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Communication: Stochastic evaluation of explicitly correlated second-order many-body perturbation energy

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A stochastic algorithm is proposed that can compute the basis-set-incompleteness correction to the second-order many-body perturbation (MP2) energy of a polyatomic molecule. It evaluates the sum of two-, three-, and four-electron integrals over an explicit function of electron-electron distances by a Monte Carlo (MC) integration at an operation cost per MC step increasing only quadratically with size. The method can reproduce the corrections to the MP2/cc-pVTZ energies of H_2O, CH_4, and C_6H_6 within a few mE_h after several million MC steps. It circumvents the resolution-of-the-identity approximation to the nonfactorable three-electron integrals usually necessary in the conventional explicitly correlated (R12 or F12) methods. © *2014 AIP Publishing LLC.*
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The second-order many-body perturbation (MP2) energy of a molecule in the near complete-basis-set (CBS) limit can be accurately and inexpensively estimated by the explicitly correlated (F12, née R12) method.[1–6] The correlation energy in the MP2-F12 method is the sum of the MP2 correlation energy in the orbital basis set (OBS) and the F12 correction:

$$E_{\text{MP2-F12}} \equiv E_{\text{MP2}} + E_{\text{F12}}. \tag{1}$$

For a closed-shell molecule, the latter is given as

$$
\begin{aligned}
E_{\text{F12}} = {} & 2 \sum_{i,j,m,n}^{\text{occ.}} V_{mn}^{ij}\big(2t_{ij}^{mn} - t_{ji}^{mn}\big) \\
& + \sum_{i,j,k,l,m,n}^{\text{occ.}} t_{mn}^{kl} B_{kl}^{ij}\big(2t_{ij}^{mn} - t_{ji}^{mn}\big) \\
& - \sum_{i,j,k,l,m,n}^{\text{occ.}} (\epsilon_m + \epsilon_n) t_{mn}^{kl} X_{kl}^{ij}\big(2t_{ij}^{mn} - t_{ji}^{mn}\big),
\end{aligned} \tag{2}
$$

with

$$V_{mn}^{ij} = \langle ij | r_{12}^{-1} \hat{Q}_{12} f_{12} | mn \rangle, \tag{3}$$

$$B_{kl}^{ij} = \langle ij | f_{12} \hat{Q}_{12} (\hat{F}_1 + \hat{F}_2) \hat{Q}_{12} f_{12} | kl \rangle, \tag{4}$$

$$X_{kl}^{ij} = \langle ij | f_{12} \hat{Q}_{12} f_{12} | kl \rangle, \tag{5}$$

where t_{kl}^{ij} is a geminal amplitude, f_{12} is the correlation factor, which is an explicit function of the electron-electron distance r_{12}, and $\hat{F}_n$ is the Fock operator of the nth electron. Here, $\hat{Q}_{12}$ is a projector that makes $f_{12}|ij\rangle$ geminals "strongly

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orthogonal"[7] in addition to being orthogonal to products of two virtual orbitals,

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2) - \hat{V}_1 \hat{V}_2, \tag{6}$$

with

$$\hat{O}_n = \sum_i^{\text{occ.}} |\varphi_i(\boldsymbol{r}_n)\rangle \langle \varphi_i(\boldsymbol{r}_n)|, \tag{7}$$

$$\hat{V}_n = \sum_a^{\text{vir.}} |\varphi_a(\boldsymbol{r}_n)\rangle \langle \varphi_a(\boldsymbol{r}_n)|, \tag{8}$$

where $\varphi_i(\boldsymbol{r}_n)$ is the ith spatial orbital of the nth electron. As the correlation factor, Ten-no's Slater-type geminal,[2] $f_{12} = \{1 - \exp(-\gamma r_{12})\}/\gamma$, is widely adopted as it consistently outperforms $f_{12} = r_{12}$,[1,8] when $\gamma \approx 1$.

