text{FN}}) \tilde{\psi}}{\psi_T} | \psi_T \rangle = 0, \quad (29)$$

where E_0^{FN} is the fixed-node energy. Denoting Ω a nodal domain of the fixed-node solution we can write

$$\langle \tilde{F} \rangle - \langle F \rangle = \int_{\Omega} d\mathbf{x} \phi_0^{\text{FN}} (H - E_0^{\text{FN}}) \tilde{\psi}. \quad (30)$$

Now, decomposing H under its kinetic and potential parts and invoking Green’s formula this quantity can be rewritten as an integral over the nodal hypersurface

$$\langle \tilde{F} \rangle - \langle F \rangle = -\frac{1}{2} \int_{\partial\Omega} (\phi_0^{\text{FN}} \tilde{\nabla} \tilde{\psi} - \tilde{\psi} \tilde{\nabla} \phi_0^{\text{FN}}) dS. \quad (31)$$

From this expression it is seen that a nonzero bias may indeed appear in a fixed-node calculation of the renormalized force. Clearly, a simple way of removing this bias is to use auxiliary functions $\tilde{\psi}$ having the same nodes as ψ_T and, therefore, the same nodes as ϕ_0^{FN} . The actual simulations presented below fulfill this condition.

Finally, let us end this section with some words about the nature of the errors introduced. Since the exact nodes are not known there is some difference between the exact and fixed-node functions

TABLE I. Total energies in variational Monte Carlo [$E_0(\text{VMC})$] and diffusion Monte Carlo [$E_0(\text{DMC})$] with the trial wave functions employed here. $E_c^{\text{VMC}}(\%)$ and $E_c^{\text{DMC}}(\%)$ are the percentages of correlation energy recovered in VMC and DMC. $\sigma^2(\text{VMC})$ is the variance of the local energy in VMC. Bond lengths are in Bohrs and energies in Hartree atomic units. Statistical uncertainties on the last digit are indicated in parentheses.

Molecule	$E_0(\text{HF})$	E_0	$E_0(\text{VMC})$	$\sigma^2(\text{VMC})$	$E_c^{\text{VMC}}(\%)$	$E_0(\text{DMC})$	$E_c^{\text{DMC}}(\%)$
H_2 ($R=1.4$)	-1.133 63	-1.174 475	-1.172 80(7.7)	0.0050(1)	95.8(2)	-1.174 45(6.7)	99.9(2)
LiH ($R=3.015$)	-7.987	-8.070 21	-8.055 54(26)	0.070(2)	82.37(3)	-8.067 57(70)	96.8(8)
Li_2 ($R=5.051$)	-14.871 52	-14.9954	-14.9429(46)	0.196(1.2)	57.6(4)	-14.9910(3.7)	96.4(3)
C_2 ($R=2.3481$)	-75.4062	-75.923(5)	-75.581(2.9)	1.088(6)	33.8(6)	-75.854(5.2)	87(1)

^aFrom experimental data analysis.

$$\delta\phi \equiv \phi_0^{\text{FN}} - \phi_0, \quad (32)$$

where ϕ_0 and ϕ_0^{FN} are the normalized exact and fixed-node solutions. The fixed-node bias can be evaluated as

$$\langle \phi_0^{\text{FN}} | \mathcal{F} | \phi_0^{\text{FN}} \rangle - \langle \phi_0 | \mathcal{F} | \phi_0 \rangle = 2 \langle \delta\phi | \mathcal{F} | \phi_0 \rangle + O(\delta\phi^2). \quad (33)$$

In other words, the fixed-node bias for $\mathcal{F}$ is of order 1 in $\delta\phi$ in contrast with the FN bias on the energy which is of order 2 in the same quantity. Finally, it is easy to see that the bias on the mixed average, Eq. (27), is of order $O(\psi_T - \phi_0^{\text{FN}}) + O(\delta\phi)$ while the bias on the ‘‘hybrid’’ estimator, Eq. (28), is of order $O[(\psi_T - \phi_0^{\text{FN}})^2] + O(\delta\phi)$.

