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Computing Response Properties with Quantum Monte Carlo

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Abstract

In this paper we describe a recently proposed formalism for computing quantum response properties with quantum Monte Carlo (QMC) techniques. It is explained how this general formalism may be used to compute dynamic multipole polarizabilities as well as perturbational components of intermolecular interaction energies. Illustrative calculations for the dynamic dipole polarizability of the helium atom and for the perturbational components of the interaction energy of He_2 are presented. The practical limitations of this new scheme are discussed.

I. Introduction

Quantum Monte Carlo (QMC) methods are powerful techniques for solving the Schrödinger equation. They have been applied with success to a variety of problems including quantum liquids and solids, the electron gas, nuclear matter, quantum spin systems, and the electronic structure of small molecules. For a review of the various aspects and applications of QMC methods, the interested reader is referred to [1]. Although some properties other than the energy have been considered, most of the applications of QMC to quantum chemistry have concerned calculations of total energies of small molecules. In this work, we present a recently proposed method to compute response properties of atomic and molecular systems with QMC.[2]

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Unlike ordinary expectation values involving only one state, response properties formally involve all the excited states of the system and for that reason are known to be quite difficult to evaluate. The method we present is based on a new formulation of the Rayleigh-Schrödinger perturbation theory suitable for quantum Monte Carlo simulations. In this formalism the n-th order Rayleigh-Schrödinger perturbation term is expressed in closed form in terms of stochastic correlation functions of the perturbing operator. These correlation functions may be easily evaluated along stochastic trajectories generated by using standard Langevin techniques. This approach is quite general and may be applied to various problems involving response properties of quantum systems. The basic theoretical ideas of the method are presented in Sec. II. For a more detailed presentation the reader is referred to [2]. In Sec. III we discuss the application of this formalism to the calculation of dynamic multipole polarizabilities. An illustrative calculation for the dynamic dipole polarizability of the He atom is presented. Our results are in excellent agreement with the accurate results of Glover and Weinhold.[3] Section IV describes how to compute the perturbational components of intermolecular interaction energies. Some illustrative calculations for the dimer He_2 are presented. Finally, the practical limitations of the approach are discussed in Sec. V.

II. Expressing the n-th RS perturbational component in terms of stochastic correlation functions

Consider a system described by its Hamiltonian H. A first step consists in constructing a diffusion process from the ground-state wave function, ϕ_0, of H. This construction, which has been presented in detail in Refs. 4 and 5, is in fact present explicitly or implicitly in any Monte Carlo scheme based on importance sampling. A possible way of characterizing a diffusion process is to exhibit its Langevin equation. In the present case, we have

$$d\vec{R}(t) = \vec{b}(\vec{R}(t))dt + d\vec{W}(t) \qquad (1)$$

where $\vec{R}(t)$ is a compact notation for representing a point (at time t) in the 3N-dimensional configuration space, that is $\vec{R} = (\vec{r}_1, ..., \vec{r}_N)$, where N is the number of particles of the system; $\vec{W}$ represents the multi-dimensional

Wiener process and $\vec{b}$, the drift vector, is the only quantity depending on the ground-state wave function ϕ_0:

$$\vec{b} = \vec{\nabla}\phi_0/\phi_0. \tag{2}$$

By employing a discretized version of the Langevin equation, stochastic trajectories corresponding to the diffusion process may be easily constructed numerically by using a step-wise procedure.

A basic quantity in the theory of Markovian diffusion processes is the transition probability density which determines the dynamics of such processes. It is possible to show (see Refs. 2,4 and 5) that in the present case this quantity is closely related to the (imaginary) time-dependent Green's function of the quantum problem. More precisely, we have

$$p(\vec{R} \rightarrow \vec{R}', t) = \frac{\phi_0(\vec{R}')}{\phi_0(\vec{R})} \sum_i \phi_i(\vec{R})\phi_i(\vec{R}')e^{-t(E_i - E_0)} \tag{3}$$

where ϕ_i are the eigenfunctions of H with the corresponding energies E_i. It should be noticed that the stationary density, $p(\vec{R})$, of the diffusion process (obtained by letting t go to infinity in the preceding formula) is nothing but the usual quantum-mechanical probability density associated with the ground-state wave function