Equation (2) is a Hylleraas functional[5] and is bounded from below with respect to the variation of the geminal amplitudes t and of γ. Their values should, therefore, be determined so as to minimize E_{F12}. At the minimum, Eq. (2) reduces[5] to

$$E_{\text{F12}} = \sum_{i,j,m,n}^{\text{occ.}} V_{mn}^{ij}\big(2t_{ij}^{mn} - t_{ji}^{mn}\big). \tag{9}$$

Ten-no proposed[2,3] holding the geminal amplitudes fixed at the values that satisfy the first-order cusp condition:

$$t_{ij}^{mn} = \frac{3}{8}\delta_{mi}\delta_{nj} + \frac{1}{8}\delta_{mj}\delta_{ni}. \tag{10}$$

This has eliminated the cumbersome variational determination of the geminal amplitudes without significant loss of accuracy. It is widely adopted in MP2-F12 and other F12 methods.[6,9]

With the fixed amplitudes, it is advisable to use the original bounded expression (Eq. (2)) rather than the minimum expression (Eq. (9)), when evaluating E_{F12}. Nonetheless,

Eq. (9) with Ten-no's fixed amplitudes leads to a convenient expression, which can be subjected to an Monte Carlo (MC) integration:

$$E_{F12} = \frac{5}{8} \sum_{i,j}^{occ.} \langle ij|r_{12}^{-1} \hat{Q}_{12} f_{12}|ij\rangle - \frac{1}{8} \sum_{i,j}^{occ.} \langle ij|r_{12}^{-1} \hat{Q}_{12} f_{12}|ji\rangle. \tag{11}$$

Expanded, this becomes the sum of two-, three-, and four-electron integrals, $E_{F12} = E_{2e} + E_{3e} + E_{4e}$, where

$$E_{2e} = \frac{5}{8} \sum_{i,j}^{occ.} \langle ij|\frac{f_{12}}{r_{12}}|ij\rangle - \frac{1}{8} \sum_{i,j}^{occ.} \langle ij|\frac{f_{12}}{r_{12}}|ji\rangle, \tag{12}$$

$$E_{3e} = -\frac{5}{4} \sum_{i,j,k}^{occ.} \langle ijk|\frac{f_{23}}{r_{12}}|kji\rangle + \frac{1}{4} \sum_{i,j,k}^{occ.} \langle ijk|\frac{f_{23}}{r_{12}}|kij\rangle, \tag{13}$$

$$\begin{aligned} E_{4e} &= \frac{5}{8} \sum_{i,j,k,l}^{occ.} \langle ijkl|\frac{f_{34}}{r_{12}}|klij\rangle - \frac{1}{8} \sum_{i,j,k,l}^{occ.} \langle ijkl|\frac{f_{34}}{r_{12}}|klji\rangle \\ &\quad - \frac{5}{8} \sum_{i,j}^{occ.} \sum_{a,b}^{vir.} \langle ijab|\frac{f_{34}}{r_{12}}|abij\rangle \\ &\quad + \frac{1}{8} \sum_{i,j}^{occ.} \sum_{a,b}^{vir.} \langle ijab|\frac{f_{34}}{r_{12}}|abji\rangle. \end{aligned} \tag{14}$$

Although the four-electron integrals can be factored into products of two-electron integrals, they are left unfactored to facilitate their MC integration. Here, we report a highly scalable MP2-F12 algorithm that evaluates these 6-, 9-, and 12-dimensional integrals stochastically, while E_{MP2} to be added with E_{F12} is computed either deterministically or stochastically.[10,11] We call this algorithm Monte Carlo explicitly correlated MP2 or MC-MP2-F12.

This method has the following advantages over the conventional, deterministic MP2-F12 algorithms:

In the conventional MP2-F12, the dimension of the non-factorable high-dimensional integrals needs to be reduced by the resolution-of-the-identity (RI) approximation,[1,3,12,13] although it is also possible to evaluate the three-electron integrals exactly.[14,15] The RI approximation requires an auxiliary basis set such as a complementary auxiliary basis set (CABS),[7,13] which is much greater than the OBS. In MC-MP2-F12, there is no need for RI or an auxiliary basis set because the high-dimensional integrals are evaluated (not individually but as their sum) directly.