IV. RESULTS AND DISCUSSION

We present a number of variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC) calculations for the diatomic molecules H_2 , LiH , Li_2 , and C_2 . Standard implementations of the VMC and DMC methods have been used and will not be detailed here. For some general presentation of these approaches the interested reader is referred for example to Refs. 1, 3, and 16. As already indicated in the preceding section all DMC calculations have been done within the fixed-node approach. Numerical experience shows that the fixed-node error on the energy resulting from the approximate location of the trial nodes is rather small when good enough trial wave functions are used. As we shall see later, this will also turn out to be true when calculating forces. In order to remove the short-time error all DMC calculations have been systematically performed with different time-steps and extrapolated to zero time-step. Regarding the trial wave function we have chosen a standard form consisting of a determinant of single-particle orbitals multiplied by a Jastrow factor

$$\psi_T = D^\dagger D^\downarrow \exp \sum_\alpha \sum_{\langle i,j \rangle} U(r_{i\alpha}, r_{j\alpha}, r_{ij}), \quad (34)$$

where the sum over α denotes a sum over the nuclei and $\sum_{\langle i,j \rangle}$ a sum over the pair of electrons. Here, the function U is chosen to be

$$U(r_{i\alpha}, r_{j\alpha}, r_{ij}) = s(x_{ij}) + p^{(\alpha)}(x_{i\alpha}) + c_1 x_{i\alpha}^2 x_{j\alpha}^2 + c_2 (x_{i\alpha}^2 + x_{j\alpha}^2) x_{ij}^2 + c_3 x_{ij}^2 \quad (35)$$

with

$$x_{ij} = \frac{r_{ij}}{1 + b_\sigma r_{ij}}, \quad x_{i\alpha} = \frac{r_{i\alpha}}{1 + b_\alpha r_{i\alpha}},$$

$$s(x) = s_1 x + s_2 x^2 + s_3 x^3 + s_4 x^4,$$

$$p^{(\alpha)}(x) = p_1^{(\alpha)} x + p_2^{(\alpha)} x^2 + p_3^{(\alpha)} x^3 + p_4^{(\alpha)} x^4.$$

b_σ can take two different values depending on the spin of the pairs of electrons considered. The different parameters of the trial wave function have been optimized using the correlated sampling method of Umrigar *et al.*¹⁷ The total energies obtained at the variational and DMC levels are presented in Table I.

The calculations have been done at the experimental bond lengths. The quality of our trial wave functions is good since a non-negligible part of the correlation energy is recovered at the variational level. Note that more sophisticated trial wave functions could be used (see, e.g., Ref. 18).

At the heart of the zero-variance principle employed here is the choice of the auxiliary quantities $\tilde{H}$ and $\tilde{\psi}$. Exactly in the same way as for the total energy we need to construct some optimal choice guided by a zero-variance equation. In the case of the energy the zero-variance equation is nothing but the usual Schrödinger equation

$$E_L(x) = H \psi_T / \psi_T = \langle E_L \rangle, \quad (36)$$

and the optimal choice (zero-variance) for ψ_T is $\psi_T = \phi_0$. Here, the ideal zero-variance condition is written as

$$\tilde{F}_q(\mathbf{x}) = \langle F_q \rangle. \quad (37)$$

In the variational case, using expression (11) this equation can be written as

$$\left[\tilde{H} - \frac{\tilde{H} \psi_T}{\psi_T} \right] \tilde{\psi} = -[\tilde{F}_q(\mathbf{x}) - \langle \tilde{F}_q \rangle] \psi_T. \quad (38)$$

In the DMC case, we have

$$[H - E_0] \tilde{\psi} = -[\tilde{F}_q(\mathbf{x}) - \langle \tilde{F}_q \rangle] \psi_T. \quad (39)$$

In this latter case we just need to construct an ‘‘accurate’’ solution of this equation. In the variational case we have more freedom since the auxiliary operator $\tilde{H}$ is also to be chosen. Here, in order to demonstrate the feasibility and the simplicity of the approach we will consider the simplest choice possible for the auxiliary quantities. Regarding the auxiliary operator we will just choose $\tilde{H} = H$. Regarding $\tilde{\psi}$ we choose the minimal form required to get a finite variance of the force, namely Q as given by (24). Note that using such forms for the auxiliary quantities there are no free parameters left. Our results are presented in Table II. Before discussing these results let us first look at the convergence of the vari-

TABLE II. Forces at the experimental bond lengths (atomic units) for the four diatomic molecules considered. $\langle F \rangle_{\text{VMC}}$ and $\langle F \rangle_{\text{mixed}}$ are the standard forces obtained with VMC and DMC. $\langle \tilde{F} \rangle_{\text{VMC,mixed}}$ are the same quantities obtained with the “renormalized” expression of the force, Eq. (18). $\langle \tilde{F} \rangle$ is the “hybrid” estimator combining the VMC and DMC results, Eq. (28). Statistical uncertainties on the last digit are indicated in parentheses.