$$p(\vec{R}) = {\phi_0}^2. \tag{4}$$

Since any stochastic average may be expressed in terms of the transition probability density and any quantum property in terms of the eigensolutions of H, expression (3) may be used to connect both types of average. Let us illustrate this idea on a specific example. In the following we are interested in computing n-time autocorrelation functions of a local potential V. Such correlation functions are expressed in terms of the stationary and transition probability densities as follows:

$$< V(\vec{R}(0))...V(\vec{R}(u_{k-1})) >=$$

$$\int d\vec{R}_0...d\vec{R}_{k-1} V(\vec{R}_0)p(\vec{R}_0) \prod_{i=1}^{k-1} p(\vec{R}_{i-1} \rightarrow \vec{R}_i, u_i - u_{i-1})V(\vec{R}_i), \tag{5}$$

with $u_0 \equiv 0$. Here, $< ... >$ denotes the average with respect to stochastic trajectories. By using Eqs. (3) and (4) these correlation functions may be given in terms of the eigensolutions of H and, after integrating out the time dependency, may be finally expressed as perturbational quantities. For the simple case of the second-order Rayleigh-Schrödinger perturbational term, we have

$$\Delta E_{RS}^{(2)} = -\int_0^{+\infty} d\tau < (V - < V >)(\vec{R}(0))(V - < V >)(\vec{R}(\tau)) > \quad (6)$$

Indeed, by resorting to the basic definition of stochastic averages in terms of probabilities, Eq. (5), by using expressions (3) and (4) for the probability densities, and finally performing the trivial time-integral, we find

$$\Delta E_{RS}^{(2)} = \sum_{i \neq 0} \frac{|< \phi_0 \mid V \mid \phi_i >|^2}{E_0 - E_i}, \quad (7)$$

which is nothing but the usual expression for the second-order term. It has been shown that similar expressions may be obtained for higher-order perturbational terms. The general formula is written

$$\Delta E_{RS}^{(n)} = (-1)^{n+1} \int_0^{+\infty} du_{n-1} \int_0^{u_{n-1}} du_{n-2} \ldots \int_0^{u_2} du_1 \\ < V(\vec{R}(0)) V(\vec{R}(u_1)) \ldots V(\vec{R}(u_{n-1})) >_C . \quad (8)$$

The derivation of this formula is given in Ref. 2. Here, the notation $< .... >_C$ refers to the usual cumulant averages given by some well defined linear combination of products of same and lower order moments.

At this point this scheme might appear rather formal since the ground-state wave function of H (whose expression is needed to construct the drift vector (2)) is generally not known. In fact, it is possible to avoid this problem by introducing a new diffusion process defined from a known trial wave function ψ_T instead of the exact one. In order to compute the same correlation functions, it is possible to show that one just has to introduce a suitable weight factor in the preceding averages. For example, the n-time

correlation functions are expressed as

$$< V(\vec{R}(0))...V(\vec{R}(u_{k-1})) >=$$

$$\lim_{t\to+\infty} \frac{< V(\vec{R}(0))...V(\vec{R}(u_{k-1}))e^{-\int_{-t/2}^{t/2}(E_L(\vec{R}(s))ds} >_{\psi_T}}{< e^{-\int_{-t/2}^{t/2}(E_L(\vec{R}(s))ds} >_{\psi_T}} \qquad (9)$$

with $0 \leq u_1 \leq ... \leq u_{k-1}$, and where averages in the right-hand side of the equation are defined with respect to the trajectories of the diffusion process built from the trial wave function ψ_T. In fact, formula (9) is nothing but a generalization of the well-known Feynman-Kac formula.[4,5] The quantity E_L appearing in the weight (Feynman-Kac) factor is defined as $H\Psi_T/\Psi_T$ and is usually referred to as the local energy.

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

(1) Use formula (8) to express $\Delta E_{RS}^{(n)}$ in terms of some suitable combination of time-correlation functions of the perturbing potential with respect to the diffusion process constructed from ϕ_0.

(2) Resort to formula (9) to express stochastic averages defined over the diffusion process built from the generally unknown exact wave function in terms of stochastic averages defined over the diffusion process built from a trial wave function ψ_T.

(3) Calculate stochastic averages from stochastic trajectories generated by using a discretized version of the Langevin equation (1) (the drift vector being constructed from ψ_T).

