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23 May 1997

Chemical Physics Letters 270 (1997) 382–386

CHEMICAL PHYSICS LETTERS

Shifted-contour auxiliary-field Monte Carlo: circumventing the sign difficulty for electronic-structure calculations

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Received 5 February 1997

Abstract

A converged Monte Carlo approach for electronic-structure calculations of ground and low-lying excited-states is developed. The method, Shifted-Contour Auxiliary-Field Monte Carlo (SCAFMC), is an extension of the Auxiliary-Field Monte Carlo (AFMC) approach, and is based on a shift of the auxiliary-field contour of integration to pass through the (imaginary) stationary point. It eliminates sign difficulties for systems with a strong contribution from the mean field, such as electronic-structure applications. The method is examplified for ground and excited-states calculations of Ne.

1. Introduction

The Auxiliary-Field Monte Carlo (AFMC) method [1–16] is an approach to simulate many-body systems for particles of arbitrary symmetry interacting by pair potentials. The method uses the Hubbard–Stratonovich (HS) transformation [7,8] that replaces the exact multiparticle propagator by an ensemble average of independent-particle propagators, in each of which the particle–particle interaction is replaced by interaction of a particle with an ensemble-dependent auxiliary-field (see below). This approach has established itself as a powerful tool for many physical applications, including the Hubbard model [3,9,10] and nuclear-shell model [2] simulations. Recent exact AFMC simulations for molecular structure [15–17] were restricted, however, to very small systems (H_2, He, and Be — with the exception of a homogeneous Jellium model [15,17] [3]) since the method suffered from a sign problem [5].

Here we demonstrate that most of the sign problem in AFMC may easily and effectively be circumvented for electronic-structure applications, by shifting the contour of integration over the auxiliary-field to pass through the stationary point. The resulting approach, labelled shifted-contour AFMC, or SCAFMC, is applied successfully for extracting ground and excited states of Ne.

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[3] The success of the Jellium model simulations for 14 electrons without modification is due to the fact that the mean field is constant in space.

PII S0009-2614(97)00370-9

2. Auxiliary-field Monte Carlo — Review

The basic electronic-structure pair-interaction Coulomb Hamiltonian in a second quantization formalism can be written in the form

$$H = h_1 + h_2 \equiv \sum_{\alpha\beta} K_{\alpha\beta}\rho_{\alpha\beta} + \frac{1}{2}\sum_{\alpha\beta\gamma\delta} v_{\alpha\beta\gamma\delta}\rho_{\alpha\beta}\rho_{\gamma\delta}\,, \tag{1}$$

where α, β, γ, and δ denote spatial orbital indices (extending up to the size of the orbital basis, N). K includes the kinetic, electron–nucleus and part of the electron–electron repulsion terms, and v is the appropriate matrix element of the electron–electron repulsion (note the order of indices we use for v). $\rho_{\alpha\beta}$ is defined in terms of the creation/destruction operators as $\rho_{\alpha\beta} = a_\alpha^+ a_\beta(\text{spin up}) + a_\alpha^+ a_\beta$ (spin down).

Next we turn to the imaginary time (τ) propagator, $e^{-H\tau}$, which is usually broken into a large number (L) of small time-steps dt, with a Trotter separation to h_1 and h_2 used ($e^{-H\tau} \approx e^{-h_1 dt}e^{-h_2 dt}...e^{-h_1 dt}e^{-h_2 dt}$). The basic HS identity is

$$e^{-(c/2)y^2} = \sqrt{\frac{c}{2\pi}}\int e^{ic\sigma y}e^{-(c/2)\sigma^2}d\sigma\,, \tag{2}$$

where c is a positive number and y can be an operator. This identity can be readily shown to yield:

$$e^{-h_2 dt} = \text{const.}\cdot\int e^{-(1/2)(\sigma,v\sigma)dt}e^{i(\sigma,v\rho)dt}\prod_{\alpha\beta}(d\sigma_{\alpha\beta})\,, \tag{3}$$

with $(\sigma,v\rho) \equiv \sum_{\alpha\beta\gamma\delta}\sigma_{\alpha\beta}v_{\alpha\beta\gamma\delta}\rho_{\gamma\delta}$, and $(\sigma,v\sigma)$ defined analogously. Collecting the last two equations and noting that a separate field $\sigma_{\alpha\beta}(t_l)$ needs to be used at each time ($t_l = ldt$, $l = 1,\ldots,L$, and $\tau = Ldt$), it follows that the propagator $e^{-H\tau}$ can be described as an ensemble average of one-body propagators, in each of which the electron–electron repulsion has been converted into an interaction with a fluctuating (time- and space-dependent) field