Molecule	$\langle F \rangle_{\text{VMC}}$	$\langle \tilde{F} \rangle_{\text{VMC}}$	$\langle F \rangle_{\text{mixed}}$	$\langle \tilde{F} \rangle_{\text{mixed}}$	$\langle \tilde{F} \rangle$
H ₂ ($R=1.4$)	0.06(7)	−0.0047(1.5)	−0.0034(10)	−0.0041(3.6)	−0.0035(5)
LiH ($R=3.015$)	−0.037(12)	−0.0263(2)	−0.03(2)	−0.0125(9)	−0.0013(11)
Li ₂ ($R=5.051$)	−0.8(4)	−0.196(1.8)	−0.2(2)	−0.096(2.5)	−0.004(4)
C ₂ ($R=2.3481$)	2(3)	−0.101(22)	1.(4)	−0.05(2)	−0.00(4)

ous estimators. Typical behaviors are shown in Figs. 1 and 2. Calculations are VMC calculations of the force (at experimental length) for the two larger molecules treated here, namely Li₂ and C₂.

Both figures show the convergence of the estimators of the bare and renormalized forces, respectively, as a function of the simulation time (a quantity proportional to the number of Monte Carlo steps). In both cases the difference between the two curves obtained is striking. In the case of the bare force the estimator of the force converges with a lot of difficulty. The fluctuations are very large and at some places “jumps” in the curves are observed. These jumps correspond in the simulation to some configurations where an electron approaches a nucleus. Their location and their magnitude are very dependent on the sequence of random numbers and initial conditions used. In fact, there is no hope to obtain a converged value of the bare force in a finite simulation time (whatever its length be). This behavior is of course related to the infinite variance of the estimator. The second curve associated with the renormalized force, Eq. (11), has an entirely different behavior. In sharp contrast with the bare case the convergence is now reached very easily. At the scale of the figure the fluctuations of the curve have almost disappeared.

Table II summarizes the various calculations we have performed. All calculations have been done at the experimental bond lengths, the expectation values of the force are therefore expected to be very close to zero.

The bare VMC and DMC values presented are reported as given by the output of our program. However, as just remarked they have to be considered with a lot of caution. Indeed, the values are not and cannot be converged due to the infinite variance. Consequently, the values quoted just give a very rough estimate. Their actual values depends strongly on the initial conditions and on the series of random numbers used. In contrast, the renormalized value are perfectly well-defined and the estimate of the average and of the statistical error are converged. At the variational level the average values of the renormalized forces are significantly different from zero. These values depend on the choice of the trial wave function. The mixed estimators are less dependent. In our calculations the results display a systematic error about 2 times smaller than the variational ones. Combining both sets of values and using formula (28) to remove as much as possible the dependence on the trial function we obtain very accurate estimates of the forces (column $\langle \tilde{F} \rangle$). Except for the molecule H₂ for which very small statistical

errors have been obtained, our estimates of the force are essentially exact (≈ 0) within error bars. Note that in the three cases where a fixed-node error on the result is expected (LiH, Li₂, and C₂) no significant bias on the results is observed. As already remarked in the introduction there are very few results to compare with in the literature. Regarding H₂ we can cite the work by Reynolds *et al.*⁵ At the equilibrium distance, they obtained for the force a value of 0.0009(24). Note that within statistical errors our (slightly biased) result is compatible with this value. However, our statistical error is about 5 times smaller. In the case of LiH we get a much more accurate value than the one given by Vrbik and Rothstein,⁶ namely $F=0.12(16)$. Quite remarkably, our statistical error is about two orders of magnitude smaller. Comparisons with the very recent results obtained by Filippi and Umrigar⁷ are not easy because the quantities calculated are different. In their work the authors present the error in the bond lengths obtained in their correlated DMC calculations and not the force like in the present work. In order to make some quantitative comparisons it is necessary to compute the dependence of our results on the distance and