It should be emphasized that this approach has some important advantages with respect to commonly employed *ab initio* methods:

(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 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 occurence of infinite sets of intermediate wave functions in the usual formalism) is implicitly taken into account through the transition probability density of the diffusion process (Eq. (3)). In practice, the transition probability density may be easily simulated (using the Langevin equation (1)) by employing only an approximate form for the ground-state wave function of the problem.

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

However, there also exists a number of problems which make this scheme rather difficult to apply to realistic molecular systems at the present time. The most challenging difficulty is certainly to apply the Fermi statistics in an efficient way. The discussion of this very important issue is postponed to Sect. V. Let us first present the application of this formalism to the computation of dynamic polarizabilities and perturbational components of intermolecular interaction energies.

III. Computing dynamic multipole polarizabilities

Although it is possible to derive formulas for computing general response properties such as dynamic hyperpolarizabilities or field-gradient polarizabilities we shall restrict ourselves to the problem of evaluating dynamic multipole polarizabilities. Dynamic multipole polarizabilities of a N-electron system at frequency ω are

$$\alpha_l(\omega) = \alpha_l^+(\omega) + \alpha_l^-(\omega) \tag{10}$$

with

$$\alpha_l^{\pm}(\omega) = N \sum_{i \neq 0} \frac{|< \phi_0 \mid Q_l \mid \phi_i >|^2}{E_i - E_0 \pm \omega} \tag{11}$$

where Q_l stands for the multipole operator $r^l P_l(\cos\theta)$. Now, by using the same arguments as above in the derivation of Eq. (7) it is easy to see that $\alpha_l^+(\omega)$ is essentially given by the Laplace-transform of the centered two-time autocorrelation function of Q_l, namely

$$\alpha_l^+(\omega) = -N \int_0^{+\infty} d\tau e^{-\tau\omega} \bar{C}_{Q_l Q_l}(\tau) \tag{12}$$

with

$$\bar{C}_{Q_lQ_l}(\tau) \equiv < (Q_l - < Q_l >)(\vec{R}(0))(Q_l - < Q_l >)(\vec{R}(\tau)) > . \qquad (13)$$

By employing formula (9), this correlation function may be exactly computed from the stochastic trajectories of the diffusion process built from an approximate trial wave function. It is important to realize that by using the basic definition of stochastic averages in terms of probability densities (Eq. (5)) and by resorting to expressions (3) and (4) for these densities, the following form for $\bar{C}_{Q_lQ_l}(\tau)$ is obtained

$$\bar{C}_{Q_lQ_l}(\tau) = \sum_i |< \phi_0 \mid (Q_l - < Q_l >) \mid \phi_i >|^2 e^{-\tau(E_i - E_0)}. \qquad (14)$$

Accordingly, it is seen that this correlation function is written as an infinite sum of real exponentials with true excitations energies of the unperturbed system as exponents, and squared centered transition moments as amplitudes. Due to this form, it is natural to fit the calculated correlation function by a function expressed as a sum of a finite number of real exponentials, namely

$$\bar{C}_{Q_lQ_l}(\tau) = \sum_{i=1}^{N} c_i e^{-\lambda_i \tau}. \qquad (15)$$

Having an analytical expression of the autocorrelation function, $\alpha_l(\omega)$ is readily obtained from Eqs. (10)-(12) and (15), one obtains

$$\alpha_l(\omega) = \sum_{i=1}^{N} \frac{2N\lambda_i c_i}{{\lambda_i}^2 - \omega^2} \qquad (16)$$

We have applied this scheme to compute the dynamic dipole (l=1) polarizability of the helium atom. We found out that a three real exponentials description was sufficient to correctly describe our data (that is, the autocorrelation function (13) evaluated at different times). Results which are presented in Table I are in excellent agreement with the almost exact results of Glover and Weinhold based on rigorous upper and lower bounds for $\alpha_{l=1}(\omega)$.[3]

Table I. Dynamic dipole polarizability for the ground-state of He. "Exact" results are taken from Ref. 3. Statistical errors are indicated in parentheses. All quantities in atomic units.