$$e^{-H\tau} = \text{const.}\cdot\int e^{-(1/2)((\sigma v\sigma))}U_\sigma(\tau)D\sigma\,, \tag{4}$$

where $((\sigma v\sigma)) \equiv dt\cdot\sum_l(\sigma(t_l),v\sigma(t_l))$, $D\sigma = \prod_{l,\alpha\beta}d\sigma_{\alpha\beta}(t_l)$, and U_σ is a time-dependent one-body propagator, $U_\sigma(t_l) = \exp(-h^\sigma(t_l)dt)U_\sigma(t_{l-1})$, associated with the time-dependent one-body Hamiltonian

$$[h^\sigma(t_l)]_{\alpha\beta} = K_{\alpha\beta} + i\sum_{\gamma\delta} v_{\alpha\beta\gamma\delta}\sigma_{\gamma\delta}(t_l)\,. \tag{5}$$

Thus, the randomly chosen σ plays the role of an external charge distribution, which folds with v to yield an auxiliary electric-field potential.

It is straightforward to show that ground and excited states energies can be extracted by subspace diagonalization [18], a general method which in this context applies by starting with M initial determinants, $|\Phi_m\rangle$, and solving the eigenvalue equation

$$\mathbf{HC} = \mathbf{SCE} \tag{6}$$

where $\mathbf{H}$ and $\mathbf{S}$ are $M\times M$ matrices defined as

$$\mathbf{H}_{m,m'}(\tau) = \langle\Phi_m|He^{-H\tau}|\Phi_{m'}\rangle \tag{7}$$

and

$$\mathbf{S}_{m,m'}(\tau) = \langle\Phi_m|e^{-H\tau}|\Phi_{m'}\rangle \tag{8}$$

(for extracting the ground state, E_0, M can be as small as 1, in which case the usual expression $E_0 = \lim_{\tau\,\text{large}}\langle\Phi_0|He^{-H\tau}|\Phi_0\rangle/\langle\Phi_0|e^{-H\tau}|\Phi_0\rangle$ is recovered). The expression for $\mathbf{S}_{m,m'}(\tau)$ gets the convenient form of a weighted overlap of determinants

$$\langle\Phi_m|e^{-H\tau}|\Phi_{m'}\rangle \to \int e^{-(1/2)((\sigma v\sigma))}\langle\Phi_m|U_\sigma(\tau)|\Phi_{m'}\rangle D\sigma\,. \tag{9}$$

Note that $U_\sigma|\Phi_{m'}\rangle$ is also a Slater-determinant, where each orbital is propagated under h^σ. The numerator is similarly defined, and the whole expression (Eqs. (6–9)) can then be evaluated using a Monte Carlo algorithm. As mentioned, however, sign difficulties (cancellations in the evaluation of Eq. (9)) start already for Be [16].

3. Shifted contour AFMC

Our approach to overcome the sign difficulties is to modify the contour of integration in the σ plane to pass through a stationary point. Formally, i times the HF density furnishes approximately a stationary

point [11]. To see this from a direct physical argument we note that H can be rewritten as

$$H = \tilde{h}_1 + \tilde{h}_2 \equiv \sum_{\alpha\beta} \left(K_{\alpha\beta} + W^0_{\alpha\beta} \right) \rho_{\alpha\beta} + \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \left(\rho_{\alpha\beta} - \eta_{\alpha\beta} \right) v_{\alpha\beta\gamma\delta} \times \left(\rho_{\gamma\delta} - \eta_{\gamma\delta} \right) + \text{const.}, \quad (10)$$

where $W^0_{\alpha\beta} = \Sigma_{\gamma\delta} v_{\alpha\beta\gamma\delta} \eta_{\gamma\delta}$. $\eta_{\alpha\beta}$, in principle arbitrary, is clearly well chosen as the expectation value of $\rho_{\alpha\beta}$ in the Hartree–Fock ground state. Thus, $\tilde{h}_1$ includes also the direct part of the electron–electron repulsion, while only exchange and correlation remain in $\tilde{h}_2$. The AFMC transformation for Eq. (10) develops analogously to Eq. (1), and yields

$$\langle \Phi_m | e^{-H\tau} | \phi_{m'} \rangle = \text{const.} \cdot \int e^{-(1/2)((\sigma - i\eta)|v|\sigma - i\eta))} \langle \Phi_m | \tilde{U}_\sigma | \Phi_{m'} \rangle D\sigma , \quad (11)$$

where now $\tilde{U}_\sigma$ is similar to U_σ, except that the one-body Hamiltonian in Eq. (5) gains an additional term, $W^0_{\alpha\beta}$. The eventual effect of the change in the division of H (Eq. (10)) is thus simply to shift the auxiliary density $(\sigma_{\gamma\delta}(t_l))$ to a line with a constant imaginary part $(-i\eta_{\gamma\delta})$.