In the conventional MP2-F12 (hereafter referred to as RI-MP2-F12), the form of the correlation factor is limited to those that lend themselves to semi-analytical integration over Gaussian-type orbitals (GTOs). In MC-MP2-F12, virtually any correlation factor can be used with a trivial modification to the computer code.

Most importantly, as demonstrated below, MC-MP2-F12 is fundamentally more scalable with respect to both system size and computer size. Its operation cost per MC step increases only quadratically with system size.

The demerits of MC-MP2-F12 include the inevitable statistical errors, which decay slowly as the inverse square root of the number of MC steps. Also, integrals such as B (Eq. (4)) are not easily subjected to MC integrations because of the derivative operator in its definition. We, therefore, rely on Eq. (9) instead, which, as we shall see below, is less stable than Eq. (2), but reliable and useful nonetheless.

Next, we describe the Metropolis algorithm of the MC integrations of Eqs. (12)–(14). They are evaluated as

$$\begin{aligned} E_{2e} &= \iint d\boldsymbol{r}_1 d\boldsymbol{r}_2 \, F_2(\boldsymbol{r}_1, \boldsymbol{r}_2) \\ &\approx \frac{1}{N} \sum_{n=1}^{N} \frac{F_2(\boldsymbol{r}_1^{[n]}, \boldsymbol{r}_2^{[n]})}{w_2(\boldsymbol{r}_1^{[n]}, \boldsymbol{r}_2^{[n]})}, \end{aligned} \tag{15}$$

$$\begin{aligned} E_{3e} &= \iiint d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 \, F_3(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) \\ &\approx \frac{1}{N} \sum_{n=1}^{N} \frac{F_3(\boldsymbol{r}_1^{[n]}, \boldsymbol{r}_2^{[n]}, \boldsymbol{r}_3^{[n]})}{w_3(\boldsymbol{r}_1^{[n]}, \boldsymbol{r}_2^{[n]}, \boldsymbol{r}_3^{[n]})}, \end{aligned} \tag{16}$$

$$\begin{aligned} E_{4e} &= \iiint d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 d\boldsymbol{r}_4 \, F_4(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4) \\ &\approx \frac{1}{N} \sum_{n=1}^{N} \frac{F_4(\boldsymbol{r}_1^{[n]}, \boldsymbol{r}_2^{[n]}, \boldsymbol{r}_3^{[n]}, \boldsymbol{r}_4^{[n]})}{w_4(\boldsymbol{r}_1^{[n]}, \boldsymbol{r}_2^{[n]}, \boldsymbol{r}_3^{[n]}, \boldsymbol{r}_4^{[n]})}, \end{aligned} \tag{17}$$

where the integrands are defined by

$$F_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{5}{8} \frac{f_{12} O_{11} O_{22}}{r_{12}} - \frac{1}{8} \frac{f_{12} O_{12} O_{21}}{r_{12}}, \tag{18}$$

$$\begin{aligned} F_3(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) &= -\frac{5}{4} \frac{f_{23} O_{13} O_{22} O_{31}}{r_{12}} \\ &\quad + \frac{1}{4} \frac{f_{23} O_{12} O_{23} O_{31}}{r_{12}}, \end{aligned} \tag{19}$$

$$\begin{aligned} &F_4(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4) \\ &= \frac{5}{8} \frac{f_{34} O_{13} O_{24} O_{31} O_{42}}{r_{12}} \\ &\quad - \frac{1}{8} \frac{f_{34} O_{14} O_{23} O_{31} O_{42}}{r_{12}} - \frac{5}{8} \frac{f_{34} O_{13} O_{24} V_{31} V_{42}}{r_{12}} \\ &\quad + \frac{1}{8} \frac{f_{34} O_{14} O_{23} V_{31} V_{42}}{r_{12}}, \end{aligned} \tag{20}$$

with

$$O_{pq} = \sum_{i}^{occ.} \varphi_i^*(\boldsymbol{r}_p)\varphi_i(\boldsymbol{r}_q), \quad V_{pq} = \sum_{a}^{vir.} \varphi_a^*(\boldsymbol{r}_p)\varphi_a(\boldsymbol{r}_q). \tag{21}$$