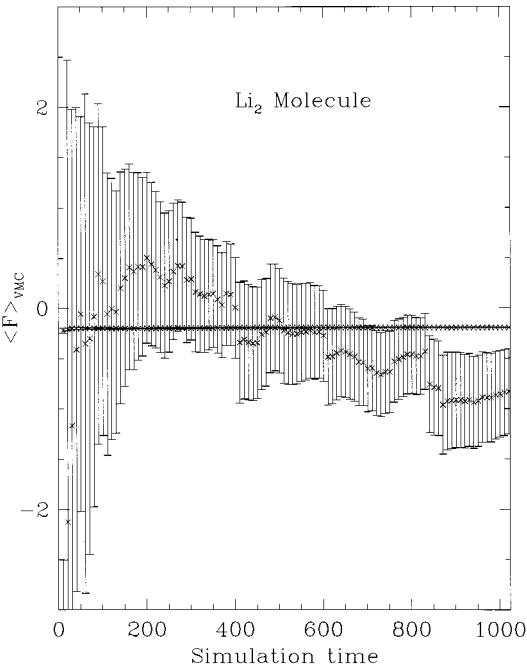


FIG. 1. Convergence of $\langle F \rangle_{\text{VMC}}$ and $\langle \tilde{F} \rangle_{\text{VMC}}$ as a function of the simulation time (proportional to the number of Monte Carlo steps) for the Li₂ molecule at the equilibrium geometry, $R=3.015$.

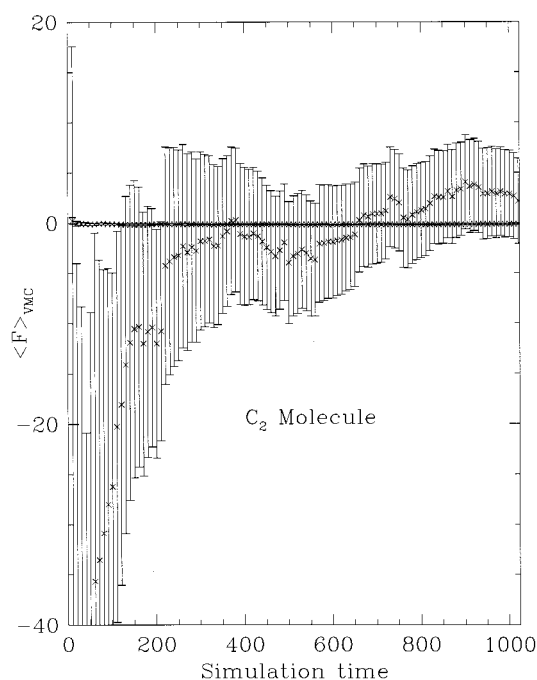


FIG. 2. Convergence of $\langle F \rangle_{\text{VMC}}$ and $\langle \tilde{F} \rangle_{\text{VMC}}$ as a function of the simulation time (proportional to the number of Monte Carlo steps) for the C_2 molecule at the equilibrium geometry, $R=5.051$.

define some estimate of the equilibrium distance. Such a study is out of purpose here and is left for future investigation. Finally, let us emphasize that the auxiliary function used here is the simplest form allowing the reduction of the variance of the local force to a finite value. Clearly, more general and sophisticated forms for the auxiliary function can be introduced and optimized. There is no doubt that significantly smaller errors on the computed forces can be achieved.

In summary, we have presented a simple and stable approach for computing forces within a QMC scheme. To do that, we propose to use the Hellmann–Feynman theorem to re-express the force as a standard local average of the gradient of the potential. The force is computed approximately using standard variational Monte Carlo and fixed-node diffusion Monte Carlo approaches. To remove as much as possible the dependence of the results on the trial wave functions we resort to the commonly used “hybrid” estimator combining both VMC and DMC results. In order to suppress the unbounded statistical fluctuations associated with the lo-

cal force we apply to this observable a generalized zero-variance property. In practice, this idea is implemented by replacing the bare local force by some renormalized expression depending on some auxiliary quantities. A simple procedure to construct the renormalized force (choice of auxiliary quantities) is presented. As emphasized, it is a general procedure: It can be performed without practical difficulty for an arbitrary molecular system. Introducing the simplest form possible for the renormalized force (minimal form, no free parameters) and using standard forms for the trial functions we get very satisfactory results for some simple diatomic molecules. Applications to bigger systems and calculations away from the equilibrium geometry are now under investigation.

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