Frequency ω	This work	"Exact"
0.00	1.39(2)	1.383
0.05	1.39(2)	1.387
0.10	1.40(2)	1.399
0.15	1.42(2)	1.419
0.20	1.45(2)	1.449
0.25	1.49(2)	1.489
0.30	1.54(2)	1.541
0.35	1.61(2)	1.610
0.40	1.69(3)	1.698
0.45	1.81(3)	1.815

In order to illustrate the great flexibility of this approach, it is interesting to present the calculation of the standard c_6 van der Waals coefficient given by

$$c_6 = \frac{3}{\pi}\int_0^\infty \mid \alpha_{l=1}(i\omega) \mid^2 d\omega \quad . \tag{17}$$

It is remarkable that in this approach no additional calculations are needed in order to evaluate this quantity. The only thing to do is to insert expression (16) for $\alpha_l(\omega)$ into (17) and to perform exactly the integration. When this is done we obtain $c_6 = 1.46(2)$ in excellent agreement with the result of 1.46 quoted in Ref. 6.

IV. Computing perturbational components of the intermolecular interaction energy

Computation of intermolecular interactions is another application of the general formalism presented in Sec. II. The unperturbed Hamiltonian is now given by the sum of the Hamiltonian of the noninteracting monomers

and the perturbing operator is nothing but the usual intermolecular interaction potential. Expressions of Sec. II may be readily used after replacing the eigensolutions of the unperturbed Hamiltonian by the eigenfunctions of the noninteracting system, $\phi_i^A \phi_j^B$, with the corresponding energies $E_i^A + E_j^B$, where ϕ_i^M and E_i^M (M=A,B) denote the eigensolutions of the isolated monomers (for simplicity we consider only two interacting monomers A and B). It should be remarked that the diffusion process contructed from the ground-state wave function $\phi_0^A \phi_0^B$ in fact decomposes into two independent sub-processes corresponding to both noninteracting monomers. This is particularly interesting since it enables one to use a common set of stochastic trajectories for computing perturbational components corresponding to different relative orientation of the monomers.

The only new aspect involved is the problem of calculating exchange contributions responsible for the repulsion at short distances. An approximate expression for the first-order exchange interaction energy (by far the leading component) has been presented in Ref. 2. This formula enables one to introduce most of the intramonomer electron-electron correlation contribution. However, we shall not enter here in the quite involved details of this formulation; for that the reader is referred to [2].

This formalism has been applied to the calculation of the first- and second-order perturbational components of the interaction energy of two helium atoms at very short distances. Results taken from Ref. 2 are presented in Tables II and III. Table II presents results obtained by using different wave functions for the monomers, namely the Hartree-Fock solution, a highly-correlated wave function (giving 87% of the correlation energy) and the exact wave function through the application of formula (9). Results show that intra-atomic correlation contribution to the first-order RS interaction energy is certainly very small at these very short distances. Table III presents the result obtained for the second-order RS contribution at the interatomic distance of 2 a.u.. This result is compared with an *ab initio* SCF perturbational calculation of the same quantity (method presented in Refs. 7 and 8). It is seen that the intra-atomic correlation contribution to this quantity is in fact important since it accounts for about 20 % of the exact value.

Table II. First-order RS interaction energy for the helium dimer calculated with different wave functions. Statistical errors indicated in parentheses. All quantities in atomic units.

R	HF w.f.	Corr. w.f.	Exact w.f.
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(4)	-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)

Table III. Second-order RS interaction energy for the helium dimer. Statistical errors indicated in parentheses. All quantities in atomic units.

R	$\Delta E^{(2)}_{RS}(QMC)$	$\Delta E^{(2)}_{RS}(SCF)$
2.0	-0.0375(11)	-0.030

V. Present limitations

At first glance, it might appear that the method presented here has little limitations and, consequently, should be the method of choice for computing response properties. In fact, this is not yet true. We shall give two major reasons for that.

i) Our first reason takes its origin in the difficulties encountered by quantum Monte Carlo approaches for treating the electronic structure of atoms or molecules. Indeed, it is known that a serious increase of statistical fluctuations with the number of electrons treated is observed for atoms and molecules (see, e.g., discussion in Ref. 9). In the present method, this means that an increase of statistical fluctuations on intramonomer local energies should be expected when treating systems of increasing size. In practice, calculating systems having up to a dozen of electrons is considered as a reasonable limit at the present time.