The sets of electron coordinates in Eqs. (15), (16), and (17) are sampled randomly from weight functions, w_2, w_3, and w_4, respectively. The weight functions must be analytically integrable, be positive everywhere, and cancel all singularities in the integrands exactly.[16] We propose the following

that satisfy all these conditions:

$$w_3(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) = w_2(\boldsymbol{r}_1, \boldsymbol{r}_2)w_1(\boldsymbol{r}_3), \qquad (22)$$

$$w_4(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4) = w_2(\boldsymbol{r}_1, \boldsymbol{r}_2)w_1(\boldsymbol{r}_3)w_1(\boldsymbol{r}_4), \qquad (23)$$

and

$$w_1(\boldsymbol{r}_1) = \frac{1}{N_1}g(\boldsymbol{r}_1), \quad w_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{N_2}\frac{g(\boldsymbol{r}_1)g(\boldsymbol{r}_2)}{r_{12}}, \qquad (24)$$

where $g(\boldsymbol{r})$ is a sum of s-type GTOs centered at constituent atoms and

$$N_1 = \int d\boldsymbol{r}_1\, g(\boldsymbol{r}_1), \quad N_2 = \iint d\boldsymbol{r}_1 d\boldsymbol{r}_2 \frac{g(\boldsymbol{r}_1)g(\boldsymbol{r}_2)}{r_{12}}, \qquad (25)$$

which can be evaluated analytically.[17] It is easy to verify that w_3 and w_4 cancel exactly the r_{12}^{-1} singularities in F_3 and F_4. In F_2, the singularity is already eliminated by f_{12}, but we elect to retain the r_{12}^{-1} factor in w_2 to facilitate the redundant-walker convergence acceleration.[11]

It is important[11] to generate many (redundant) sets of electron coordinates (walkers) and to substitute all distinct permutations of them into the integrands to boost the MC sampling efficiency. The working equation is adjusted to invoke the redundant-walker algorithm:

$$E_{\text{F12}} \approx \frac{1}{N}\sum_{n=1}^{N} I_n \equiv I_N, \qquad (26)$$

$$I_n = \frac{1}{m_2}\sum_{i=1}^{m_2} J_i\big(\boldsymbol{r}_{1i}^{[n]}, \boldsymbol{r}_{2i}^{[n]}\big), \qquad (27)$$

and

$$J_i\big(\boldsymbol{r}_{1i}^{[n]}, \boldsymbol{r}_{2i}^{[n]}\big) = \frac{F_2\big(\boldsymbol{r}_{1i}^{[n]}, \boldsymbol{r}_{2i}^{[n]}\big)}{w_2\big(\boldsymbol{r}_{1i}^{[n]}, \boldsymbol{r}_{2i}^{[n]}\big)} + \frac{1}{m_1}\sum_{j=1}^{m_1}\frac{F_3\big(\boldsymbol{r}_{1i}^{[n]}, \boldsymbol{r}_{2i}^{[n]}, \boldsymbol{r}_{j}^{[n]}\big)}{w_3\big(\boldsymbol{r}_{1i}^{[n]}, \boldsymbol{r}_{2i}^{[n]}, \boldsymbol{r}_{j}^{[n]}\big)}$$
$$+\frac{1}{m_1(m_1-1)}\sum_{j=1}^{m_1}\sum_{k\neq j}^{m_1}\frac{F_4\big(\boldsymbol{r}_{1i}^{[n]}, \boldsymbol{r}_{2i}^{[n]}, \boldsymbol{r}_{j}^{[n]}, \boldsymbol{r}_{k}^{[n]}\big)}{w_4\big(\boldsymbol{r}_{1i}^{[n]}, \boldsymbol{r}_{2i}^{[n]}, \boldsymbol{r}_{j}^{[n]}, \boldsymbol{r}_{k}^{[n]}\big)}. \qquad (28)$$