Table 1
Ground and excited states energies (in a.u.) of Ne using full-CI and subspace diagonalization SCAFMC at $\tau = 1$ a.u. (when a plateau in the E_m vs. τ curve is reached). $M = 9$ initial determinants are taken (see text). The basis set used is 4-31G with $N = 9$ basis functions. Also shown are the eigenvalues E_m (see Eq. (6)) for $\tau \sim 0$ (the SCAFMC calculation of the ground and excited-states energies starts at $\tau = 0$ from these values, and decays to the values shown in the second column after τ). The number in parentheses shows the error in the last digit. 9000 Monte-Carlo samples were used, and the time-step was $dt = 0.1$ a.u.

m	$E_m(\tau = 0)$	$E_m(\tau = 1)$	E_m(full-CI)
0	0.000	−0.116(4)	−0.116
1	1.639	1.563(4)	1.562
2	1.782	1.713(4)	1.712
3	1.782	1.713(4)	1.712
4	1.868	1.802(4)	1.800
5	1.869	1.802(4)	1.800
6	2.606	2.42(2)	2.432
7	3.11	3.02(1)	3.02
8	3.46	3.26(2)	3.27

Table 2
Similar to Table 1 (excluding full CI results), but with a larger basis set: 6-31G** with $N = 15$ basis functions, and the SCAFMC results are taken from $\tau = 1.2$ a.u. 13,000 Monte-Carlo samples were used, and the time-step was $dt = 0.1$ a.u.

m	$E_m(\rho = 0)$	$E_m(\tau = 1.2)$
0	0.000	−0.155(5)
1	1.640	1.524(2)
2	1.781	1.659(3)
3	1.782	1.660(3)
4	1.868	1.745(2)
5	1.868	1.746(2)
6	2.605	2.344(4)
7	3.07	2.843(4)
8	3.40	3.119(6)

In practice, we use in the evaluation of the SCAFMC expressions (Eqs. (6)–(8), (11)) a Monte Carlo algorithm with the weight here being $e^{-((\sigma v \sigma))/2}$. The calculated eigenenergies for Ne are shown in Tables 1 and 2 for two cases: A 4-31G basis with $N = 9$ basis functions, for which we performed also a full-CI calculation, and a 6-31G** basis with $N = 15$. Both calculations used $M = 9$ initial determinants, associated with the ground Hartree–Fock state and single-orbital excitations (with the excited orbital having the same spatial symmetry and spin as the original (hole) orbital). All energies are given relative to the Hartree–Fock energy.

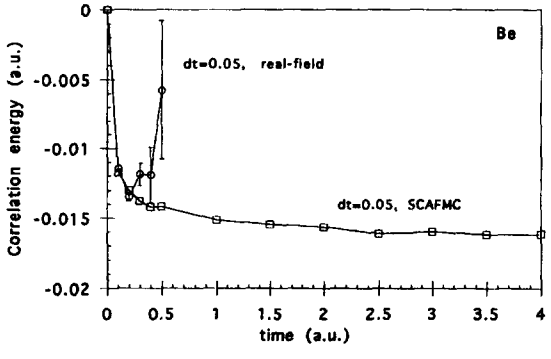

Fig. 1. The improved performance of the SCAFMC vs. the real-field version is shown through the dependence of the ground state correlation energy on τ for Be (with $N = 6$ S-only Slater orbitals), for a time-step $dt = 0.05$. 10,000 Monte Carlo samples were used here and in Fig. 2. Error bars are indicated for the real-field calculation; for the SCAFMC calculation they are smaller than the symbol size.