ii) There is in fact a much more serious problem which makes this original formalism still more difficult to apply to systems having more than 2 electrons. This problem results from the necessity of introducing Fermi statistics for monomers in an appropriate way. In Ref. 2 it has been explained that, in contrast with QMC approaches designed for computing ordinary quantum averages (such as the total energy, the dipole moment, etc ...), correlation functions involving operators evaluated at different times cannot be computed with the usual stable fixed-node approach. This means that formulas presented in Sec. II, where the ground-state wave function was supposed to have the correct fermionic antisymmetry properties, cannot be directly applied as given. The basic reason is that nodal hypersurfaces of the trial wave function play the role of infinitely repulsive barriers for the stochastic trajectories (the drift vector (2) diverges at nodes). As a consequence, eigenfunctions of H appearing in Eq. (3) are not the correct ones but instead some new eigensolutions vanishing wherever the ground-state wave function vanishes. Accordingly, response properties sensitive to all excited states are biased. It is important to realize that the resulting bias may be quite important and that it would exist even if *exact* nodes for the trial wave function were used. In fact, there exists a natural solution to this problem within the framework of QMC approaches. It consists in using a bosonic-type trial wave function and making use of fermionic-type projection functions in the averages to restore the Fermi statistics (nodal-release type of approaches; see, e.g., Refs. 5,10-12). Let us denote as f and g two such projections functions, the exact non-biased autocorrelation function of the perturbing operator is then written

$$< V(\vec{R}(0))...V(\vec{R}(u_{k-1})) >=$$

$$\lim_{t\to+\infty} \frac{< f(\vec{R}(-t/2))V(\vec{R}(0))...V(\vec{R}(u_{k-1}))g(\vec{R}(t/2))e^{-\int_{-t/2}^{t/2}(E_L(\vec{R}(s))ds} >_{\psi_T}}{< f(\vec{R}(-t/2))g(\vec{R}(t/2))e^{-\int_{-t/2}^{t/2}(E_L(\vec{R}(s))ds} >_{\psi_T}} \tag{18}$$

However, the main difficulty in applying this scheme is that it is known to be very unstable from a numerical point of view. The reason is that

for large times t positive and negative contributions of Eq. (18) (corresponding to bosonic-type contributions) nearly cancel and the resulting fermion contribution becomes rapidly exponentially smaller than the statistical fluctuations. This well-known problem is generally referred to as the "sign problem". Very recently, Caffarel *et al.* have proposed a new approach to extract more information from QMC correlation functions.[13] In this approach a Lanczos-type algorithm is used to increase the rate of convergence of the long-time limit involved in Eq. (18), thus avoiding the use of large times associated with large statistical fluctuations. The possibility of applying such a scheme to compute nodal-release correlation functions is presently examined.

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References

1. See, e.g., contributions in *J. Stat. Phys.* **43** (1986). See also *Monte Carlo Methods in Statistical Physics* ed. by K. Binder (Springer-Verlag, Berlin, 1977) and *ibid.* Vol. II (1984). For applications to the electronic structure of atoms and molecules, see, e.g., W.A. Lester, Jr., and B.L. Hammond, *Ann. Rev. Phys. Chem.* **41**, 283 (1990) and references therein.

2. M. Caffarel and O. Hess, *Phys. Rev. A* (to be published).

3. R.M Glover and F. Weinhold, *J. Chem. Phys.* **65**, 4913 (1976).

4. M. Caffarel and P. Claverie, *J. Stat. Phys.* **43**, 797 (1986).

5. M. Caffarel and P. Claverie, *J. Chem. Phys.* **88**, 1088 (1988); M. Caffarel and P. Claverie, *ibid.* **88**, 1100 (1988).

6. R.M Glover and F. Weinhold, *J. Chem. Phys.* **66**, 191 (1977).

7. B. Jeziorski and M. van Hemert, *Mol. Phys.* **31**, 713 (1976).

8. O. Hess, M. Caffarel, C. Huiszoon, and P. Claverie, *J. Chem. Phys.* **92**, 6049 (1990).

9. D.M. Ceperley, *J. Stat. Phys.* **43**, 815 (1986).

10. M.H. Kalos in *Monte Carlo Methods in Quantum Problems*, NATO ASI Series C (Reidel, Dordrecht, 1982).

11. D.M. Ceperley and B.J. Alder, *J. Chem. Phys.* **64**, 5833 (1984).

12. K.E. Schmidt and M.H. Kalos in *Monte Carlo Methods in Statistical Physics* ed. by K. Binder (Springer-Verlag, Berlin, 1984).

13. M. Caffarel, F.X. Gadea, and D.M Ceperley, *Europhys. Lett.*, submitted.