To evaluate the right-hand side, we must have m_1 independent sets of walkers $\{\boldsymbol{r}_i^{[n]}|1 \leq i \leq m_1\}$ at the nth MC step, each of which is distributed according to the three-dimensional weight function w_1 of Eq. (24). We also need m_2 independent sets of walker pairs $\{\boldsymbol{r}_{1i}^{[n]}, \boldsymbol{r}_{2i}^{[n]}|1 \leq i \leq m_2\}$ generated according to the six-dimensional weight function w_2 of Eq. (24). These correct distributions are ensured by the Metropolis algorithm.[11,18]

The statistical uncertainty ε in I_N is given by

$$\varepsilon^2 = \frac{1}{N(N-1)}\sum_{n=1}^{N}(I_n - I_N)^2. \qquad (29)$$

This definition makes use of the reblocking algorithm of Flyvbjerg and Petersen[19] with the blocking length increasing with the degrees of redundancy m_1 and m_2.

In each MC cycle, the algorithm has three steps. The first step is the Metropolis propagation of m_1 single walkers and m_2 walker pairs according to their respective weight functions. This involves the evaluation of the weight functions, which is inexpensive. The second step is where the ampli-

TABLE I. The F12 correction (in mE_{h}) to the MP2/cc-pVDZ energy of H_2O as a function of γ (in a.u.) in the Slater-type geminal.

γ	RI (VBX)[a]	RI (V)[b]	RI (V)[c]	MC (V)[d]
0.4	−21.80	−123.27	−124.46	−122.36 (0.49)
0.8	−75.61	−101.29	−102.02	−100.90 (0.33)
1.2	−83.90	−82.31	−82.80	−82.08 (0.24)
2.0	−71.03	−53.74	−54.01	−53.60 (0.15)
2.5	−59.45	−41.40	−41.59	−41.28 (0.13)

[a]Using Eq. (2) and uncontracted aug-cc-pVQZ as CABS.
[b]Using Eq. (9) and uncontracted aug-cc-pVQZ as CABS.
[c]Using Eq. (9) and cc-pVDZ-F12/OptRI as CABS.[22]
[d]Using Eq. (9) with $m_1 = m_2 = 40$ and $N = 2 \times 10^6$. The values in parentheses are the statistical uncertainty in mE_{h}.

tudes of molecular orbitals (MOs) and the O and V matrices are evaluated at newly accepted coordinates of walkers. This nominally costs $O(m_1 M^2 + 2m_2 M^2)$ because, to evaluate M MO amplitudes, one needs to compute M atomic-orbital (AO) amplitudes at an $O(M)$ cost and then transform them to the MO amplitudes at an $O(M^2)$ cost per each walker. The third step is to compute I_n in Eq. (27), of which the cost scales as $O(m_1^2 m_2 M^0)$. The theoretical performance increase brought by the redundant-walker algorithm is $(m_1^2 m_2)/(m_1 + 2m_2)$. In each step, the memory cost is negligibly small. The whole algorithm can be easily and efficiently parallelized.

The RI- and MC-MP2-F12 calculations on H_2O, CH_4, and C_6H_6 have been performed with the geometries and weight functions given in the supplementary material.[20] The RI-MP2-F12 calculations utilized the open-source MPQC package,[21] in which the Slater-type geminal was approximated as a linear combination of Gaussians. The 1s core orbitals were frozen in all calculations.

Table I shows the dependence of E_{F12} on various parameters of the calculations. Comparing the second and third columns, we see that the "VBX" expression (Eq. (2)) gives E_{F12} that varies less with γ with the minimum occurring at around $\gamma = 1.2$, whereas the "V" expression (Eq. (9)) is correct only in the vicinity of $\gamma = 1.2$. MC-MP2-F12 based on the "V" expression is, therefore, predicated on the knowledge of the optimal value of γ and its transferability across a variety of molecules, which has been established.[2] Furthermore, the γ dependence of the "V" data is likely exaggerated by the smallness of the OBS, which may be understood by noting that the functional form of f_{12} depends strongly on γ only away from the cusp, where the basis-set dependence of correlation is relatively small.