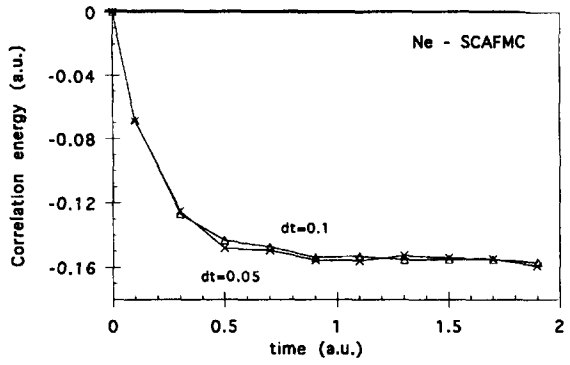

Fig. 2. The ground state correlation energy in SCAFMC for Ne ($N = 15$) is shown to converge both as a function of time and as a function of time-step for relatively large values of dt. A real-field calculation is not shown since even after a single time-step its error bars exceed the scale of the figure.

Figs. 1 and 2 show the ground state correlation energy (in a.u.) as a function of τ with a single initial determinant, $|\Phi_0\rangle$. For purposes of comparsion with the previous (real-field) version [16], we performed a calculation on Be which shows that much longer times (τ) can now be reached. The effect is even more important for Ne — with real fields the calculation was highly unstable even for one time-step.

4. Discussion

To explore further the improved performance of SCAFMC, we note that for one time slice, the real-field calculation gives for the propagator: const.$\cdot \int P(\sigma) e^{-i\sigma V \rho dt} D\sigma$, while the shifted contour modification gives the single time step propagator (with a different constant) as: const.$\cdot \int P(\sigma) e^{-i\sigma V(\rho-\eta)dt} e^{-W_0 \rho dt} D\sigma$. We thus see that the shifted contour reduces strongly fluctuations in the integrand (since the argument in the complex integrand is now proportional to $\rho - \eta$, rather than ρ). The wild fluctuations of the exponent are replaced by a damping factor, $e^{-W_0 \rho dt}$, due to the direct interaction, combined with fluctuations associated with auxiliary-fields that probe the detailed correlation energy.

The accuracy obtained here is 3×10^{-6} times smaller than the total energy ($\sim$ 128 a.u. for Ne). The shifted contour accounts explicitly for the direct energy. The remaining correlation is quite complicated in nature, but is handled efficiently by the numerical aspect of the calculation. The system has a host of energy scales, and the shifted contour allows accounting for the important small energy scale without being masked by the trivial high-energy scale due to the direct energy part.

5. Conclusions

In conclusion, by modifying the integration contour to pass through an imaginary stationary point in the auxiliary-field space, associated with the Hartree–Fock density, a numerically stable SCAFMC algorithm results for repulsive interactions. At this stage there are several improvements which can be conjectured: first, in order to reduce the formal N^4 scaling of the method (see Eq. (5)) to A^3 (due to the determinants calculation) one may use a grid "x" [15] or a pseudo spectral based approach [16,19]; in both cases the equivalent of Eq. (5) is evaluated very fast and the shift into the complex plane would be simply $\sigma(x,t_l) \rightarrow \sigma(x,t_l) - i n(x)$ [4], where n is the electron density in the ground state (which can be evaluated from Density Functional Theory [20]). In addition, different types of mean fields, including exchange effects [5], can also be used. Further, although the method as an all-electron approach has successfully converged for Ne, a use of effective or frozen core potentials may improve its convergence even more. A basis-set based approach, as developed here, may prove to be useful for large-scale Complete Active Space calculations. We note that SCAFMC can also be used within the AFMC-basis sampling approach of Ref. [14], or with walker-sampling (see, e.g., Ref. [13]). In addition to the ground and excited state energies, other expectation values (or components of the full wavefunction) may be

[4] Real time calculations using a shifted contour (with a shift proportional to $n(x,t)$) may be conjectured although the stability properties of the approach is not guaranteed then.

[5] For example, a shifted field with $W_0 = F - h_1$, with F being the Fock matrix, can be used to incorporate exchange effects into the mean field.

extracted [6]. Finally, note that the SCAFMC method is not restricted to electronic structure calculations and may prove useful for other systems.

Acknowledgements

We gratefully acknowledge discussions with E.A. Carter and T.J. Martinez (who also supplied us with the electronic-structure code for evaluating the Ne potential matrix elements), with R. Baer who proposed an explanation for the improved performance, and with R.D. Coalson, R. Kosloff, and J.C. Wells. This research was supported by an NSF grant CHE 93-14320, an NSF Early Career Award and a Sloan Fellowship (D.N.).

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[6] More technical improvements would be exploring extraction of E from the decay of the expectation value of $e^{-H\tau}$.