The rightmost column shows that E_{F12} from MC-MP2-F12 can be easily made to converge within 1 mE_{h} of the correct limits after 2×10^6 MC steps for all values of γ. The rapid convergence may be traced to the smallness of the magnitude of E_{F12} and the fact that integrand F_2 is already free of singularities by virtue of f_{12} and thus more easily integrable.

Table II summarizes E_{F12} obtained by RI- and MC-MP2-F12 with a range of molecules and OBS. MC-MP2-F12 reproduces the correct (RI) values within a few mE_{h} for H_2O and CH_4 after 2×10^6 MC steps with $m_1 = m_2 = 40$. For C_6H_6, a larger degree of redundancy ($m_1 = m_2 = 80$) and more MC steps (8×10^6) are necessary to achieve comparable accuracy. The uncertainties also increase with the size

TABLE II. The F12 correction E_{F12} and statistical uncertainty ε (in mE_h) obtained by RI- and MC-MP2-F12 ($\gamma = 1.2$; $m_1 = m_2 = 40$, and $N = 2 \times 10^6$ for H_2O and CH_4; and $m_1 = m_2 = 80$ and $N = 8 \times 10^6$ for C_6H_6).

Molecule	OBS	E_{F12} (RI)	E_{F12} (MC)	ε
H_2O	cc-pVDZ	− 82.2	− 82.1	0.3
H_2O	cc-pVTZ	− 35.0	− 34.5	0.7
H_2O	cc-pVQZ	− 16.1	− 16.3	1.6
CH_4	cc-pVDZ	− 46.0	− 46.2	0.3
CH_4	cc-pVTZ	− 18.5	− 19.3	1.1
CH_4	cc-pVQZ	− 8.3	− 9.2	2.6
C_6H_6	cc-pVDZ	− 215.4	− 214.7	1.3
C_6H_6	cc-pVTZ	− 95.0	− 94.9	4.3
C_6H_6	cc-pVQZ	− 44.5	− 35.8	9.9

of OBS to the extent that they become significant portions of E_{F12} when cc-pVQZ is used. However, since the objective of the F12 correction is to avoid large OBS, smaller statistical uncertainties for smaller OBS (despite the greater magnitudes of E_{F12}) are encouraging. The uncertainties are indeed sufficiently small to render MC-MP2-F12 a viable alternative to RI-MP2-F12, although a systematic application of MC-MP2-F12 to energy differences such as reaction enthalpies is still needed and underway.

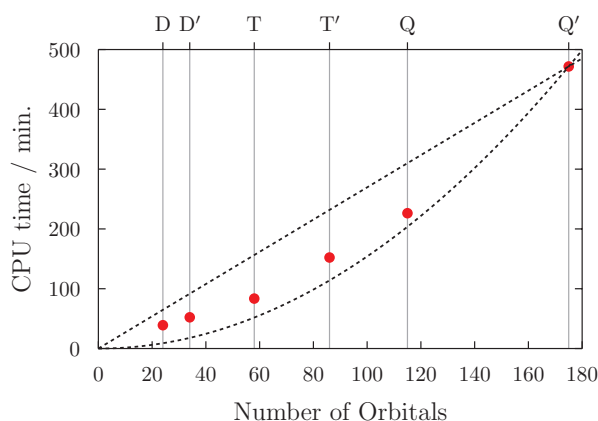Figure 1 plots the operation cost of MC-MP2-F12 per 5×10^5 MC steps as a function of the number of MOs (M).

FIG. 1. The CPU time (in minutes) spent in 5×10^5 MC steps of the MC-MP2-F12/cc-pVXZ calculations for H_2O (D, T, and Q) and for CH_4 (D′, T′, and Q′). The dashed line and curve are linear and quadratic functions.

The measured costs display quadratic dependence on size, suggesting that the evaluation of MO amplitudes is the rate-determining step in each MC step. This may be contrasted with the $O(M^5)$ dependence of the cost of the RI-MP2-F12 algorithm.

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